# Heat and Mass Limitations in an Anaerobic Digestion Process

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*Abstract:* - In this study, heat and mass limitations in an anaerobic reactor containing domestic solids were researched in batch reactors. The dynamic and static anaerobic data for 365 days showed that the methane production for the dynamic digestion reactor was measured as 176.86 m<sup>3</sup> which is extremely high for static anaerobic one (102.78 m<sup>3</sup>). As the heat transfer data increased with elevated temperature the methane productions also were highlighted. The external mass transfer was observed for easily degradable solids. In the calculation of external mass transfer during the degradation of organics dissolved with difficulty some semiempirical regressions were used. In the calculation of internal mass transfer the microorganisms in the solids were taken into consideration and the diffusion was defined with Fick's law. The diffusion coefficient D, was found to be constant. Generally, the diffusion coefficient of solids in water (Dw) was < 1.0. The effect of the total solid (TS) concentration in anaerobic batch reactors (TS between 12% and 39%) was investigated. The methane gas production decreased minorly when the TS levels elevated to 30%. At a TS percentage of 39%, the methane generation decreased significantly. At high TS, the mass transfer was inhibited and ended with lowered methane generations while the hydrolysis process did not affect significantly at high TS concentrations.

*Key-Words:* - Anaerobic treatment; Methane (CH<sub>4</sub>) gas generation; Diffusion coefficient; Dynamic and static anaerobic processes; Fick's law; Heat and mass limitations; Solid anaerobic batch treatment; Hydrolysis; Liquid/gas mass transfer; Domestic solid wastes.

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# **1** Introduction

The solid wastes can be removed with different processes like biochemical incineration. gasification, composting, landfill, and anaerobic digestion, [1], [2], [3]. Anaerobic treatment is a complicated process and has three steps: (1) microbial digestion, (2) physicochemical processes and (3) mass transfer of some gaseous end substances. Anaerobic digestion is an excellent effective technology with low cost for energy reuse from organic wastes with elevated moisture ratio ending with gasification and pyrolysis, [4]. Based on solid ratio; anaerobic treatment can be classified as wet (< 19% TS) and dry ( $\geq$ 19% TS) processes, [5].

Dry remediation technologies, solid-state or high-solids anaerobic processes were very significant since the ratio of water put to the raw waste is impostantly lowered since the volume of the digester is lowered. This process has success with minor waste volume and the waste transport emissions decreased. As a result, small digester capacities with elevated organic loading rates were processed, [6]. Some problem was detected at anaerobic digesters with high total solids. The utilization of anaerobic digester with high solids is limited due to low heat and mass transfer rates during long times and inhibitions due to presence of toxic compounds such as volatile fatty acids and ammonia, [7]. The anaerobic processes with high solids were slow processes for releasing of hydrolysed organics and microbial degradations, [8]. In order to industrialization of this process the heat and mass transfer should be improved. The anaerobic digestion processes with high solid ratios was studied in of crop waste, [9], and animal manures, [10]. The effects of operational conditions, [11], feedstock properties, [12], and pre-treatment steps, [13], the benefits of co-digestion, [12], the stability of the process, [14], and the lowcost benefits of anaerobic digestion with high solid were investigated, [7].

Anaerobic digestion is very sensitive to increases in temperature by lowering the steady-state condition in the process ending with low biogas productions. The temperature in the anaerobic reactor is related on the heat exchange between the anaerobic digester and environment. During biogas generation anaerobic digestion produce clean power and provide sanitation by degrading the organic compounds, [15]. During anaerobic digestion the dominated microorganisms degrade ultimately the organic compounds to methane and carbondioxide gas under anaerobic conditions, [16]. This phenomenon is used to degrade the domestic sludge and the municipal and industrial solid wastes in the sludges, [17].

Mixing has a big importance for gas generation in the anaerobic digesters. Without mixing, the organic substances were not distributed, the fluidity was pure, and the mass transfer was not cccurred during static digestion process, [18], [19], [20], [21]. Mixing in the dynamic anaerobic digestion cause to excellent methane generations. The mixing process were as follows: mechanical mixing, [22], mixing by slurry recirculation, [23], and mixing with gas recirculation, [24], [25]. The importance of mechanical mixing were elevated heat and mass transfer percentages, with low hydraulic dead space, and high metabolism rate of anaerobic bacteria.

Mass transfer of gaseous products affect significantly the transportation of total and methane gases from the liquid phase. Furhermore. transportation of gases from the liquid media affects the pH value of the reactor and the buffer capacity of the carbonate system since the thermodynamics and kinetics of microbiological reactions governed by pH value and CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> gases. Mixing in the liquid phase governed the substrate mass transfer and sludge retention, [26], and gas volume percentages in high rate degradation processes, [27]. A lot of data containing gas generation in anaerobic digesters were based on the liquid-gas steady-state conditions. This has a pozitive effect for poorly soluble gases such as CH<sub>4</sub>, and to CO<sub>2</sub> and H<sub>2</sub>S gas solubilities.

In bad mixed anaerobic digesters, the gas void ratio and the dose of substrates were studied, [28], [29]. The hydrodynamic mass transfer of different digesters using a viscous Newtonian and non-Newtonian fluid was studied, [30]. The studies showed that mechanical mixing has elevated mass transfer rates and have good homogeneity of the anaerobic reactors, [30]. Three mixing procedures were compared and it was noted that the mixing energy level was highest in mechanical mixing, [31]. Mechanical mixing improves the homogeneity and quick mass transfer at a reduced mixing duration, for a non-Newtonian fluid with excess organic loadings. Limitations in slurry and gas recovering were elevated apparatus costs at digesters with high solid wastes, [32]. A slurry recirculation digester for anaerobic digestion of straw granules was studied, [33]. It was found blockage to transfer the straw particles to the liquid surface even though the particle size was smaller than 3 mm, [33]. Reuse of gas in hay digestion; It has been noted that it tends to bring straw particles to the liquid surface and accumulate crusts on the liquid surface that are not effective for anaerobic digestion, [34]. Therefore, these processs has limited improvements in biogas generations at high capacity digestion systems, [35].

Among the currently used anaerobic digestion processes; The most perfect model has been designed, [36]. To ensure anaerobic two-stage digestion of sewage sludge; It is intended to simulate the dynamic activity of a semi-continuous pilot scale reactor, [37]. The modified anaerobic digestion model for olive mill solid waste and olive mill wastewater at thermophilic temperature; Anaerobic semi-continuous tubular digesters have been found to provide steady-state behaviour, [38]. The data indicated that the modified anaerobic model could predict the steady-state results of gas flows, total gas and methane percentages, pH, and volatile fatty acids extensively. In another model, degradation of grass silage occurred in two semicontinuous digesters under mesophilic conditions, [39]. This model was calibrated by a Genetic Algorithm in MATLAB/ SIMULINK, [39].

In this study, heat and mass variations in the anaerobic processes with high solid content process with anaerobiv model for municipal solid wastes in anaerobic batch reactors were reaserched. Anaerobic batch reactor experiments were carried out with solid dose ranging from 19% to 45%. CH<sub>4</sub>(g) production performances were evaluated. Anaerobic digestion model No.1 was used to compare the experimental results to detect the impact of water ratio on the performance of anaerobic degradation. The effect of total solids on the yields of anaerobic digestion was investigated. The impact of the hydrolysis and transportation of liquid/gas mass transfer on anaerobic digestion was resaearched. The significance of the experimental data was correlated with ANOVA statistical analysis method.

# 2 Materials and Methods

# 2.1 Properties of Compounds

Cellulose, hemicellulose and lignin ratios of domestic solid wastes were also measured by the method specified in the literature, [40]. The hemicellulose type substrates were solved by an acid (36 g/l C<sub>19</sub>H<sub>42</sub>NBr and 32.9 ml/lH<sub>2</sub>SO<sub>4</sub> (99.99%)) for 80 min at 130°C. The soluble organics were measured by extraction with a detergent (40 g/l C<sub>12</sub>H<sub>25</sub>NaO<sub>4</sub>S, 23.88 g/l C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>8.2</sub>H<sub>2</sub>O, 9.23 g/l Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.10H<sub>2</sub>O, 6.88 g/l Na<sub>2</sub>HPO<sub>4</sub> and 16 ml/l C<sub>6</sub>H<sub>14</sub>O<sub>4</sub>) at 130°C for 90 min and the lignin type organics were measured by discarting the cellulose type organics for 4 h with H<sub>2</sub>SO<sub>4</sub> (99.99%), respectively. At the last step, the extracted samples were washed with deionized water and dried at 130°C before to the next step.

# 2.2 Studies Performed During Tests

A cardboard with a density of 1.58 kg/m<sup>3</sup>, was used as an organic compound with a ratio of 35% in municipal solid waste. The cardboard was cutted and sieved at 1.2 mm. The studies were performed in 1000 ml batch glass reactors with a working volume of 400 ml. A mixture of cardboard, water, microorganisms and trace metals was prepared to have different total solid percentage contents from "wet" to "dry" anaerobic conditions as given in follows: 12%, 19%, 25%, 32%, 39%, 45%. An organic substrate /microorganism ratio of 50 (w/w) was used to control the negative effects of starter microorganisms. The microorganisms were taken from a leachate of municipale solid wastes in an industrial treatment plant degrading municipal solid wastes. 2.5 ml trace element solution was added to the mixture. This trace element solution comprised of: 3 g/l FeCl<sub>2</sub>.4H<sub>2</sub>O, 0.9 g/l CoCl<sub>2</sub>.6H<sub>2</sub>O, 0.5 g/l NiCl<sub>2</sub>.6H<sub>2</sub>O, 0.5 g/l MnCl<sub>2</sub>.4H<sub>2</sub>O, 0.09 g/l H<sub>3</sub>BO<sub>3</sub>, 0.09 g/l ZnCl<sub>2</sub>, 0.09 g/l Na<sub>2</sub>SeO<sub>3</sub>, 0.09 g/l CuCl<sub>2</sub>.2H<sub>2</sub>O and 0.09 g/l Na<sub>2</sub>MoO<sub>4</sub>.2H<sub>2</sub>O, respectively. The analyses were performed during 450 days under mesophilic conditions (35°C) without mixing.

# 2.3 Analytical Procedures

The total gas generations and the gas composition were measured in the strat-up period while the metnane generation was measured under staedy state conditions in the digester. The total gas generation was detected by the water displacement method The biogas composition was analysed by a gas chromatography–mass spectrometry (GC-MS); a gas chromatograph (GC) (Agilent Technology Model 8890N GC equipped with a mass selective detector (Agilent Technology Model 5989 inert MSD) by injecting a sample volume of 2 ml. Mass spectra were recorded using a VGTS 250 spectrometer equipped with a capillary SE 52 column (HP5-MS 30 m, 0.25 mm ID, 0.25  $\mu$ m) at 220°C with an isothermal program for 10 min. The initial oven temperature was kept at 55°C for 1 min during 2 min, then the time was increased to 5.5 min. Helium (He) was used as the carrier gas at constant flow mode (1.7 ml/min, 49 cm/s linear velocity). The calibration was carried out with a standard gas composed of 29% CO<sub>2</sub>(g), 3% O<sub>2</sub>(g), 8% N<sub>2</sub>(g) and 60% CH<sub>4</sub>(g), respectively.

Volatile fatty acid concentrations were measured after centrifugation of samples at 14000 rpm for 40 min. in a GC-MS (Agilent 8890N GC – Agilent 5989 inert MSD). As carrier gas nitrogen  $[N_2(g)]$ was used. All other pollutant assays were performed according to the Standard Methods (2022), [41].

# 2.4 Measurement of Methane Productions

Biochemical methane potential was measured according to the method stated in the literature, [42]. The tests were performed in 600 ml glass serum bottles at 35°C. The glass bottles were filled with synthetic medium containing nutrients and trace elements, and granular sludge from a mesophilic anaerobic digester treating yeast industry wastewater in İzmir, Turkey. The final sludge concentration in the bottles was 45 gVS/l. The bottles were loaded with 1 g of cardboard (0.95 gVS). The calculated biochemical methane gas productions were accounted daily.

# 2.5 Anaerobic Degradation

The steps of anaerobic degradation consist from hydrolysis, acidogenesis, acetogenesis, and methanogenesis as shown in Figure 1 (Appendix). In hydrolysis, big molecular weigth compounds were break down too much smaller compounds. In the acidogenesis step, long-chain fatty acids transformed to short-chain volatile fatty acids, while in the acetogenesis step, acetate,  $CO_2$ , and/or hydrogen (H<sub>2</sub>) are formed via the fermentation of the volatile fatty acids. The produced acetate,  $CO_2(g)$  and/or H<sub>2</sub>(g) were transformed to methane via methanogen bacteria.

Anaerobic degradation process is affected by the temperature variations yielding with lowering of methane gas productions. The temperature in the anaerobic reactor affects the heat exchange between anaerobic reactor and anaerobic environment and a constant and appropriate temperature is required to sustain digesti. In the anaerobic digesters high

generations was detected the methane as temperature was elevated, [43], [44]. In order to increase the energy demand of the anaerobic Archae; an elevated heat transfer ratio is necessary. The static heating was performed by transporting of thermal energy to the anaerobic reactor with hot water in the reactor. For this a heat exchange coil device is necessary in the reactor. The negative points of static heating were low thermal yields cause to lowering of steady-state conditions during methane generation. When studying the static heating process during anaerobic digestion, polyethylene coiled tubing was used and a large temperature change was observed when operating in the vertical direction after heating, [45]. The dynamic heating process contains the releasing of thermal energy to the anaerobic reactor during direct heating of the recycled slurry. This cause to rapid heat transfer and homogenous increase of The dynamic digestion heating temperature. methods exhibited limitations during the pipeline transport, [46].

A lot of anaerobic digestion process was extensively used in the literature according to anaerobic digestion model No.1 model. This model is an effective for methane productions, [47], [48], [49], and includes a lot of steps. The growth and decay of different types of microorganisms were also taken into considerations, [50]. To simulate digestion in the presence of high solids during the digestion of organic matter of domestic solid waste; A new model was created based on the anaerobic digestion model No.1, [51]. In the comparison of conventional 'wet' anaerobic digestion model No.1, simulates the reactor mass to volume variation depending of high degradation of total solids. The model contains the relationships between total solid yields and methane generations. Municipal waste sizes, organic rate and organic matter load; A dynamic mathematical model was developed that includes the effects of anaerobic co-digestion of organic matter in municipal waste and domestic sludge on methane production and COD yield, [52]. The anaerobic degradation of the sewage sludge is simulated using the anaerobic digestion model No.1, while the degradation step of the organic substances was modelled by a surface-based kinetic, depending on the diameter of the composite substance.

# 2.6 Anaerobic Digestion Model No.1

A lot of mathematical models were present to determine the anaerobic digestion. These models were usefull to determine the anaerobic reactor dynamics. Anaerobic digestion model No.1 model four steps were present during degradation of organics: hydrolysis, acidogenesis, acetogenesis, and methanogenesis with generation and decay of microorganisms present in the anaerobic reactor, [36].

Physicochemical steps such as acid-base and notral pH variations and gas-liquid emissions. Due to high numbers of processes, and high 100 value of parameters, the calibration of the anaerobic reactor is difficult during methane productions. The anaerobic digestion model No.1 was utilized for optimization of the anaerobic methane gas productions A standardized anaerobic digestion model No.1 can be effective to solve the inhibitions during settling of volatile fatty acids. Since anaerobic digestion process is very sensitive due to anaerobic Archae bacteria the mathematical equibrium can not be solve the problems. The efficiency of the model was related to the data used for fitting of the model data. It was a relathionship between the inlet and output data. Each inlet value introducing to the methane reactor at a duration t is correlated with the output and leaves the digester at a time  $t + \Delta t$ . This time can be defined as retention duration. A lot of operational conditions such as flows and mixing regime, composition of the organics and substrate concentrations affects the yield. Therefore, complex ploblems originated from the parameters given above should be solved by expert researchers.

A lot of intelligence model techniques like artificial networks, fuzzy logic and expert models can be used to monitore and predict the anaerobic digestion. Nature-inspired methods were produced for specific biological systems relevant to biomass properties affects significantly the methane gas production in the anaerobic processes. It is important to note that which suitable models can be used to simulate the methane productions in anaerobic reactors.

# 2.7 Intelligence Models

Artificial intelligence models can be used in environmental. agricultural applications. in anthropological experiences, in medical fields, and in different types of engineering applications. These models can be utilized for modeling, predicting, and simulating to find meaningful solutions. Modeling is very difficult due to the complexity of the processes which were nonlinear, [53]. Therefore, with artificial intelligence models it is easy to predict nonlinear equations. Last studies in computing results decreased the time which is necessary to develop the equations, and to combine the new results based on new modifications.

Artificial intelligence can be applied to the new data developed in micro-scale. In the anaerobic digestion, when the relationships is complicated it is not possible to generate new mechanistic process models. Contrarily, some researchers were used artificial intelligence models to study under steadystate conditions during digestion process, [53]. By utilization of these model methane gas generation should be improved. Nature-inspired computing is a recently developed model for artificial intelligence techniques. Living and nonliving natural models can be able to study with the same or different data. When a central administration was not present, the processing was distributed. Steady-state conditions should be maintained during solving of the problems in engineering applications. Algorithms are iterative procedures to solve the problems step by step for specific aims. With computational optimization the algorithms can be designed, implemented and improved by solving the optimization problems, [54].

Optimization steps includes the improvement of the yields, of the efficiency, and decrease the energy and cost spent for the processs. If enuogh time was present, the problems can be solved under laboratory conditions while it is difficult to solve the problems in real applications such as anaerobic digestion. It is necessary some computer simulations.

# 2.8 Performed Statistical Data

ANOVA test were applied to the experimental data to determine F and P values and to show the significance between dependent and independent variables, [55]. Variation of the experimental data mean and standard deviation values was indicated by F ratio. F explain the variation of the data averages/expected variation of the date averages. P indicates the significance data, and d.f showes the freedom degrees. Regression analysis was applied to the experimental data to detect the regression coefficient  $R^2$ , [56]. These data were calculated using Microsoft Excel Program.

All experiments were carried out three times and the results are given as the means of triplicate samplings. The data relevant to the individual pollutant parameters are given as the mean with standard deviation (SD) values.

# **3** Results and Discussions

# 3.1 Why Heat Transfer is Important?

Heat transfer shows the flow of thermal energy managed by a non-equilibrium and non-uniform temperature in the processes. Factors affecting the heat transfer in an anaerobic digester with high solid content were as follows: microorganisms in starter (temperature, physiology, biomass maximum growth rates, catabolic heat generation), substrate type (particle diameter, type, porosity), equipment diameter (length and apparatus type) and operational conditions (biomass percentage in the starter culture, pH, temperature and humidity of the gas), [57], [58], [59]. Interphase mass transfer of methane gas from a liquid substrate was illustrated in Figure 2 (Appendix).

The heat transfer in an anaerobic digester with high solid content was relevant with the activity of metabolic rates. The substrates with low thermal conductivities cause to small heat transfer rates. Mechanical mixing and air supply with gas are two efficient methods to improve substrate agitation and provides suitable heat and mass transfer during the anaerobic digestion, [60]. During mechanical mixing, the size of the impeller and mixing properties affect significantly the, impeller, [61], [62]. Flow rates were affected by the speed and have not an important effect on the mixing rates. No more studies were found researching the specific impacts of the mixing methods on the performance of anaerobic digesters with high solid content, [61], [62].

# **3.2** Why Mass Transfer is Important?

Many efforts have been made due to the important A lot of studies were performed to detect the advice of mass transfer on the reaction yields. Mass transfer yields is relevant with concentration gradient of gases and substrates during advection or diffusion. In anaerobic processes the yields depend to mass transfers, to grafting, to the types of the organics, to temperature, to moisture ratio, and to mixing yields. In the compairison with wet anaerobic digestion reactors with high solid wate ratio exhibited some problems due to mass transfer was inhibited. To improve the relathionship between biodegradable substrates and anaerobic Archae bacteria it is important to provide suitable mass transfer, [63].

An anaerobic digester with high solid wastes has solids, liquids, and gas steps (Figure 2, Appendix) relevant to a solid organic compound, starter anaerobic culture, water, and gases namely methane, CO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>S). The organic solid compound should have a porous structure. Furthermore, the the shape and the diameter of the organic compounds, the void space for gas in tranferring were important parameters. The surface area of the substrates for bacterial methabolism and solid substrate uptaken yields are affected by the porosity of the substrates, [64].

The start-up of anaerobic digester having high solid content performed by a starter bacterial mass followed by the generation of a complex reaction and ultimately advances u up to stabilization of the solid wastes, [65]. In these studies, a minimum size of seed should be used, and the anaerobic yields are related with the activity of the of reactions. Volatile fatty acid was released and diffused to methanogenic Archae bacteria. In order to effective metabolism of Archae bacteria the presence of an alkaline buffer solution protect these bacteria from the volatile fatty acid accumulation and inhibition, [66], [67].

The volumetric mass transfer coefficient kLa is correlated with kL (mass transfer coefficient), and with specific surface area. In dry and semi-dry anaerobic digesters, the volumetric mass transfer coefficient kLa is significantly lowered depending to two items: (1) The solid–liquid/gas interface is small, since low biogas bubble and inadequate mixing. (2) The mass transfer coefficient was relevant with low moisture percentage. Eq. 1 indicates the difference between the diffusivity coefficients of readily degradable organics in the D<sub>i</sub> digester and in the water D<sub>i</sub> (Eq. 1):

$$k_{L}(digestate) = k_{L}(water) \left(\frac{D_{i}(digestate)}{D_{i}(water)}\right)^{0.5}$$
(1)

Diffusivity coefficients significantly lowered with lowering of porosity depending to water percentage and the elevated viscosity which is significantly depend to the solid content, [68], [69], [70].

Based on these assumptions, the maximum yield of the volumetric mass transfer coefficient is dependent to the total solids. A  $k_T = 0.5 d^{-1}$  was taken into consideration for the alalysis at TS = 10%.

#### 3.2.1 Operational Conditions Internal Mass Transfer

Mass transfer in the anaerobic digester was modeled by taken into consideration the diffusion alone and utilizint the Fick's law. The diffusion coefficient D in Fick's law is relevant to a constant or is not dependent to substrate dose. D is not measurable parameter and it can be calculated by multiplying the diffusion coefficient (Dw) of the solids in aqueous digester by a constant (< 1). No extensive knowledge was obtained about diffusion coefficient of solides in anaerobic digester utilizing Fick's law as showed in in Eq. (2), [71]:

$$J = -D\frac{d\varphi}{dx} \tag{2}$$

where, J: is the diffusion flux with an expression of amount of substrate per unit space per unit time. J indicates the dose of the substrate through a unit space during a unit duration. D: is the diffusion coefficient or diffusivity. Its dimension is space per unit duration.  $d\phi/dx$ : is the concentration gradient,  $\phi$ : is the dose of the concentration of substrate per unit volume. x: is the size of the length.

Internal mass transport inhibits the biofilm growth and bacteria types and affects the porosity and the cohesiveness, [72]. Dense bacterial growth can be defined by slow diffusion percentages. The porous media in bacterial growth increase the diffusion, [73]. Furthermore, extracellular polymeric material in bacterial growth impede the diffusion, and improved the resistance to antimicrobial chemicals, [74].

#### 3.2.2 Operational Conditions in External Mass Transporting

External mass transfer in granulated bacteria c can defined with small dimensions, while he complicated biomass negatively affects the bacteria. During the transferring of organic materials from the bulk liquid to the surface of a gigester, separated transport ways should be taken into consideration based on the diameter of the organic compounds. Since the complex hydrodynamic parameters generated problems some semiempirical relathionships should be taken into consideration to detecte rate of external mass transfer, [75]. An important problem was detected during operation of the anaerobic processes. In the absence of gaseous products shows the failing of the biologic process If the diffusion from the mass to the liquid phase is slow; the products are in the gas phase and the external mass transfer resistance is elevated and affects the whole reaction rate. The external mass transfer resistance is significantly affected by flow conditions; temperature, pressure, superficial velocity and particle size of substrate in the digester, [76]. By variation of the parameters mentioned above external mass transfer resistance can be decreased.

As a result, with the information of new data some fundamentel points led to improve mass transfer in anaerobic microorganisms. Under these conditions it is important to understand the effective paramaters to maintain elevated biogas generation in anaerobic digesters.

# **3.3 Impact of Some Factors Affecting of Heat** and Mass Transfer

In order to excellent optimize the anaerobic digesters with high solid wastes the influences of some inhibitory compounds should be taken into consideration to elevate the mass and heat transfer ratios, the biogas efficiency and substrate degradation yields. On the other hand, some factors in effluent like chemical and rheological, total solid levels, the ratio of organic compound to biological mass, adsorbents and surfactants concentrations, and mixing ratios affected the mass and heat transfer in anaerobic digester with high solid wastes. Different kind of waste inoculums can be used in anaerobic digester with high solid wastes such as organic substrates in domestic solid, food wastes, agricultural wastes, animal manures or organic industrial wastes. Various types of wastes cause to change of physicochemical properties and the anaerobic yields. The composition of waste bacteria varies with particle dimentions, structure and moisture percentages. Similarly, substrate type, crystal shape porosity, particle dimention, surface area and homogeneity also affect the yield of anaerobic digestion.

#### 3.3.1 Factors Affecting the Particle Dimention of Feedstock

The particle size is significant for biodegradation of substrate and growth of microorganisms. The surface area, density, heat/mass transfer, and microbial metabolites affect the particle dimention of feedstock. In a wet anaerobic digestion, lowering of particle diameter improves significantly the biodegradation kinetics and treatment yields, [77]. The degradation of bacteria with substrates and decreasing of particle size exhibited the pretreatment of organics to water and chemical substances. This cause to homogeneity and not clogging was detected. The impact of particle size changes on biogas generation for anaerobic digesters containing high solids should be researched very well, [6]. The lowering of particle size highligted the specific surface space and accelerates the microbial contact and improve the methane generation for the organic compounds with an elevated fiber ratio and degraded with difficulty, [6]. The big specific surface space affect significantly the growth and activity of bacteria. The bacterial metabolizing starts from the surface, penetrating the particle's interior and the porosity of the microorganisms is important for aquous flow versus solid organics in anaerobic disgester with high solid ratio.

Despite small grinding elevated the organic compound substrate contacting and conversion ratio, it elevated the problem originated from volatile fatty acids due to decanting of volatile fatty acids, [78]. In order to take some measures, the decanting of the inhibitory compounds on the asurface area should be prevented. The steady-state size affects the biodegradability and seed/organic material ratio, [79], [80]. Different suggestions were reported in recent literature about particle size affecting the methane generations, [81], the particle size distribution of input wastes for mechanistic and data-driven models, the paricle size is relevant with gas production for Biot numbers for heat transferring as mentioned in Eq. (3):

$$Bi_{heat} = \frac{h \cdot L}{\lambda} \tag{3}$$

and, Biot numbers for mass transfer was given in Eq. (4):

$$Bi_{mass} = \frac{k_m \cdot D}{L} \tag{4}$$

Biot numbers provide to obtain the competitive importance of internal resistance versus to external resistance. The length scale L in the expression for Bi is was accepted as the particle size,  $\lambda$  and D, are the thermal and mass diffusivities of solid wastes, and h and k<sub>m</sub> are the heat and mass transfer coefficients of solid wastess, respectively.

# 3.3.2 The Effect of Total Solid Content in Feedstock

The solid content significantly contributes to the diffusion and reaction kinetics, for quick diffusion and biodegradaion efficiencies, [82]. When the total solids elevated, the viscosity increased extremely, [83], while when the diffusivity coefficient showed a significant decrease, [84], the reduced mass transfer led to the accumulation of acids leading to the fail anaerobic digester having high solid ratio. Under semi-dry conditions, the volatile fatty acids elevated and the volatile solid ratio lowered. This limits the methane generations, [85]. When pH was between 4.0 and 6.9 the volatile acids not

dissociated since were inhibitory to the bacterial Archae, [86].

The diffusion coefficient, affecting the mass transfer, was investigated by a lot of studies containing wet conditions. Contarily, this coefficient in dry anaerobic digesters lowered immediately in anaerobic digesters with high solid ratio since the the diffusion phenomenon affect significantly the microorganism's rates, [87], [88]. Diffusion of liquides in in anaerobic digesters with high solid ratio was operated slowly when mixing was not used. When the total solids are greater than 19% and mixing is low, organic compounds originated from waste biota react and further degraded. The bacteria should be dispersed before the reactor start-up and for a suitable metabolic kinetic the seed and bacteria should be homogenized. The limitation of the transfer cause accumulation of acids during biodegradation, ending with the limitations in whole microbial activity, [89].

High total solid ratios contribute to the physical properties of the bacteria and waste seeds. The rheological properties of the digestere containing viscoelastic compounds elevated the problems relevant with yields especially at high total solids reactors. This situation affects the yield of mass transfer and sludge viscosity increased extremely when the diffusive coefficient decreased at digeters containing high solid content. Decreasing of mass transfer cause to the decanting of fatty acids and ammonia. This cause to fail of the process stabiliy resulting in variations of dominated bacteria metabolic reactions.

#### **3.3.3 Variation of Reactor Temperature**

The temperature of an anaerobic digested reactor with high solid content affect the microbial reactions in the feedstock and cause to heat losses. The anaerobic reactors were operated in 3 temperature types;

- 1. Psychrophilic (8°C 33°C),
- 2. Mesophilic (35°C 42°C),
- 3. Thermophilic (55°C 65°C).

Among them mesophilic and thermophilic conditions are extensively used, [90]. It is important to choose an operating temperature versus to type of feedstock such as food waste, straw derivative, domestic sludge and woody waste. This should improve thereaction kinetic, reactor stability, and biogas efficiencies. The feedstock composition is important to provide effective conditions for anaerobic digestion processes. In digester with high solid content the feedstock exhibited poor mass transfer, while a thermophilic temperature can be improving the anaerobic degradation yields resulting in high methane generations, [91]. Heat losses in thermophilic digesters is importantly sensitive to the disturbances in environmental conditions. In a thermophilic digester, the hydrolysis process decreased significantly with elevated fatty acid decantation ending with low stability, [92].

#### **3.3.4** Hydrodynamics Properties of the Digester

In anaerobic digesters with high solid ratio, the homogenation of the mechanical stirring reactor was attributed to long digestion time and poor substrates removal rates due to mass transfer inhibitions. These negative effects can be overcomed by leachate or digestate reuse, [12]. The mass transfer for digesters can be characterized by the Sherwood number as shown in Eq. (5):

$$S_h = f. \left( R_e \, . \, S_c \right) \tag{5}$$

which presents the ratio of advective mass transport to diffusive mass transport, [93]. Since Sh is significantly affect the Reynolds number Re and Schmidt number Sc (the ratio of kinematic viscosity to biomass diffusivity) variation of mixing rate the an advective mass transfer should be made for a good diffusivity. The influent waste with a high solid content can be characterized by its rheological structure likes high viscosity, shear-thinning, and thixotropy, [83]. The value of Sc for digesters with a high solid content was importantly elevated than wet anaerobic digesters. This phenomenon, inhibits the mass diffusion. For a constant ratio of total solids in the digesters with high solid content the Sc will be fixed since increasing of Sh cause to elevate of Re. The Re for mechanical strirring for high solid content digesters with non-Newtonian fluid is illustrated in Eq. (6), [61]:

$$Re = \frac{\rho N^{2-n} D^2}{K} \tag{6}$$

where,  $\rho$ : is the density of the fluid (kg/m<sup>3</sup>), N: is the rotational frequency (1/s), D: is the diameter of the mixing apparatus (m), K: is the consistency (Pa s<sup>n</sup>), and n: is the rheological flow index.

The digesters with high solid ratio have more unfermented metabolites. Due to inhibited heat and mass transfer compared to normal anaerobic digesters, recirculation of organic matter, nitrogen, phosphorus and anaerobic bacteria the digesters with high solid content digestated more efficiently ending with high organic compound degradation and extended digestion and more methane gas productions.

#### 3.3.5 Implementation of the Adsorbents or Surfactants

Non-ionic surfactants can be changed the organic material structure and make it hydrophilic and more accessible to enzymes with low-toxicity and more H<sub>2</sub> generation. This improve the yield of hydrolysis of bacteria, [94]. In order to minimize the treatment cost in anaerobic digesters without pretreatment iron can be added to the digester. Fe<sup>0</sup> powder can be used to increase the methane efficiency by 17%. Compared with Fe<sup>0</sup> powder, Fe is more effective in improving the reaction rate by 23% due to its elevated mass transfer yields with aquous and biomass. Fe in powder form can cause microbial  $Fe^{3+}$  depletion. This ultimately led to the highest methane production yields like 34.80% and the biggest reduction in volatile suspended solids (52.90%). The methane generation percentage can be elevated by implementation of limonite. This elevated the removal of soluble organic metabolites and increasing the distributions of bacteria contacting with protein and amino acids, [95]. Implementation of Fe and Ni can elevate the methane generation highlihting by the concentrations of archaeal bacteria, [96]. Porous adsorbents like biochar and activated carbon can be utilized to vary the types of bacteria and improve the biodegradation of substrates and buffering ratio and mass transfer and increasing the electron transfer ratio ending with high diffusion yields, [97], [98], [99], [100]. The presence of biochar also increases the numbers of Syntrophomonas and methanogens Methanosarcina and Methanocelleus, and acetoclastic/hydrogenotrophic bacteria.

# **3.4 Modelling of the Anaerobic Digesters**

Anaerobic digestion is a mixture of biochemical reaction between feedstock hydrodynamics and bacteria to produce methane gas as effluent. The modelling of these phenomenon is difficult. When anerobic digestion was modelled in order to elevate the reactor performance some suitable scenarios should be performed for a good optimization, design control by taken some measures by preventing the falling of operation of anaerobic reactors. Three types of models can be utilized to operate the anaerobic digesters: (a) biochemical kinetic models, [101], (b) computational fluid flow models, [102], and (c) data-driven models, [103].

# 3.5 Maximum Methane Generation Percentages

The maximum methane generation percentages were measured at 12% TS, 19% TS, 25% TS, 32%

TS, 39% TS and 45% TS, respectively, after 365 days operation duration (Table 1, Appendix). The methane yields were relevant to TS ratio in the digesters. Analyses of variance were performed. The role of TS content on anaerobic digestion was investigated in anaerobic batch reactors. A range of TS contents from 12% to 45% was evaluated. 4.9, 3.2, 2.9, 1.9 and 0.9 ml/g VS/d maximum methane gas generation percentages were detected after 19% TS, 25% TS, 32% TS, 39% TS and 45% TS, respectively, after 365 days. The total methane generations slightly lowered with increasing TS concentrations as the TS ratio was increased from 12% to 32% TS. Two different explanations can be performed at 39% TS while methane percentage was inhibited. These limits can be explained by the inhibition of anaerobic digestion at high solids ratio since the accumulation of volatile acids. 7.16 ml/g VS/d maximum methane production was detected at 12% TS ratio after 365 days. The methane generation was inversely correlated with total solid doses (Table 1, Appendix).

In batch tests, higher methane production was found in digesters containing 22% TS compared to 33% TS for mesophilic conditions, [104]. Similarly, increased methane production was mentioned in thermophilic batch tests at 22% TS compared to 29% TS and even higher than 34% TS, [105]. Low methane yields of  $\approx$  21 ml/g VS were obtained at 39% TS.

# 3.6 Measured pH and Volatile Fatty Acid Levels

pH values and VFA concentrations were observed after 365 days at anaerobic digesters containing 12% TS, 19% TS, 25% TS, 32% TS, 39% TS and 45% TS, respectively (Table 1, Appendix).

7.2, 7.4, 7.9 7.8 and 6.6 pH values were measured at digesters containing 12% TS, 19% TS, 25% TS, 39% TS and 45% TS, respectively, after 365 days of operation time. The pH=8.0 value was found at digesters containing 32% TS after 365 days (Table 1, Appendix).

27, 29, 33, 39 and 16 g/l volatile fatty acid concentrations were obtained at digesters containing 12% TS, 19% TS, 32% TS, 39% TS and 45% TS contents, respectively, after 350 days of operation time (Table 1, Appendix). The maximum 43 g/l VFA concentration was obtained at digesters containing 25% TS after 365 days operation time (Table 1, Appendix).

# **3.7** Cumulative Methane Generations

The cumulative methane levels at digesters containing 32% TS and 39% TS, were 149 and 142

ml/g VS/d, respectively, after 365 days operation time (Figure 3, Appendix). The maximum cumulative methane production was measured as 55, 129, 152, 159 and 186 ml/g VS/d at digesters containing 12% TS after 53 days, 120 days, 159 days, 230 days and 365 days operation times, respectively. The cumulative methane generations data slightly decreased at digesters containing 12% TS and 39% TS (Figure 3, Appendix).

# **3.8** Properties of Dynamic Digestion

The resaerchers studied with anaerobic digesters containing high solid ratio at anaerobic digestion model No.1 mentioned that two gas generation maximums were detected at anaerobic digestion with medium temperature  $(30^{\circ}\text{C} - 38^{\circ}\text{C})$  and elevated temperature  $(50^{\circ}\text{C} - 55^{\circ}\text{C})$ , [92], [106]. For minor and medium-types biogas processes, the medium temperature digestion process was found to be the most economical one with a temperature of  $35^{\circ}$  C. As a result,  $35^{\circ}$ C was selected as the digestion temperature for determine the impacts of dinamic digestion researchers for anaerobic digestion containing high solid wastes process at anaerobic digestion model No.1.

The cumulative biogas generation ratio of the dinamic digestion researchers with anaerobic digestion containing high solid wastes process at anaerobic digestion model No.1 during 365-day assays was operated at 35°C (Figure 4, Appendix). 0.19, 0.37, 0.46, 0.55, 0.56, 0.49, 0.48, 0.38 and 0.32 m<sup>3</sup>/m<sup>3</sup>.d maximum biogas production rates were found for dinamic digester researchers for anaerobic digestion model No.1 after 29, 55, 85, 121, 159, 179, 210, 230 and 259 days operation times, respectively, at 35°C (Figure 4, Appendix). 0.69 m<sup>3</sup>/m<sup>3</sup>.d maximum biogas production rate of dinamic digester for anaerobic digestion containing high solid wastes process at anaerobic digestion model No.1 was detected after 145 days operation time, at 35°C (Figure 4, Appendix).

Figure 4 (Appendix) shows the biogas generation ratio of dinamic digester researchers: 0.134  $m^3/m^3.d$ ) and standard digestion researchers: 0.165  $m^3/m^3.d$ ). The biogas generation ratio of dinamic digester researchers was importantly bigger than that of static digestion researchers (Figure 4, Appendix).

3.9 Data Analysis of Static Digestion Researchers for Anaerobic Digestion Containing High Solid Wastes Process at Anaerobic Digestion Model No.1.

The cumulative biogas production rate of static digestion researchers for anaerobic digestion containing high solid wastes process at anaerobic digestion model No.1 during the 365-day experiment at 35°C digestion temperature was determined and is summarized in Figure 5 (Appendix). 0.04, 0.26, 0.20, 0.17, 0.25, 0.24, 0.21, 0.20 and 0.19 m<sup>3</sup>/m<sup>3</sup>.d maximum biogas generation ratios were detected for static digestion researchers for high solid wastes process at anaerobic digestion model No.1 model after 25, 50, 75, 100, 150, 175, 200, 225 and 250 days operation times, respectively, at 35°C (Figure 5, Appendix).

0.36 m<sup>3</sup>/m<sup>3</sup>.d maximum biogas production rate of static digestion researchers for anaerobic digestion containing high solid wastes process at anaerobic digestion model No.1 was detected after 160 days duration at 35°C (Figure 5, Appendix).

Mixing is an important point affecting significantly the gas generation ratio of anaerobic digestion. With no mixing, several problems like uneven material distribution, poor fluidity, and difficulties in the heat and mass transportations in the static digestion process were detected, [107], [108], [109], [110]. Contrarily, mixing by dinamic digester significantly accelerate the digestion yield and biogas generation ratio.

Static digestion models can be utilized as a limiting method, when a lot of tests were necessary for complicated anaerobic systems. In order to explain in detail, the digestive process, son unravelling mechanisms should be taken into consideration in molecular scale. For example, phospholipids dissolved by the gastric mucosa mentioned that to contact with globular proteins like  $\beta$ -lactoglobulin to streigtenentgh its shape and inhibits to the role of pepsin, [111].

A wide variety of static digestion models have been investigated by utilizing some parameters like pH, ionic strength, time of each step and enzymatic studies and the data obtained was not extensively explained and compared with other references. In order to solve the problem, the data should be compared with other data. It is necessary to mention a digestion menu for all scientific communities. Furthermore, the international researchers group namely INFOGEST consisting of all scientists working about digestion was declared a consensus about static digestion for public health, [112], [113].

# 3.10 Differences between Dinamic Digestion and Static Digestion Resaerchers for Anaerobic Digester Containing High Solid Compounds for Anaerobic Digestion Method No.1.

The dinamic digestion and static digestion resaerchers for anaerobic digester resaerchers high solid compounds process with anaerobic digestion method No.1 was tabulated in Table 2 (Appendix). The digesters of both researchers were operated under a temperature of 35°C, by different temperatures. A high static-curve fitting interaction was found between the cumulative biogas generation and duration. The cumulative biogas generation of dinamic digester researchers (standard deviation of 74.24 m<sup>3</sup>) and static digestion researchers (standard deviation of 33.86 m<sup>3</sup>) process were 222.88 m<sup>3</sup> and 88.56 m<sup>3</sup>, respectively. This showed that cumulative biogas generation of dinamic digester researchers was importantly elevated than that of static digester researchers Table 2 (Appendix). After 550 days of the assays, dinamic digester reaserchers elevated the the outlet of digestion. Contrarily, the cumulative biogas generation provided the quick growth in static digestion researchers. This showed that the anaerobic digestion with high solid content for dinamic digester researchers was not long compared to anaerobic digestion with high solid content process for static digestion researchers. In this last process, a lot of organics were not transformed ultimately due to lower mass release in static digestion researchers for anaerobic digestion with high solid content at anaerobic digestion model No.1 Table 2 (Appendix).

The energy results of dinamic digestion and static digester researchers for anaerobic digestion containing high solids ratio process at anaerobic digestion model No.1 are illustrated in Table 2 (Appendix). Assuming that the calorific value of the fresh liquid was calculated as 4267 kJ/kg, [114]. The total energy of liquid for dinamic digestion and static digestion researchers for anaerobic reactor having high solid ratio process at anaerobic digestion model No.1 were calculated as 28645.8 MJ (Table 2, Appendix). It can be concluded that the ingredients of dinamic and static digestion researchers was calculated as 60%. Total biogas generation of dinamic digestion and static digestion reserchers for anaerobic digestion containing high ratio process at anaerobic digestion solids containing high solid ratio model were calculated as 223.88 and 95.33 m<sup>3</sup>, respectively (Table 2, Appendix). Based on these data, the biomass energy

transformation yields of the liquid calculated for the dinamic digestion and static digestion researchers for process at anaerobic digestion containing high solid ratio model were 19.89% and 8.56%, respectively (Table 2, Appendix).

# 4 Conclusions

When we compare the data obtained from dynamic digestion and static digestion researchers after 365 days showed that the biogas generation for dynamic digestion researchers was 134.32 m<sup>3</sup> or 151.67% bigger than that of static digestion researchers with the same digestion temperature for municipal solid wastes with the anaerobic digestion model No.1 for anaerobic digestion containing high solid ratio in anaerobic digestion process in anaerobic batch reactors. The role of total solid content on anaerobic digestion with high solid waste was researched in anaerobic batch reactors. A ratio of total solids varying from 12% to 45% was evaluated.

7.16 ml/g VS/d maximum methane generation yield was detected at 12% TS content after 365 days duration. Methane generation was not correlated to the Total Solid dose. The maximum pH of 8.0 was found at 32% TS content after 365 days duration. The maximum 43 g/l VFA dose was measured at 25% TS content after 365 days duration. The maximum cumulative methane generation data were detected at 12% TS content for 57, 129, 152, 159, and 186 ml/gVS cumulative methane generation after 53 days, 120 days, 159 days, 230 days, and 365 days durations, respectively.

The cumulative methane generation data slightly lowered with the TS ratio increasing from 12% TS to 39% TS. The total methane generation slightly lowered as the TS doses were increased from 12% to 32% TS. Two different items happened at 39% TS: Methane generation was decreased as found at 39% TS. This can be explained as follows: In the hydrolysis scale and liquid/gas mass transportation was researched and it was found that the mass transfer inhibition could be attributed to low methane generation at elevated TS, and that hydrolysis yield constant slightly lowered by elevating TS.

A simple anaerobic digestion model is useful to assume the methane generation. To lower the addition of fossil fuels to energy requirements some solar thermal collectors can be utilized to provide thermal energy in anaerobic digesters. Photovoltaic (PV) panels can be used as electricity source. Different approaches, like the development of a sustainable mobility scenario on the utilization of methane on vehicles, will provide to detect elevated yields from anaerobic digesters.

For elevated yields from the generated anaerobic digestion model No.1 integrations to the vehicles, to thermal tanks, to solar thermal collectors, to PV panels, to amplification devices, and high-pressure devices liquefied methane can be collected.

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# **APPENDIX**



Fig. 1: Generalized representation of the steps involved in anaerobic digestion; (LCFA: Long chain fatty acids, VFAs; Volatile fatty acids. Reproduced with permission from Ref., [92].



Fig. 2: Interphase mass transfer of biogas from a liquid substrate (e.g., waste stream), G<sub>j</sub> and G<sub>D,j</sub> are the jth undissolved and dissolved biogas species. Reproduced with permission from Ref., [92].

Table 1. Effect of TS content on HSA	AD performance for maximum C	CH <sub>4</sub> (g) production rate, CH <sub>4</sub> (g) production
yield,	pH and VFA concentrations, res	spectively.

TS Content	Maximum CH <sub>4</sub> (g) Production Yield	Time	рН	VFA Concentrations
(%)	(ml/g VS/d)	(days)	Values	(g/l)
12%	7.16	365	7.2	27
19%	4.9	365	7.4	29
25%	3.2	365	7.9	43
32%	2.9	365	8.0	33
39%	1.9	365	7.8	39
45%	0.9	365	6.6	16



Fig. 3: The values of cumulative CH<sub>4</sub>(g) production for different TS contents after 365 days and at 35°C.



Fig. 4: The values of biogas production rates of dynamic digestion (DD) process after 365 days and at 35°C.



Fig. 5: The values of biogas production rates of static digestion (SD) process after 365 days and at 35°C.

	Fnorm	Anaerobic Digestion Model No.1			High Solid Ratio Model		
Digestion Processes	of Slurry (MJ)	Cumulativ e Biogas Generation (m <sup>3</sup> )	Energy of Biogas (MJ)	Biogass Energy Transformatio n Yields (%)	Cumulativ e Biogass Generation (m <sup>3</sup> )	Energy of Biogas (MJ)	Biogass Energy Transformatio n Yields (%)
Dynamic digestion (DD)	28645. 8	222.88	17192.8 8	29.84	223.88	11458.3 2	19.89
Static digestion (SD)	28645. 8	88.56	11452.9 2	12.84	95.33	4927.08	8.56
Differenc e between DD and SD process $(\Delta = DD$ - SD)	0	134.32	5739.96	17.00	128.55	6531.24	11.33

Table 2. The comparison of anaerobic digestion model No.1 model with high solid ratio model for dynamic
digestion (DD) and static digestion (SD) processes.

### **Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)**

Prof. Dr. Delia Teresa Sponza and Post-Dr. Rukiye Öztekin took an active role in every stage of the preparation of this article.

The authors equally contributed in the present research, at all stages from the formulation of the problem to the final findings and solution.

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# **Conflict of Interest**

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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