Jurnal Teknologi

Full Paper

MATHEMATICAL MODELING OF EXISTING TWO STAGE ANAEROBIC DIGESTION PROCESS FOR PALM OIL MILL WASTEWATER

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Article history
Received
8 December 2015
Received in revised form
7 January 2016
Accepted
11 February 2016

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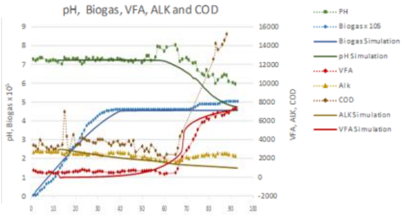
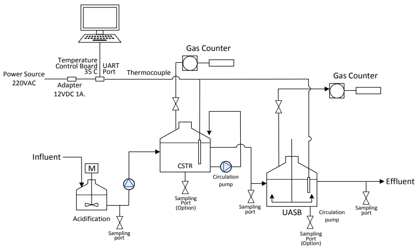
Graphical abstract



COD, VFA, Alkalinity, pH and biogas production rate vs time of a failure case



Abstract

This work is an attempt to describe the dynamics of a two-stage industrial biogas plant using palm oil mill effluent (POME) and the mixture of POME with effluent from rubber factory (LTE), both at steady state and transient peroid before system failure accurred. One incident occurred in POME treatment plant when LFE bypassed its digesters and mixed together with palm-oil-mill wastewater due to no space in the existing latex wastewater ponds under water flooding during heavy raining period. The model was developed based on simplified ADM1 incorporating the effects of ALK/VFA and pH on the microbial growth. The model prediction for such scenario was in agreement with the actual data from the incident which occurred during November 2014. The Steady state simulation estimated that Ss reduced from 74,917 to 2856 mg/l at HRT 15 d which agreed well with the actual data. Dynamic simulation after adding LTE predicted that the Ss reduced to 20,300 at HRT 10.71 d which was the correct trend albeit rather imprecise. That was considered satisfactory for future operational purpose. This discrepancy was due to the difficulty in estimating many process parameters. In general the model demonstrates the usefulness of the ADM1 in describing behavior of an anaerobic wastewater treatment system from palm oil mill industry and can be used for the purpose of future design and operating of the existing plants.

Keywords: Anaerobic digestion, Biogas production, Co-digestion, Biogas Modeling

1.0 INTRODUCTION

In Thailand, the production of biogas from agro-industrial wastewater is one option to increase significantly the share of renewable energy. The anaerobic digestion of organic waste material is widely used not only to reduce organic matter in wastewater, but also to generate biogas. Energy production from biogas can conserve fossil fuel use as well as mitigate the extent of global warming [1]. Thus the Royal Thai Government promotes and subsidizes the renewable energy projects particularly biogas and biomass energy [2]. The long term objective is not only to reduce water pollution, but also to gain maximum economic value from wastewater and waste in general.

In Southern Thailand, palm oil mill effluent (POME), wastewater from animal farm, domestic wastewater and latex-factory effluent (LFE) provides a great potential for producing biogas due to their large volume and high organic matters. Currently, existing biogas plants from POME and animal farms are the main sources of biogas for converting to electricity because of its high organic substances and volume, easily degradable and non-toxic. One of a problematic wastewater for biogas production is that from latex factory. It has very low pH, high sulfate and ammonia content. It was suggested that mixing small portion of wastewater from latex factory with POME would reduce its toxicity and may enhance the overall biogas production due to more optimized C/N ratio. However, there has been no attempt in doing so in practice because having both wastewater in the same proximity is rare. Even they are within the same proximity, the management may be too reluctant to allow this non-proven practice. In general it is too risky to disturb well-behaved and stable biogas plants by introducing alien substrate sources even though good monitoring and control is in-place. In this article, we present a case study when a portion of wastewater from a latex factory was mixed with a larger amount of POME in biogas plant and caused the whole system to fail because the monitoring system did not sufficiently signal the operators to take proper action until too late. Here we develop a mathematical model to describe the dynamics of the system, both for normal continuous operation and after the sudden change in feed composition because of the incident.

2.0 METHODOLOGY

2.1 Full Scale Operation

Thaisritong company limited located in southern Thailand consists of two factories: palm oil factory and latex factory in the same area. Wastewater from palm oil factory was treated under anaerobic treatment process by the two-stage reactors, CSTR (Continuous Stirrer Tank Reactor) in series as shows a simplified schematic diagram in Figure 1 and normal steady state condition in Figure 2. In normal operation COD was reduced by 90%. Note that we do not consider UASB reactor in this article because only two-reactors-in-series (Acidification tank and CSTR) are sufficient for our discussion. Moreover, including UASB into our model development would make the model and discussion over-complicated.

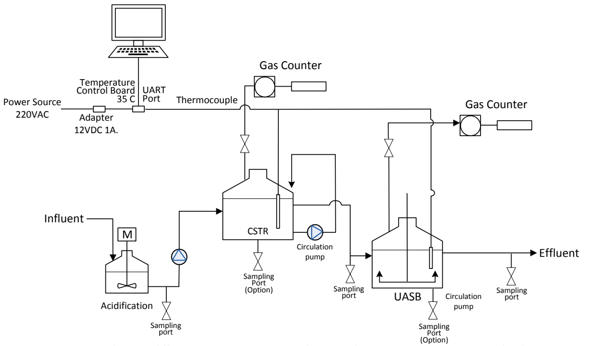


Figure 1 a simplified schematic diagram describing the biogas plant under the case study

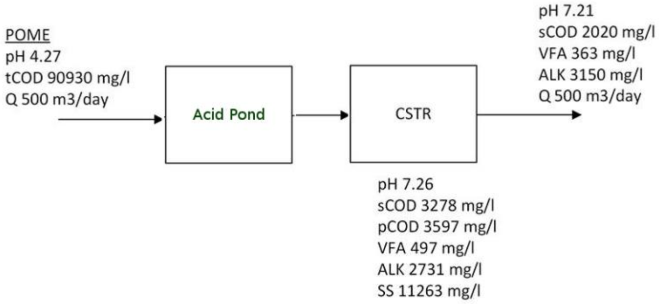


Figure 2 Variables at normal steady state condition (day 1 to day 11, with only POME feed)

Normally, both biogas and methane production increased propotionally with the total COD removal [3]. But the treatment failed when a wastewater from latex factory mixed into POME due to heavy raining season. The flood caused latex wastewater pond full of wastewater and thus the management took decision to mix POME with LFE (day 12 in Figure 8). The failure of the system occurred after continuous mixing for two months when VFA began to increase. The mixing was suddenly stopped but the VFA still continued to rise up steadily while the rate of biogas produced was diminishing as a proportion of H_2S got higher. Figure 3 below show a mixing conditions on day 12 to day 64.

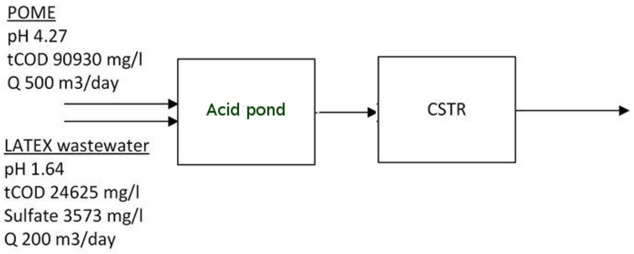


Figure 3 Mixing conditions on day 12 to day 64

In all experiments, we analyzed pH, Chemical Oxygen Demand (COD), Suspended Solids (SS), Alkalinity and Volatile Fatty Acids (VFA). All analytical procedures are performed in accordance with standard methods for examination of water and wastewater APHA [4].

2.2 Simplified Mathematic Modelling

ADM1 model, developed by IWA task group for mathematical modelling of anaerobic digestion processes, is well established but very difficult to use in practice. It divides the influent into several specific constituents which is rarely known in the detail [5]. In this articles, a simplified model was developed from mass balance of anaerobic treatment processes and their kinetics [6] in an increasing complexity manner. The resulting mathematical structure includes multiple steps describing biochemical and physico-chemical processes [7] in a similar fashion as that of ADM1. In the formulation, we modified some rate terms to include the effect of ALK/VFA ratio on pH which in turn changed the growth rate of acidogens and methanogens. Other physico-chemical states are also important because a number of biological inhibitions can be expressed [8]. For instance, the latex wastewater had high concentration of sulfate. Therefore we need to include sulfate-inhibition terms in the model. Since anaerobic digestion process has two main biological degrading stages: acidogenenesis and methanogenesis, thus requires different kinetic parameters and optimum pH for growth for different microbial groups [9]. In the formulation, it is assumed that substrate uptake reactions are Monod-type kinetics whereas the microbial death can be represented by first order kinetics [10].

2.2.1 CSTR Digester

For the acid producing biomass, a simplified form of the Anaerobic model with the sulfate inhibition term addition can be written as follows,

$$\frac{dX_{BS}}{dt}=\frac{\mu_{MS}S_S}{K_{SS}+S_S}\frac{K_{IS}}{K_{IS}+I}X_{BS}-\frac{Q}{V}X_{BS} \tag{1}$$

and similarly for the degradation of easily degradable substrate (EDS):

$$\frac{dS_S}{dt}=-\frac{1}{Y_{X_{BS}S_S}}\frac{\mu_{MS}S_S}{K_{SS}+S_S}\frac{K_{IS}}{K_{IS}+I}I_{pH1}X_{BS}+k_{hx}\frac{\frac{X_S}{X_{BS}}}{K_x+(\frac{X_S}{X_{BS}})}X_{BS}-\frac{Q}{V}(S_{Si}-S_s) \tag{2}$$

The methane producing biomass (MPB) :

$$\frac{dX_{Bm}}{dt}=\frac{\mu_{MM}S_{HA_C}}{K_{SM}+S_{HA_C}}\frac{K_{IM}}{K_{IM}+I}X_{BM}-\frac{Q}{V}X_{BM} \tag{3}$$

The rate of change in organic acid :

$$\begin{aligned}\frac{dS_{HAc}}{dt}=&-\frac{1-Y_{X_{BS}S_S}}{Y_{X_{BS}S_S}}\frac{\mu_{MS}S_S}{K_{SS}+S_S}\frac{K_{SI}}{K_{SI}+I}I_{pH1}X_{BS}\\&-\frac{1}{Y_{X_{BM}S_{HA_C}}}\frac{\mu_{MM}S_{HA_C}}{K_{SM}+S_{HA_C}}\frac{K_{IM}}{K_{IM}+I}I_{pH2}X_{BM}+\frac{Q}{V}(S_{HA_{ci}}-S_{HA_c})\end{aligned} \tag{4}$$

The rate of change in slowly degradable substrate (SDS) :

$$\frac{dX_S}{dt}=-k_{hx}\frac{\frac{X_S}{X_{BS}}}{K_x+(\frac{X_S}{X_{BS}})}X_{BS}-\frac{Q}{V}(X_{Bi}-X_S) \tag{5}$$

The rate of methane production

$$\frac{dS_{CH_4}}{dt}=-\frac{1-Y_{X_{BM}S_{HA_C}}}{Y_{X_{BM}S_{HA_C}}}\frac{\mu_{MM}S_{HA_C}}{K_{SM}+S_{HA_C}}\frac{K_{IM}}{K_{IM}+I}I_{pH2}X_{BM} \tag{6}$$

The rate of change in alkalinity

$$\begin{aligned}\frac{dS_{ALK}}{dt}=&\frac{-5.9f_{ALK}}{Y_{X_{BS}S_S}}\frac{\mu_{MS}S_S}{K_{SS}+S_S}\frac{K_{IS}}{K_{IS}+I}I_{pH1}X_{BS}\\&+\frac{5.8f_{ALK}}{Y_{X_{BM}S_{HA_C}}}\frac{\mu_{MM}S_{HA_C}}{K_{SM}+S_{HA_C}}\frac{K_{IM}}{K_{IM}+I}I_{pH2}X_{BM}+\frac{Q}{V}(S_{ALK_i}-S_{ALK})\end{aligned} \tag{7}$$

The rate of change in inhibitor (Sulfate)

$$\frac{dS_I}{dt}=-k_{hI}S_I+\frac{Q}{V}(S_{I_i}-S_I) \tag{8}$$

Here X_{BS}, S_s, S_{Si}, X_S, I, K_{SS}, K_S, μ_{MS}, K_{hx}, K_{IS}, Q, V, $Y_{X_{BS}S_S}$ are acid producing biomass (mg COD/l), EDS and inflow EDS concentration (mg COD/l), SDS concentration (mg COD/l), inhibitor concentration (sulfate) (mg/l), acid producing saturation constant (mg COD/l), SDS saturation constant, specific growth rate of APB (d^{-1}), SDS related growth constant (d^{-1}), inhibitor saturation constant (ml/l), influent flow rate (m^3d^{-1}), digester volume (m^3) and APB/EDS yield coefficient. I_{ph1} is pH inhibition effect to organic acid.

X_{BM}, K_{SM}, μ_{MM}, X_S, $Y_{X_{BM}S_{HA}}$, S_{HA}, S_I, S_{ALK}, S_{CH}, f, K_{hi} are MPB concentration (mg COD/l), MPB saturation constant (mg COD/l), MPB/acid yield coefficient, acid and its inflow concentration (mg COD/l), alkalinity and its inflow concentration (mg/l), accumulated methane, ALK conversion factor and inhibitor reaction const (d^{-1}). I_{ph2} is pH inhibition effect to methan production.

2.2.2 Acid Pond

Assuming well-mixed, the effluent introduced from the acidification pond satisfies the following ODE :

$$\frac{dS_{S_i}}{dt}=\frac{Q}{V}\left(f_m S_{SI}+(1-f_m)S_{S2}-S_{Si}\right)-\frac{1}{Y_{X_{BS}S_S}}\frac{\mu_{MS}S_{Si}}{K_{SS}+S_{Si}}\frac{K_{IS}}{K_{IS}+I}X_{BS_i} \tag{9}$$

$$\begin{aligned}\frac{dS_{HAc_i}}{dt}=&\frac{Q}{V}\left(f_m S_{HAc_i}+(1-f_m)S_{HAc2}-S_{HAci}\right)\\&-\frac{1-Y_{X_{BS}S_S}}{Y_{X_{BS}S_S}}\frac{\mu_{MS}S_{Si}}{K_{SS}+S_{Si}}\frac{K_{IS}}{K_{IS}+I}X_{BS_i}\end{aligned} \tag{10}$$

$$\frac{dX_{BSi}}{dt}=\frac{Q}{V}\left(f_m X_{BS1}+(1-f_m)X_{BS2}-X_{BSi}\right)+\frac{\mu_{MS}S_{Si}}{K_{SS}+S_{Si}}\frac{K_{IS}}{K_{IS}+I_i}X_{BS_i} \tag{11}$$

$$\frac{dX_{Si}}{dt}=\frac{Q}{V}\left(f_m X_{S1}+(1-f_m)X_{S2}-X_{Si}\right) \tag{12}$$

$$\frac{dS_{ALKi}}{dt}=\frac{Q}{V}\left(f_m S_{ALK1}+(1-f_m)S_{ALK2}-S_{ALKi}\right) \tag{13}$$

$$\frac{dS_{Ii}}{dt}=\frac{Q}{V}\left(f_m S_{I1}+(1-f_m)S_{I2}-S_{Ii}\right) \tag{14}$$

Where S_{S1}, S_{S2}, S_{HAc1}, S_{HAc2}, X_{BS1}, X_{BS2}, X_{S1}, X_{S2}, S_{ALK1}, S_{ALK2} are the corresponding concentrations in entering stream 1 for POME, 2 for latex wastewater and $f_m=\frac{Q_1}{(Q_1+Q_2)}=\frac{Q_1}{Q}$

It should be noted that actually all wastewater were introduced into an acid pond (Hydraulic Retention Time (HRT = V/Q = 1 d)) from which its outflow became the inflow of CSTR (HRT = 15 d). The hydrodynamics of both acid pond and CSTR can be assumed well-mixed due to continuous circulation.

2.3 Effect of VFA/ALK Ratio to pH

Generally, change in VFA concentration is the most sensitive parameter which causes the digester failure due to the imbalance between acidogenic, acetogenic and methanogenic activities [11]. Furthermore, in our case, the inhibitor which was in form of sulfide and amonia in the complimenting LFE brought about the reduced methanogenic activities, thus VFA accumulation exceeded the allowable limit. The increasing VFA/ALK reduced pH further until the pH dropped to a toxic level. The VFA, ALK and pH data from routine measurement were used to correlate VFA/ALK to pH using modified Gompertz equation and sigmoidal equation which have the following forms.

$$pH=\frac{4.644}{1+e^{\left(\frac{(VFA/ALK)-30.630}{-6.826}\right)}} \qquad (15)$$

and sigmoidal equation

$$pH = 2.65(1 - e^{(e^{(0.8-0.075(VFA/ALK))}+1.75)}) + 4.6 \qquad (16)$$

It was found that sigmoidal equation fit the data better than the modified Gompertz equation, thus it will used in the following simulation.

2.4 pH Inhibition Function

Biological reactions occure only within a specific pH range. The reaction rate rapidly drops to zero at too low or too high pH values [16]. It was proposed in the original ADM1 model that pH should be taken into consideration if it falls out of the optimal range (6.8 - 7.2) [12]. Low pH can inhibit acidogenesis and pH below 6.4 can be toxic for methane forming bacteria [13]. In this article we used the following equation to mimic the effect of pH on microbial activities. Note that this modification introduces empirical upper and lower pH limits which specify the optimal pH range for methane production.

$$I_{pH} = (1 + 2x10^{0.5(pH_{LL}-pH_{UL})})/ (1 + 10^{(pH-pH_{UL})} + 10^{(pH_{LL}-pH)}) \qquad (17)$$

3.0 RESULTS AND DISCUSSION

3.1 Full Scale Operation

Figure 8. shows that after mixing with LFE for 40 days, ALK started to drop from 2,600 mg/l to 1,800 mg/l and biogas production rate became very low. Then after 64 days VFA started to increase rapidly due to the cessation of methanogenic activity, following from the drop of COD removal efficiency. In overall, ALK did not change much, but stayed within 1,800-2,600 mg/l range even after 64 days. After the time that VFA rose up (77 days), LFE was not allowed to mix with POME anymore. However VFA and COD continued to increase steadily causing pH to go below 6.5.

Under anaerobic condition, the rate of sulfate reduction depends on the biological activity of sulfate-reducing bacteria [14]. Sulfate-reducing bacteria oxidizes simple organic compound by utilizing sulfate and generate sulfide and alkalinity [15]. Part of the sulfide inhibits other microbial activities, resulting to a lower overall treatment efficiency of the anaerobic digestion sytem [16]. Although alkalinity was generated in this biological acitivity which would result in an increase in the pH [17], high VFA superseded the ALK generation and cause pH to drop further [18]. With the anticipation that methanogen bacteria was dying or being washed out of the system, the operators with the consent of the management decided to stop any feed into the system and started to recover the system by adding the active sludge from another neighborhood plant. The methane production was brought back to normal optimal condition (pH value between 6.5-7.5) slowly. Otherwise, below a pH of 6.0 methane production from VFA will proceed very slowly. Acidogens will be more active which convert organic substrates to the VFA and the resulting VFA accumulation will drop the pH to a highly inhibitory levels.

3.2 Steady State Simulation

In normal steady state operation, the average inflow variables were as follows: X_{BSi}=110, S_{Si}=74,917, X_{BMi}=0, S_{HAci}=6,073, X_{Si}=9,000 and S_{ALKi}=2,000. The hydraulic retention time (HRT=$\frac{V}{Q}$) was 15 d and all values associated with second stream (LFE) were zero. The best matching between operational data (Figure 2 and 3, assuming inert COD is approximately 930 mg COD/l) and the model for steady-state condition prior to wastewater mixing (day 1 to day 11) gave the following variable estimation: X_{BS}=724.5, S_S=2,856, X_{BM}= 854.4, S_{HAc}=507.6, X_S=562.3 and S_{ALK}= 2,877. The best estimates of model parameters were: $Y_{X_{BM}S_{HAc}}$=0.01, $Y_{X_{BS}S_S}$=0.09, K_{SS}=1,000, K_{SM}=1,000, k_{hx}=1,000, K_X=1,000, μ_{MS}= 0.09, μ_{MM}= 0.198 and f_{ALK}= 0.045. Figure 4 show steady state simulation of ssi (easily degradable substrate), xsi (slowly degradable substrate), shaci (organic acid), xbsi (acid production biomass), salki (alkalinity) and sli (sulfate inhibitor).

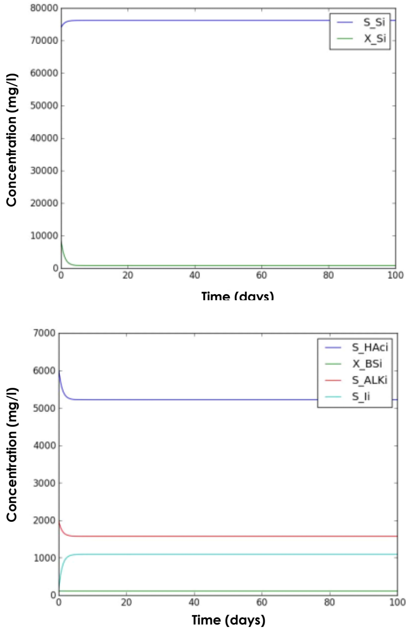


Figure 4 Steady state simulation of S_{Si} (Easily degradable substrate), X_{Si} (Slowly degradable substrate), S_{HAci} (Organic acid), X_{BSi} (Acid production biomass), S_{ALKi} (Alkalinity) and S_{Ii} (Sulfate inhibitor

3.3 Dynamic Simulation After Latex Factory Waste Water was Continuously Added to POME

Started on day 12, the second inflowing stream was suddenly added (and held on until day 76) which consisted of X_{BS2}=100, S_{S2}=20,500, S_{HAc2}=2,000, S_{ALK2}=5,000 This reduced HRT to 10.71 d. . Figure 5 dynamic simulation of xbs (acid production biomass), XBM (methane producton biomass), xsi (slowly degradable substrate) and sli (sulfate inhibitor).

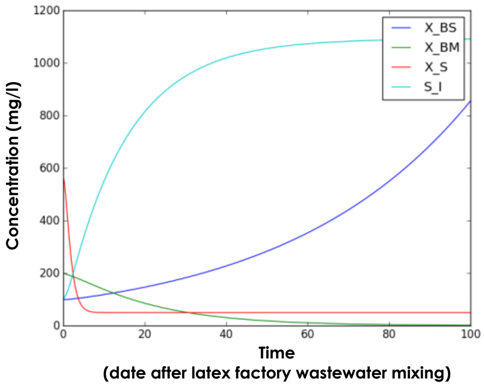


Figure 5 Dynamic Simulation of X_{BS} (Acid production biomass), X_{BM} (Methane producton biomass), X_{Si} (Slowly degradable substrate) and S_{Ii} (Sulfate inhibitor)

3.4 Effect of VFA/ALK Ratio to pH

Normally VFA/ALK ratio under anaerobic digester condition should be lower than 0.4 and it is quite dangerous if it is more than 0.8. VFA and ALK under steady state had average values of 494 and 2,731 mg/l respectively. Inhibitor, in form of amonia in added LFE caused reduction in methanogenic bacteria, thus there is not sufficient microbes to consume VFA. This caused the cumulation of VFA reach the maximum value of 9,169 mg/l although ALK did not change significantly. The increases of VFA/ALK caused the reduction of pH to a toxic level. The relationship between VFA/ALK and pH was represented by the best fit of Modified Gompertz and sigmoidal equations as shown in Figure 6.

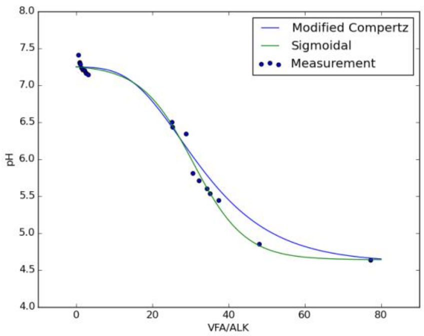


Figure 6 Effect of VFA/ALK ratio on pH

3.5 pH Inhibition Function

At pH between 6.5 to 7.5 the digesters produced methane normally. However, acidogens will be more active at pH range between 5.5 to 6.5, converting organic substrates to VFA which results to VFA accumulated in the reactor.

The simulation predicted that, after adding LFE, VFA (Figure 7) was slowly accumulated until day 60, which was in agreement with actual VFA measurement (Figure 8). Buffering capacity as reflected by ALK level (Figure 8) was still stable after mixing for sometime until about day 60 when VFA started to climb up quickly. Although the simulation gave the correct trends regarding VFA and ALK it underestimated their trends significantly. This reflects that the actual phenomena which occurred in the incident was more complicated than what the model try to represent. However, in general the model gave satisfactory predictive capacity in the sense that we would not allow the trends to go on without correction in future operation. Thus the model could form a basis for designing the control algorithm/system to deal with a similar problems.

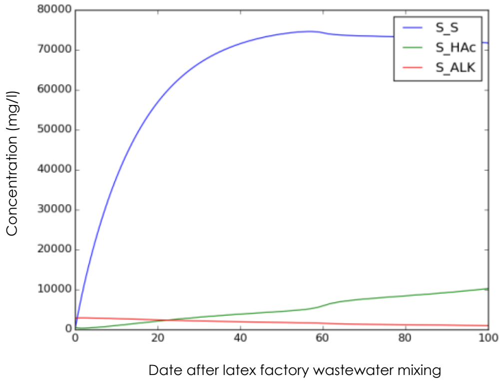


Figure 7 Dynamic Simulation for Ss (Easily degradable substrate), S_{HAc} (VFA substrate) and S_{ALK} (ALK substrate)

4.0 CONCLUSION

The results shows that the modified ADM1 was successfully developed and implemented to simulate the steady state operation of two-stage anaerobic digesters treating POME during normal operation. However after mixing with LFE, it over predicted the easily-degradable-substrate under dynamic state although gave a correct trends.

The model can also simulate the effect of VFA/ALK on pH when compared with the measured data. In this case, the sigmoidal function represented the effect more accurately than that of modified Gompertz model.

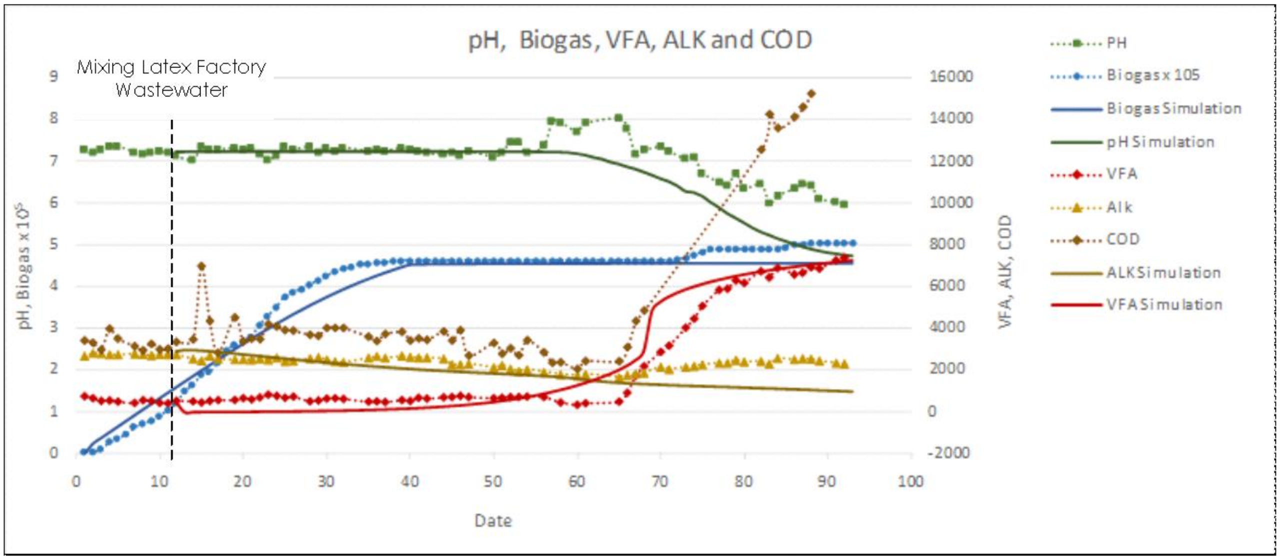


Figure 8 COD, VFA, Alkalinity, pH and biogas production rate vs time of a failure case

In overall the model successfully predicted the incident based on the current set of data. However, more intensive studies will be required to improve the performance of the mathematical model if it is to be used as a part of optimization and control algorithm in the actual biogas plant of this type in the future.

Acknowledgement

This work supported by Walailak University Fund. We would like to acknowledge the factory process information support from Thaisritong ltd. This study may not complete without co-opertion from our postgraduate student group and really grateful to acknowledge the supported provide by School of Engineering and Resources, and Renewable Energy Research unit, Walailak university.

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