CHAPTER TWO: LITERATURE REVIEW

This chapter reviews literature of Mathematical modeling and simulation of anaerobic digestion process. This Chapter consists of literature review of anaerobic digestion process, modeling of AD process, plug flow reactors used in AD and plug flow reactor modeling in anaerobic digestion.

2. Literature review

2.1 Anaerobic Digestion

Anaerobic degradation or digestion can be defined as a biological conversion process without external electron acceptor such as oxygen (Angelidaki, 2004). This technology has been recognized as core of sustainable waste management (Mahmoud, *et al*., 2004). Anaerobic digester is a reactor where the removals of organic matters are carried out with the help of microorganisms (Rowse, 2011). There are many factors which affect the design and performance of anaerobic digestion process (Zhang, *et al*., 2006).

2.2 Anaerobic digestion Process fundamentals

Anaerobic digestion is one form of the naturally occurring process of decomposition and decay, by which organic matter (animal waste or biomass) is broken down to its simpler chemical constituents (Metcalf and Eddy, 2003). Conversion of complex biomass in to methane is done under series of biochemical stages (Rathnasiri, 2009). These can be basically categorized as disintegration, hydrolysis, fermentation (acidogenesis), acetogenesis (acetate generation) and methanogenesis (methane generation) (Batstone, *et al*., 2002).

2.2.1 Disintegration and hydrolysis

Disintegration and Hydrolysis is the first step of anaerobic digestion. There are conversions of particulate matter into organic compounds like carbohydrates, protein and lipids that it involves an array of different steps such as lysis, non – enzymatic decay, phase separation and physical breakdown (Batstone, *et al*., 2002). If the substrate is in particulate form, hydrolysis will become the limiting step of the digestion process (Bouallagui, *et al*., 2005) and it is one of the key factors involved in measuring the performance and prediction of AD of complex wastes (Alvarez,

2003). Further hydrolysis rate depends of the pH, temperature, composition and concentration of intermediate compounds as well (Fantozzi and Buratti, 2009).

2.2.2 Fermentation of organic monomers (acidogenesis)

In this stage, hydrolyzed products are transformed to short chain or volatile fatty acids (VFA), like propionic and butyric acid, and subsequently into acetic acid and other VFA, hydrogen and carbon dioxide and ethanol (Marti, 2008). The same groups of microorganisms involved in hydrolysis are responsible in this conversion (Botheju, 2010). Propionic, butyric and valeric acids produced in this step are referred to here as VFA (Alvarez, 2003).

2.2.3 Acetogenesis Process

The conversion of LCFA (Long chain fatty acids) and VFA into acetate, carbon dioxide and hydrogen take place in acetogenesis phase (Batstone, *et al*., 2002). The hydrogen producing acetogenic bacteria are responsible for the anaerobic oxidation of the products generated in the acidogenic phase into substrates suitable for methanogens (Rathnasiri, 2009).

2.2.4 Methanogenesis Process

Methenogenisis phase is responsible for the production of methane and carbon dioxide from the acetates and the hydrogen. It has been found that the methane is formed by two classes of methanogenesis bacteria that hydrogenotropic methanogenesis produce methane from hydrogen (H_2) and aceticlastic methanogenesis does it by using acetates (Rathnasiri, 2009). The primary aceticlastic methanogens, *Methanosachia* and *Methanosaeta* relatively law growing genera than the hydrogenotrophs (hydrogen – Oxidation Methanogens) as the excess of hydrogen formed during the acid formation can be affected to the methanogenesis (Joseph, *et al.*, 1992).

2.3 Mathematical modeling of AD process

Anaerobic digestion systems are rather complex processes that unfortunately often suffer from instability (Lyberatos and Skiadas, 1999) . The optimization of the AD and the assessment of its operation as a function of varying feed or operating conditions are important objectives and can be pursued by using appropriate digestion models (Appels, *et al*., 2008). Therefore process modeling is a useful tool for describing and predicting the performance of anaerobic digestion systems (Siles, *et al*., 2008). In addition to that models have potentials for revealing non-linear behaviors of the system and to quantify the performance of alternative operational setups (Ossiansson and Lidholm, 2008).

There are many anaerobic digestion models available at present (Appels, *et al*., 2008). Mostly the Monod type kinetic models have been widely used to describe the process kinetics of anaerobic digesters (Siles, *et al*., 2007). Having defined the rate limiting step, early models described the digestion model under steady state conditions (Lyberatos and Skiadas, 1999; Lee, *et al*., 2009). The limiting step itself depends on various factors such as wastewater characteristics, hydraulic loading and temperature (Appels, *et al*., 2008). Thus it is obvious that "limiting step hypothesis" leads to simple and readily usable models. In fact such models, do not describe very well the digester behavior, especially under transient (Lyberatos and Skiadas, 1999)

In Graef and Andrews model (1974), the limiting step was taken as the conversion of fatty acids in to biogas and only involves acetoclastic methanogenens (Graef and Andrews, 1974, Cited by Lyberatos and Skiadas, 1999). An assumption was made on model of Hill (1982) in which methanogenesis depends on the total fatty acids and inhibition occurs due to the concentration of TFA (Hill, 1982).

Angelidaki- 1993, developed a mathematical model especially for the digestion of manure. The ammonia inhibition is focuses in the model and a detailed description of pH and temperature characteristics are included in order to accurately simulate free ammonia concentration (Angelidaki, *et al.*, 1993, Cited by Chen, *et al*., 2008).

2.3.1 Siegrist Model

Anaerobic digestion has been considered as a degradation of complex, polymeric organic materials involving combination of series and parallel reactions (Povlostathis and Giraldo-Gomez, 1991). Siegrist model provides a slightly simplified model compared with ADM 1 (Anaerobic Digestion Model 1) published by International water association (IWA) to illustrate the degradation process. Here the hydrolysis rate is modeled as a single step process with first order kinetics with respect to the concentration of particulate matter. The model parameters are based on experiments and calibration and validation of model was done by lab experiments (Lidholm and Ossiansson, 2008).

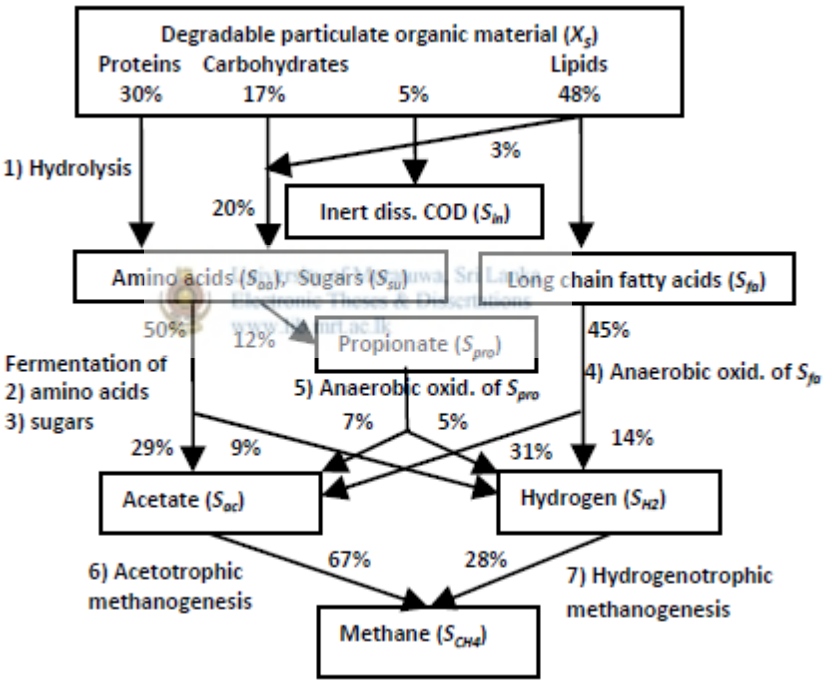

Figure 2-1: Schematic diagram of Siegrist Model

2.3.2 AM2 Model

AM2 model was developed jointly by researchers of the INRA **(**National Institute for Agricultural Research) of Narbonne and the INRIA of Sophia-Antipolis in 2001 (Olivier *et al*., 2001, Cited by Kerroum, 2010). This model is based on experimental

results obtained on the fixed bed reactor of the INRA of Narbonne. Acidogenesis and methanogenesis are the two main bacteria populations considered for the model development. The main feature of the AM2 is the consideration of the principal steps of anaerobic digestion process that are, respectively, substrate disintegration (non biological step), hydrolysis, acidogenesis, acetogenesis and finally the methanogenesis with seven different bacteria groups(Derbal, *et al*., 2009).

2.3.3 ADM1 Model

The ADM1 (Anaerobic digestion model 1) was developed by the task group for International water association (IWA) and published in 2002 (Batstone, *et al*., 2002). It is one of the most sophisticated and complex model (Dereli, *et al*., 2010).

ADM 1 contains five steps of biochemical conversion processes and eight bacterial groups as mentioned below. Those are disintegration of complex particulates, hydrolysis of particulate monomers, acidogenesis of soluble COD (sugars, AA and LCFA) to mixed VFA, hydrogen and carbon-dioxide by two acidogens bacterial species, acetogenesis of VFA (valerate, butyrate and propionate) to acetate, hydrogen and carbon-dioxide by acetogens bacteria and Finally, heterotrophic methanogenesis of acetate to methane and carbon-dioxide by acetoclastic methanogens archaea and autotrophic methanogenesis of both hydrogen and carbon-dioxide to methane by hydrogenophilic methanogens archaea (Fezzani and Cheikh, 2008). The main differences of ADM 1 from Siegrist model are the exclusion of valerate and butyrate as state variables (Lidholm and Ossiansson, 2008).

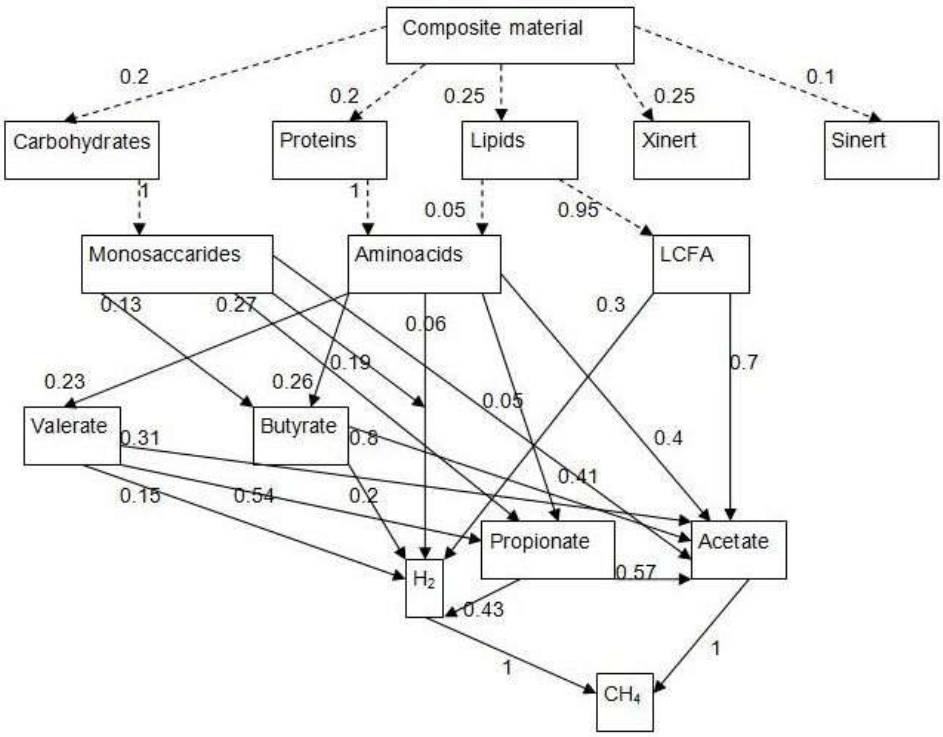

Figure 2-2: Schematic diagram of anaerobic digestion Model-1

Research on AD modeling with ADM1 helps to improve the original ADM1 via modifications in various ways such as the inclusion of lactate and ethanol into ADM1 for accurate bio-hydrogen simulations (Ratnasiri, 2009). Phenol anaerobic degradation is a complex process and extension was proposed with an inclusion of many modifications to the existing model (Fezzani and cheikh, 2009). Another extension was proposed to sulfate reduction process in AD (Fedorovich *etal*, 2003). Further ADM1 was modified to simulate AD process in high rate reactors with significant axial dispersion like in up flow anaerobic sludge bed (UASB) reactors. There the kinetics of biomass growth in ADM1 was combined with substrate transformation with axial dispersion (Mu, *etal*., 2008). In order to predict the inhibition of methanogenic process due to high TVFA concentration at low HRT, the existing inhibition function in ADM1 applied for the rate of acetate uptake was modified (Fezzani and Cheikh, 2008).

2.4 Modeling and Simulation Tools

2.4.1 Biological process modeling using AQUASIM 2.1 f

AQUASIM 2.1f is a computer program for the identification and simulation of aquatic systems. It facilitates to build mathematical models to various complex aquatic systems in an integrated environment. In addition to dynamic simulation this provides two powerful tools: linear sensitivity analysis and parameter estimation, where the latter tool was used for estimating the kinetics parameters by combining with given data (Feng, *et al*., 2006). AQUASIM is an extremely flexible in allowing the user-specified model; it provides elementary methods for simulations, for parameter estimation and for parameter sensitivity analysis (Reichert, 1998).

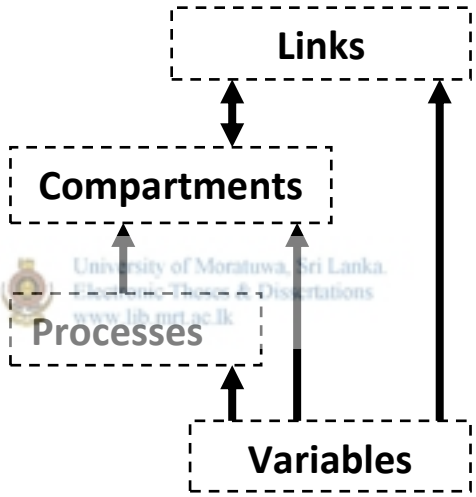

Figure 2-3: Main elements of AQUASIM model structure (Reichert, 1998)

Figure 2-3 illustrate the interaction between the four subsystems of variables, processes, compartments and links. Variables and processes must be defined before they can be activated in compartments. Finally, links can be used to connect compartments that are already defined. All these definitions together form the model used by AQUASIM for simulation and data analysis.

2.5 Anaerobic digesters for solid waste treatment

Anaerobic digesters can be categorized in terms of their operating criteria (Tchobanoglous, *etal*., 2003). According to the general characterial digestion process is categorized as either ‘wet’ or ‘dry’ system. In addition to that it can be further classified as ‘batch’ or ‘continuous’ according to the regime of loading.

Digester technology has revolved in several aspects at present day. Many number of new reactor design have been introduced and developed in order to get a significant rate of reaction per unit volume of reactor (Bouallagui, 2004). Accordingly reactor systems, further categorized as one- stage system and multiple-stage systems. Stages equal to the number of reactors in the system (Nizami and Murphy, 2010). The aim of development of multi-stage system is to improve AD by having separate reactors for the different stages. Accordingly two stage reactors are used in which first reactor for the hydrolysis/liquefaction/acetogenesis and second for methanogenesis (Monnet, 2003). This method has a capability to maximize both energy recovery and COD removal efficiency (Park *et al*., 2010).

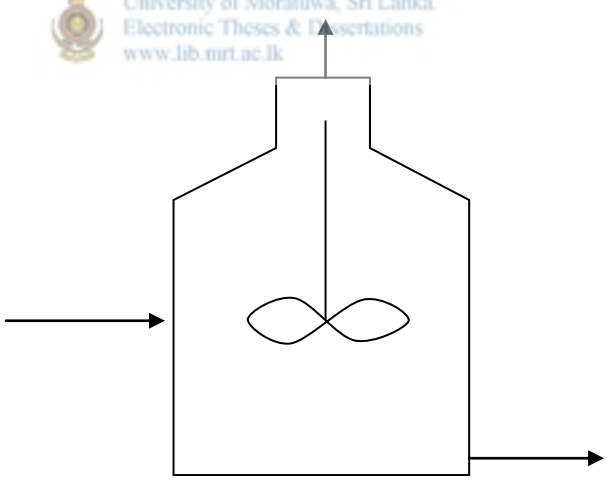

Figure 2-4: One stage system

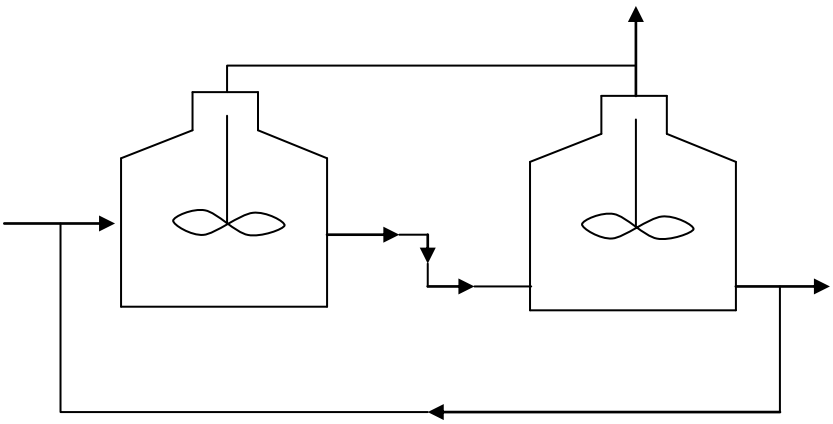

Figure 2-5: Two stage system

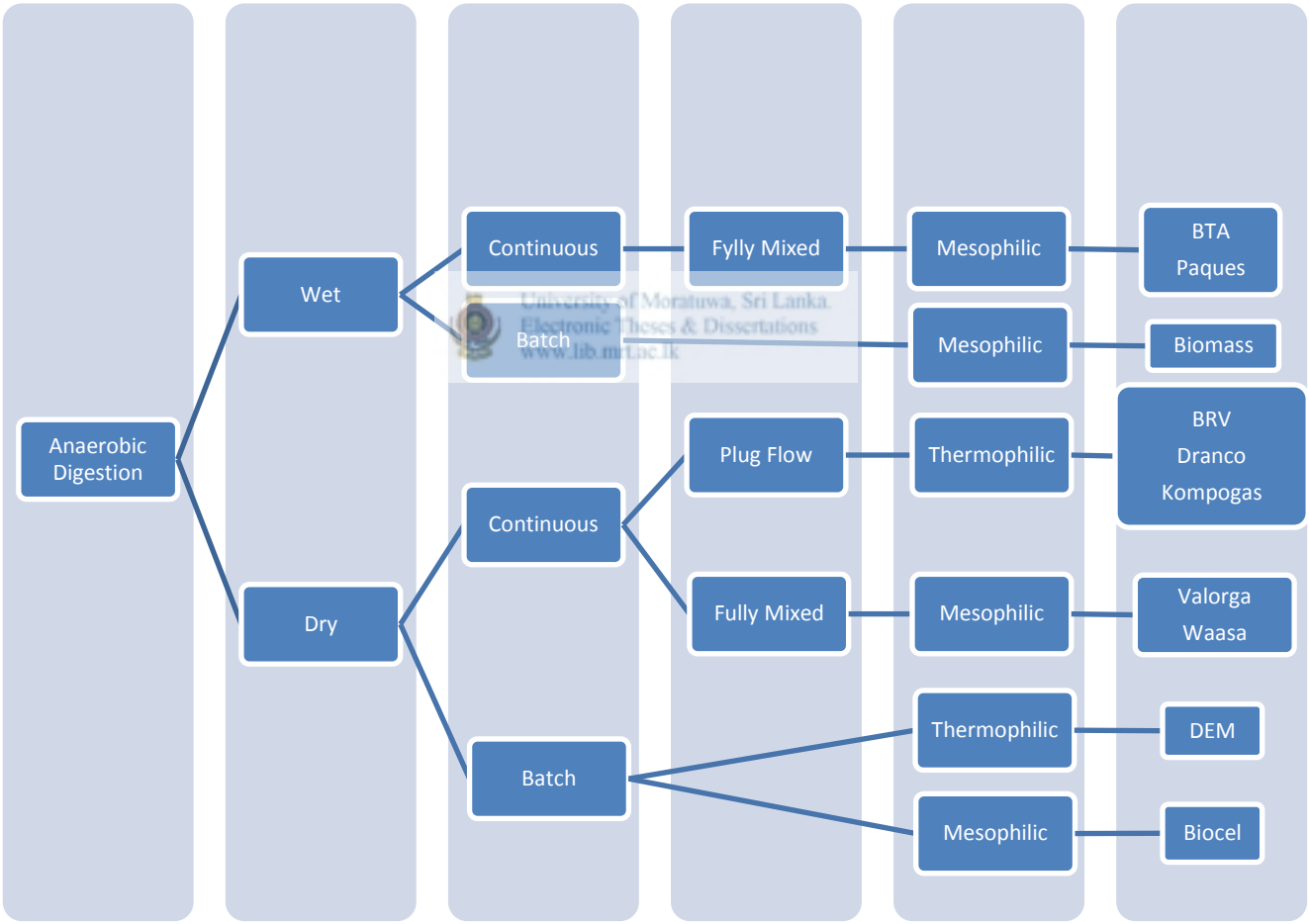

Figure 2-6: Classification of AD by operational criteria

2.5.1 Batch system

Batch digesters are filled once with fresh waste. Inoculums are added into the system in order to initiate the biological reaction process but it is not mandatory in dry batch systems (Alvarez, 2003). These systems are easy to design and control. The primary disadvantage of batch digesters is uneven gas production and lack of stability in the microbial population (Rapport, 2008).

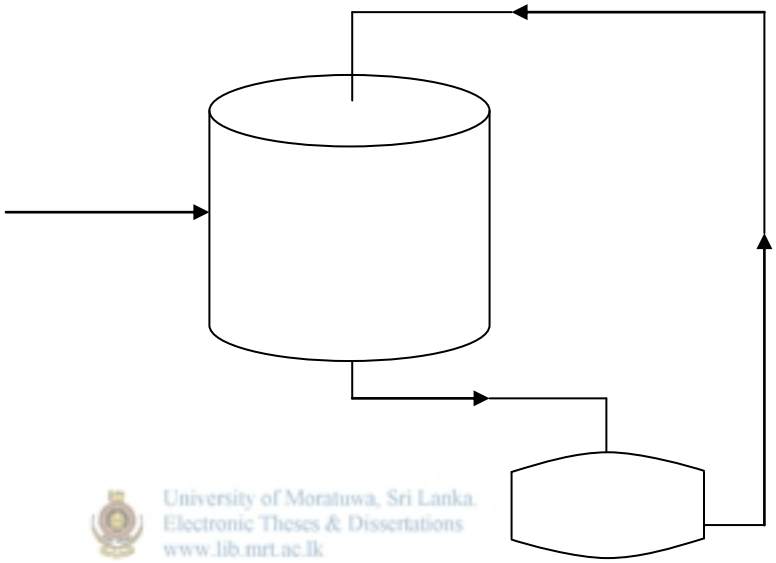

Figure 2-7: Batch system

2.5.2 Continuous system

In continuous system the feed is supplied to the reactor continuously. Continuous stirred tank reactor is the basic reactor that can be used in AD. Up flow anaerobic sludge blanket (UASB) reactor performs well in its operation. It is the most popular reactor design for the high rate anaerobic treatment of industrial waste water (Tchobanoglous, *et al.*, 2003). It can handle high volumetric rates, good CH_4 productivity and low sludge production makes the process economically and technologically attractive (Chavez, *et al.*, 2005).

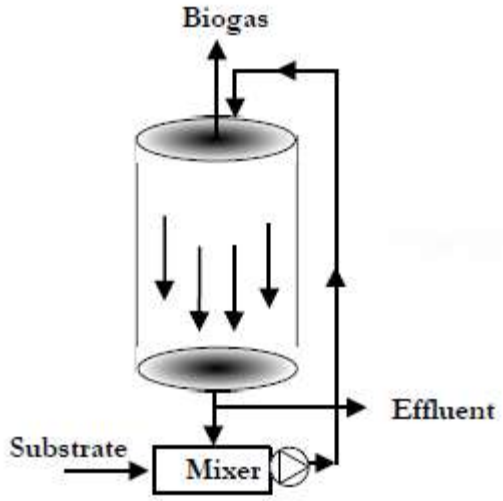

Figure 2-8: Continuous system

2.6 Plug flow reactors

In a plug flow or tubular reactor the substrate flows along an axial direction in a tubular container. Under the ideal condition, no mixing can observe in axial direction and concentration is uniform through the radial direction.

Tubular reactors have developed in many ways in order to increase the gas production and reduce the inhibition according to the various factors. At present, it can be observed that many types of tubular reactors have come up with impressive inventions targeting the both performance and cost effectiveness as well.

In most of anaerobic digesters, failures occur due to the rapid acidification following production of volatile fatty acids. This causes to decrease the pH in the reactor and consequence is the inhibition of activity of methanogenic bacteria (Namsree, 2012).

2.6.1 Mathematical modeling of plug flow reactor

The tubular flow reactor is a convenient means of approaching the performance characteristics of a batch reactor on a continuous basis (Charles, 1977). In ideal plug for reactors, it is assumed that the fluid particles pass through the reactor with little

or no longitudinal mixing and exit from the reactor in the same sequence in which they entered.

Development of a Mathematical model can be initiated by applying material balance to a small reactor segment ΔV. The C is defined as the concentration of constituent which uniformly distributed across the cross section area of the control volume and there is no longitudinal dispersion.

Material balance over differential volume element ΔV on a reactive constituent C is written as follows:

$$\text{Accumulation} = \text{Inflow} - \text{Outflow} + \text{Generation}$$

$$\frac{\partial C}{\partial t}\Delta V = QC_x - QC_{x+\Delta x} + r_c \Delta V \qquad \text{Eq(1)}$$

Figure 2-9: Schematic of plug flow reactor

Where $\frac{\partial C}{\partial t}$ = Change in average concentration with time, (g/m^3.s)

C = Constituent concentration (g/m^3)

ΔV = Differential volume element (m^3)

Q = Volumetric flow rate (m^3/s)

r_c = Reaction rate for constituent (g/m^3.s)

$$QC_{x+\Delta x} = Q(C + \frac{\Delta C}{\Delta x}\Delta x) \qquad \text{Eq(2)}$$

Substituting the differential form of $QC_{x+\Delta x}$ in Eq: 1

$$\frac{\partial C}{\partial t}\Delta V = QC_x - Q(C + \frac{\Delta C}{\Delta x}\Delta x) + r_c \Delta V \qquad \text{Eq (3)}$$

Substituting $A\Delta x$ for ΔV and dividing by A and Δx yields

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\Delta C}{\Delta x} + r_c \qquad \text{Eq(4)}$$

Taking the limit as Δx approaches zero yields

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + r_c \qquad \text{Eq(5)}$$

The Eq: 5 is the deferential format of change of constituent concentration in plug flow reactor (Metcalf and Eddy, 2003).

2.6.2 Mathematical model of Advective diffusive reactor of AQUASIM 2.1

In AQUASIM 2.1, reactor compartment known as advective-diffusive reactor describes the one dimensional advective-diffusive transport of substances, which can be used to model plug flow reactor with certain assumptions (Reichert, 1998).

The conservation law for one dimensional material flow in advective-diffusive reactor is expressed in Eq: 6.

$$\frac{\partial \hat{\rho}}{\partial t} + \frac{\partial \hat{j}}{\partial x} = \hat{r} \qquad \text{Eq(6)}$$

Where ρ is the one dimensional density (amount of conserved quantity per unit compartment length), j is the one-dimensional flux (amount of the conserved quantity transported per unit time) and r is the one dimensional source term (amount produced per unit compartment length per unit time).

Here three types of components are conserved. The array of one-dimensional densities of these types of components is given in Eq: 7.

$$\hat{\rho} = \begin{pmatrix} A \\ AC_i \\ S_i \end{pmatrix} \qquad \text{Eq(7)}$$

- The first component of equation 7 describes the conservation of water volume (volume per unit length) within the compartment (water is approximated to be incompressible).
- The second component of equation 7 describes substances transported dissolved or suspended with the water flow. Here C_i is the laterally averaged concentration of substances.
- The third component of equation 7 describes substances settled to the bottom or sorbed to surfaces within the compartment.

One dimensional flux of the quantities is described as in Eq: 8.

$$\hat{j} = \begin{pmatrix} Q \\ QC_i - AD\dfrac{\partial C_i}{\partial x} \\ 0 \end{pmatrix} \qquad \text{Eq(8)}$$

Where the Q refers to the volumetric discharge through the compartment, and D is the coefficient of longitudinal diffusion or dispersion.

One dimensional source term (r) is consisting of three components.

$$\hat{r} = \begin{pmatrix} q \\ Arc_i + \left(\dfrac{1+sign(q)}{2}\right)qC_{lat,i} + \left(\dfrac{1-sign(q)}{2}\right)qC_i \\ rs_i \end{pmatrix} \qquad \text{Eq(9)}$$

First component (q) is the lateral water inflow as volume per unit length of the compartment. Most of the time this longitudinal inflow is zero and the only inflow that is that at the compartment inlet. Here inflow is specified as a boundary condition and particular equation is defined below. The effect of transformation process and the lateral inflows or outflows is described through the second component. $C_{lat,i}$ is the concentration in the lateral flow q. Last component describe the effect of transformation process on settled of sorbed substances or of growing organism.

Combining equation 7 to 9 in the equation of conservation law for one dimensional material flow following set of three differential equations can be derived.

The first equation describes water flow through the compartment.

$$\frac{\partial Q}{\partial x} = q \qquad \text{Eq(10)}$$

Here the spatial gradient of the discharge, Q , is determined by the lateral flow, q.

Second equation describes the behavior of substances transported in the compartment.

$$\frac{\partial C_i}{\partial t} = -\frac{1}{A}\frac{\partial QC_i}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C_i}{\partial x}\right) + rC_i + \left(\frac{1+sign(Q)}{2}\right)\frac{q}{A}C_{in,i} + \left(\frac{1-sign(Q)}{2}\right)\frac{q}{A}C_i$$

Eq(11)

First term represent the convective transport of material with water flow, second term dispersion or diffusion, third term transformation process and finally from both fourth and fifth terms describe lateral inflow or out flow.

Third equation describes the behavior of settled or sorbed substances or of sessile organisms.

$$\frac{\partial s_i}{\partial t} = rs_i \qquad \text{Eq(12)}$$

In order to solve above differential equations, it is required to define relevant boundary conditions for each relevant equations. Following boundary condition can be defined for the reactor model.

Equation 13 describes the boundary condition for the differential equation of Eq: 10 and it represent the discharge through the compartment.

$$Q(x_s) = Q_{in} \qquad \text{Eq (13)}$$

At the beginning $x = x_s$

According to equation 10, due to the lateral inflow q, the discharge at the end of the compartment can be defined as

$$Q(x_e) = Q(x_s) + \int_{x_s}^{x_e} q\,dx \qquad \text{Eq(14)}$$

The boundary conditions for equation (11) are given by the continuity of the substance loadings entering the compartment and by a transmission boundary condition.

$$QC_i \left(x_s\right) - AD\frac{\partial C_i}{\partial x}\left(x_s\right) = I_{in,C_i} \qquad \text{Eq(15)}$$

$$\frac{\partial^2 C_i}{\partial x^2} = 0 \qquad \text{Eq (16)}$$

Where I_{in,C_i} is the total (given) mass input of the substance described by the concentration C_i per unit of time. The boundary conditions of Eq : 16 is omitted for dispersion-free transport.

Mathematical modeling and simulation on tubular reactor was done previously using ADM 1 for the co-digestion of Olive mill wastewater with olive mill solid waste (Fezzani and Cheikh, 2008). The simulation was carried out by implementing ADM1

in the software package MATLAB/Simulink. There the modified ADM1 was able to predict acceptable results under HRT of 24 and 36 days under TVFA of 43, 67,130 gCOD/L. further the reactor got inhibition at HRT of 12 days under 67 gCOD/L and it was well justified by modified ADM1.

2.6.3 Modeling and simulation of plug flow reactor in AD

The ADM 1 was implemented in the simulation software package MATLAB/Simulink, was adapted and applied to replicate with reasonable degree of accuracy the thermophilic anaerobic co-digestion of olive mill wastewater (OMW) with olive mill solid waste (OMSW) in a semi-continuous tubular digester. The simulations results indicated that the modified ADM1 was able to predict reasonably well the steady-state results of gas flows, methane (Fezzani and Cheith, 2007).

2.6.4 Novel PFR reactor configurations

Enhancement of biogas production can be achieved by improvement of reactor design (Namsree, 2012). Accordingly novel reactor designs have come up in different aspects.

2.6.4.1Transpaille Digester

N.Cuzin - 1991, stated that the utilization of a plug flow digester solve the problem of acidification through localization of the acidification phase in the first half of the fermenter. There is no perturbation due to cyanide (5-6 mg/l) was observed. According to the pH and COD values of liquid phase it was shown that most of the organic matter seemed to be degraded in the first part of the fermenter, whereas production of biogas occurred in the second part. The piston flow in the digester eliminates the intermediate acid compound during the transit which helps to prevent drastic acidification in the reaction zones. Ultimately this reactor shows a satisfactory capacity to cope with acidification and nitrogen enrichment of the permanent liquid phase allows the utilization of N – deficient substrate without addition of nitrogen.

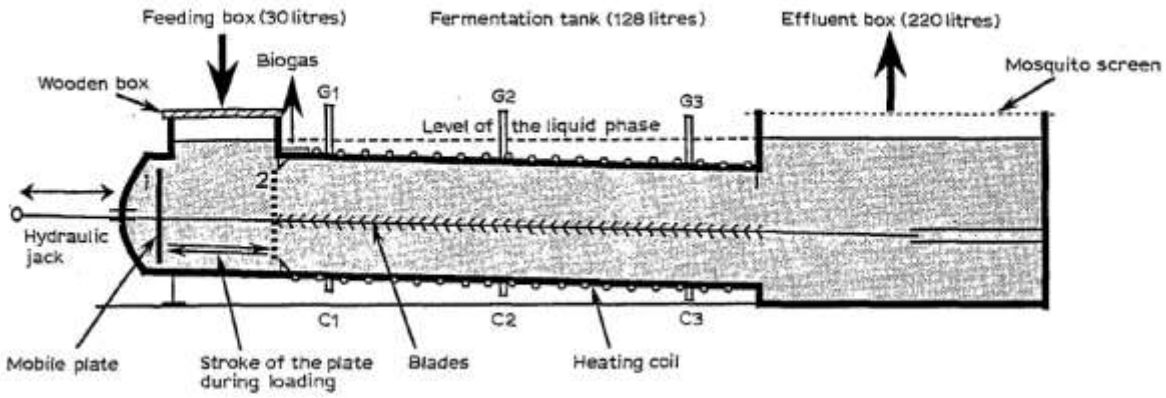

Figure 2-10: Transpaille plug flow reactor (Cuzin, et al., 1991)

2.6.4.2 Taiwan – model tubular reactor

The Taiwan – model tubular reactor is an attractive digester which is capable of producing gas at a considerable rate and it is a very cost effective way of setting up a tubular reactor. This model is a simple version of anaerobic plug flow reactor which is made of tubular polyethylene bag, PVC piping and plastic housing to transport the gas produced within it. The biogas from the digester is composed of 50-70% methane 30-40% carbon dioxide, and trace amount of other gases. The studies on this model has emphasized that it can be produced biogas with methane concentrations above 60% with temperature at or below the mesophilic range (20-40^{0}C) and it reveals that small scale agricultural digesters can produce methane at concentrations useful for cooking (Lansing *et al.*, 2008).

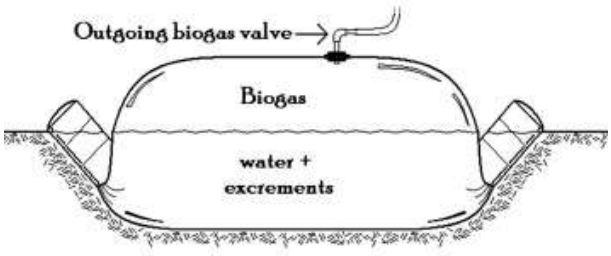

Figure 2-11: Taiwan – model tubular reactor (Lansing *et al.*, 2008)

2.6.4.3 Bioterminator

Bioterminator is another type of plug flow reactor in which baffles has been placed inside it in order to make separate chambers within it (Burnett, 2000). Hydrolysis is carried out in the first chamber in which hydrolyzing and acid forming microorganisms are largely populated to form volatile fatty acids (VFA) and other intermediate products. The subsequent chambers are responsible for methane formation from migrated VFA to it. According to the studies has been carried out, the digester is capable of reducing 93% of raw primary solids at average feed concentration of 4% even without heating it. The anaerobic baffled reactor (ABR) is one such novel reactor which makes it possible to anaerobically treat waste at short retention time (Bouallagui, 2003).

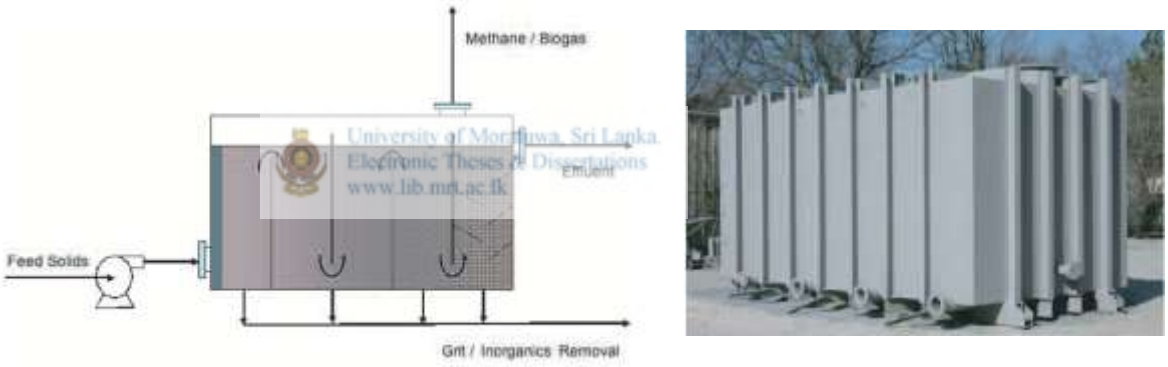

Figure 2-12: High rate bioterminator (Burnett, 2000).

2.6.4.4 Sri Lankan Plug flow reactor

In Sri Lanka, the interest on PFR in AD has increased during the past decade. Several governmental and nongovernmental organizations are engaging to make it popular in the country. Currently there are several reactors installed and most of them are used in solid waste treatment. There is a special type of PFR developed in which a part of the discharge is recycled and fed into the input stream. The main objective of having recycle stream is to increase the active biomass concentration at

the front of the PFR. It is make the initial steps of AD efficient. Figure: xx illustrate the schematic of AD plug flow reactor with recycle.

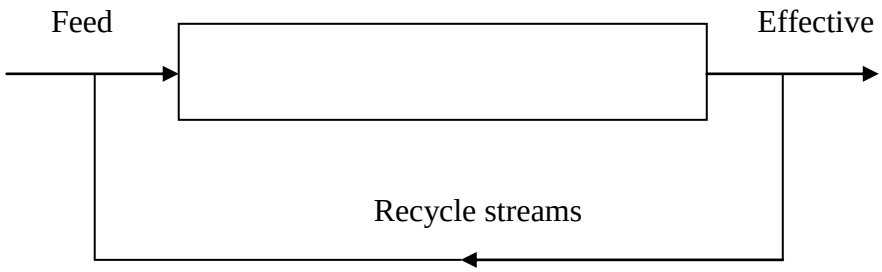

Figure 2-13: Schematic of plug flow reactor with recycle stream

In many places traditional plug flow reactors are used and observe many reactor stability issues in operation.