



Modelling of an Anaerobic Process producing Biogas from Winery Wastes

Iginio Colussi, Angelo Cortesi, Vittorino Gallo, Adriana S. Rubesa Fernandez, Rosa Vitanza*

DI3, Dipartimento di Ingegneria Industriale e dell'Informazione, Università di Trieste, Piazzale Europa, 1 – 34127 Trieste, Italy
rosa.vitanza@di3.units.it

Significant instability is often exhibited by anaerobic digesters: this problem may be avoided through appropriate control strategies. Such strategies require, usually, the development of suitable mathematical models, which adequately describe the main processes that take place.

In this paper, a simple process design model is proposed, which describes an industrial plant producing biogas by anaerobic digestion of winery wastes. The required kinetic parameters have been obtained from preliminary laboratory tests. The results of the simulation have been applied to the evaluation of the viable energy use of winery wastes (exhausted grape marc) produced by a distillery of Friuli Venezia Giulia region.

1. Introduction

Anaerobic digestion is an engineered biochemical process that mineralises organic substrates, e.g. agro-industrial wastes, to methane and carbon dioxide through a series of reactions mediated by several groups of microorganisms. Main process benefit is the biogas production with very low energy consumption. A notable agro-industrial waste generated in Italy is related to the winery activity: in 2007, Italian wet solid waste production (grape stalk, grape marc and wine lees), was about $7.0\text{-}9.0\cdot 10^5$ t (ISTAT, 2008). In a previous paper, we described the operational performance of 4 anaerobic batch reactors (5 L volume) treating winery wastes at 35 °C (Colussi et al., 2009). Bioreactors were loaded with anaerobic sludge from full scale UASB treating brewery wastewater. The work compared the behavior of suspended and attached growth biological processes under different substrate and biomass concentrations: reactors for growth biomass tests were filled with floating wood and polyethylene supports. The substrate consisted in a mixture of exhausted grape marc and wine lees (5:1 on weight basis). Experimental results showed similar performances (biogas production) for attached and suspended growth reactors.

In this paper, a simple process design model is proposed for the description of an industrial plant producing biogas by anaerobic digestion of winery wastes. The necessary kinetic parameters have been acquired from the above mentioned preliminary experimental work. The anaerobic digestion model, developed in this paper, is a simplified version of the IWA Anaerobic Digestion Model N. 1 (ADM1) in which the input COD is represented by cellulose. Simulation results have been applied to assess the self-sustainability of the energy needs of a distillery of Friuli Venezia Giulia region.

2. Reaction model

The reaction system describing an anaerobic reactor is complex because of a number of sequential and parallel biochemical and physico-chemical reactions. Biochemical reactions are the core of any model and it is possible to represent an anaerobic system using only these equations (Husain, 1998). The anaerobic digestion model developed in this work is a simplified version of the IWA Anaerobic Digestion Model N. 1 (ADM1) (Batstone et al., 2002a, 2002b) and accounts for 9 biological processes and 12 state variables. The model structure is schematized in figure 1. The input COD is related to cellulose, because the considered substrate, exhausted grape marc, is composed of insoluble organic matter with high molecular weight. Substrate uptake reactions are modelled as Monod-type equations whereas the biomass death is represented by first order kinetics. Dead biomass hydrolysis involving an increase in acetate amount and inert material is also considered. The biological kinetic rate expressions and the stoichiometric parameters are reported in Petersen matrix form in Table 1 (Vanrolleghem et al., 2005). Parameters evaluation was carried out by fitting the experimental data derived from our own preliminary experimental research (Colussi et al., 2009). The ODE system was solved by using MATLAB applying the ode23s solver function (suitable for stiff problems). The hydrogenotrophic (XH₂) impact on methane generation was considered negligible in respect to acetoclastic (XAC) contribution. The goodness of the fitting curve, relating to the experimental methane production, and the obtained parameters are reported in Figure 2 and Table 2, respectively.

3. CSTR Modeling

An anaerobic CSTR treating winery waste was simulated by using fitting parameters of Table 2. Although the considered substrate had a solid content up to 30 % (on weight basis), wet process was simulated in order to encompass also the washing wastewater from processing of grape marc. The reactor design was done considering the COD cellulose biodegradation as the limiting step of the digestion process. The plant layout is illustrated in Figure 3. The sludge recirculation (R) from the bottom of a sedimentation tank was considered as a mean in order to control the biomass concentration value in the bioreactor. The total solid (TS) content in the input flow (IN) was set to 6 %: so the supernatant recirculation flow (QD) was calculated depending on the feed (F) TS content. The system was simulated by solving mass balances, in steady-state, in the bioreactor and in the settling tank. The system of non linear equations (see Table 3) was solved by MATLAB using the trust-region dog-leg method. CSTR volume was calculated setting the cellulose and XCE concentrations of reactor outflow. Calculations were done considering two operating conditions: 90 % and 50 % of cellulose degradation. Input parameters and simulations results are presented in Tables 4 and 5.

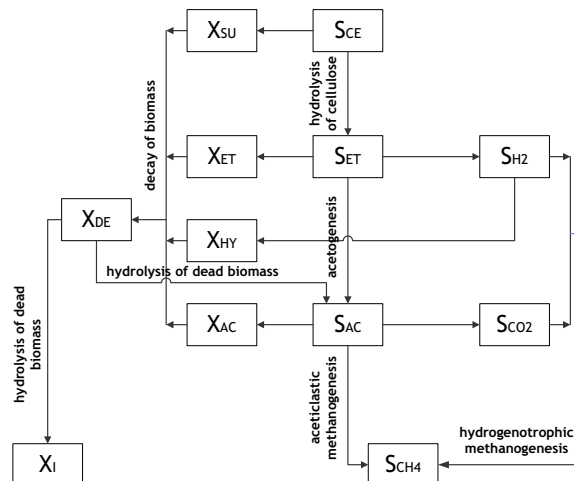


Figure 1: Model representation. X_i = generic biomass, S_i = generic substrate, CE = Cellulose, ET = Ethanol, H₂ = Hydrogen, AC = Acetic Acid, DE = Dead biomass, I = Hydrolyzed Biomass

Table 1: Biochemical rate coefficients and kinetic rate equations.

S_i = generic substrate [mgCOD·L⁻¹]; X_i = generic biomass [mgVSS·L⁻¹]; $\mu_{max\ i}$ = generic biomass maximum growth rate [d⁻¹];
 b_i = decay rate of generic biomass [d⁻¹]; K_i = half saturation constant for generic substrate [mgCOD·L⁻¹]; k = dead biomass hydrolysis rate [d⁻¹];
 Y_i = Yield coefficient for generic biomass [mgVSS·mgCOD⁻¹]; F_X = Biomass COD content [mgCOD·mgVSS⁻¹];
 F_i = biomass inert content

Components Process	S_{CE}	S_{ET}	S_{AC}	S_{CH4}	S_{CO2}	S_{H2}	X_{CE}	X_{ET}	X_{AC}	X_{HY}	X_{DE}	X_i	Process rate
Hydrolysis of cellulose	$-\frac{1}{Y_{SU}} + \frac{(1 - Y_{CE} \cdot F_X)}{Y_{CE}}$				$+\frac{(1 - Y_{CE} \cdot F_X)}{Y_{CE}}$		+1						$\mu_{maxCE} \frac{S_{CE} \cdot X_{CE}}{K_{CE} + S_{CE}}$
Uptake of ethanol (acetogenesis)		$-\frac{1}{Y_{ET}}$	$+\frac{2(1 - Y_{ET} \cdot F_X)}{3 Y_{ET}}$		$-\frac{1(1 - Y_{ET} \cdot F_X)}{3 Y_{ET}}$	$+\frac{1(1 - Y_{ET} \cdot F_X)}{3 Y_{ET}}$		+1	+1				$\mu_{maxXET} \frac{S_{ET} \cdot X_{ET}}{K_{SET} + S_{ET}}$
Uptake of acetate (acetoclastic methanogenesis)			$-\frac{1}{Y_{AC}}$	$+\frac{(1 - Y_{AC} \cdot F_X)}{Y_{AC}}$	$+\frac{(1 - Y_{AC} \cdot F_X)}{Y_{AC}}$								$\mu_{maxXAC} \frac{S_{AC} \cdot X_{AC}}{K_{SAC} + S_{AC}}$
Uptake of hydrogen (hydrogenotrophic methanogenesis)				$+\frac{(1 - Y_{H2} \cdot F_X)}{Y_{H2}}$		$-\frac{1}{Y_{H2}}$				+1			$\mu_{maxXH2} \frac{S_{H2} \cdot X_{H2}}{K_{SH2} + S_{H2}}$
Decay of X_{CE}							-1						$b_{CE} \cdot X_{CE}$
Decay of X_{ET}								-1					$b_{ET} \cdot X_{ET}$
Decay of X_{AC}									-1				$b_{AC} \cdot X_{AC}$
Decay of X_{HY}										-1			$b_{HY} \cdot X_{HY}$
Hydrolysis of dead biomass X_{DE}			$\frac{20}{23} \cdot (1 - F_i) \cdot F_X$		$-\frac{48}{368} (1 - F_i) \cdot F_X$						-1	$F_i \cdot F_X$	$k \cdot X_{DE}$

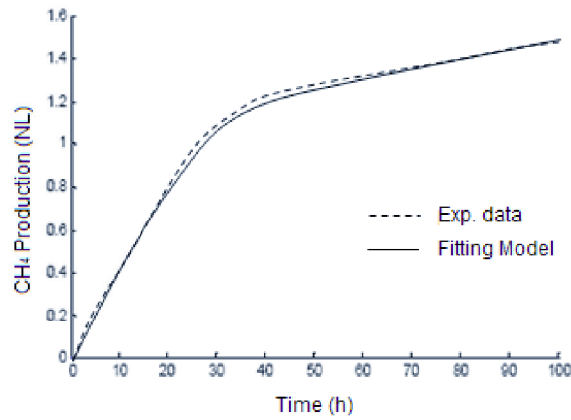


Figure 2: Fitting curve on bio-methane production from exhausted grape mark (Colussi et al., 2009)

Table 2: Calculated fitting parameters (see units in Table 1)

Parameter	Value	Parameter	Value	Parameter	Value
$\mu_{\max \text{ CE}}$	0.02	b_{AC}	0.001	Y_{CE}	0.31
$\mu_{\max \text{ ET}}$	0.02	k	0.004	Y_{ET}	0.035
$\mu_{\max \text{ AC}}$	0.02	K_{CE}	160	Y_{AC}	0.0095
b_{CE}	0.015	K_{ET}	160	F_{X}	1.42
b_{ET}	0.002	K_{AC}	160	F_{I}	0.01

Table 3: System of non linear equations

$$\begin{aligned}
 Q_D &= \frac{Q_A(TS_A - TS_{IN})}{TS_{IN}} & Q_{IN} \cdot S_{CE}^{IN} + Q_R \cdot S_{CE}^R - Q_{OUT} \cdot S_{CE}^{OUT} + \frac{r_{CE}}{Y_{CE}} \cdot V &= 0 & Q_R \cdot X_{CE}^R - Q_{OUT} \cdot X_{CE}^{OUT} + r_{CE} \cdot V &= 0 \\
 Q_{OUT} \cdot S_{CE}^{OUT} - Q_L \cdot S_{CE}^L (\cong 0) - Q_R \cdot S_{CE}^R - Q_S \cdot S_{CE}^S &= 0 & Q_{OUT} \cdot X_{CE}^{OUT} - Q_L \cdot X_{CE}^L (\cong 0) - Q_R \cdot X_{CE}^R - Q_S \cdot X_{CE}^S &= 0 & COD_{IN \text{ MAX}} &= \frac{Q_A \cdot COD_A}{Q_{IN}} \\
 S_{CE}^R + X_{CE}^R &= f_R \cdot (S_{CE}^{OUT} + X_{CE}^{OUT}) & S_{CE}^S + X_{CE}^S &= f_S \cdot (S_{CE}^{OUT} + X_{CE}^{OUT}) & \frac{X_{CE}^S}{X_{CE}^{OUT}} &= f \cdot \frac{S_{CE}^S}{S_{CE}^{OUT}} \\
 X_{CE}^S &= \frac{f \cdot f_S \cdot X_{CE}^{OUT} \cdot (S_{CE}^{OUT} + X_{CE}^{OUT})}{S_{CE}^{OUT} + f \cdot X_{CE}^{OUT}} & S_{CE}^S &= \frac{f_S \cdot S_{CE}^{OUT} \cdot (S_{CE}^{OUT} + X_{CE}^{OUT})}{S_{CE}^{OUT} + f \cdot X_{CE}^{OUT}} & Q_S &= \frac{r_{CE} \cdot V}{X_{CE}^S} \\
 Q_{IN} \cdot S_{ET}^{IN} + Q_R \cdot S_{ET}^R - Q_{OUT} \cdot S_{ET}^{OUT} + \frac{r_{ET}}{Y_{ET}} \cdot V &= 0 & Q_{IN} \cdot S_{AC}^{IN} + Q_R \cdot S_{AC}^R - Q_{OUT} \cdot S_{AC}^{OUT} + \frac{r_{AC}}{Y_{AC}} \cdot V &= 0 & Q_R \cdot X_{ET}^R - Q_{OUT} \cdot X_{ET}^{OUT} + r_{ET} \cdot V &= 0 \\
 Q_R \cdot X_{AC}^R - Q_{OUT} \cdot X_{AC}^{OUT} + r_{AC} \cdot V &= 0 & Q_R \cdot X_{DE}^R - Q_{OUT} \cdot X_{DE}^{OUT} + r_{DE} \cdot V &= 0 & \frac{X_{DE}^R}{X_{DE}^{OUT}} &= \frac{X_{CE}^R}{X_{CE}^{OUT}} \\
 \frac{X_{ET}^R}{X_{ET}^{OUT}} &= \frac{X_{CE}^R}{X_{CE}^{OUT}} & \frac{X_{AC}^R}{X_{AC}^{OUT}} &= \frac{X_{CE}^R}{X_{CE}^{OUT}} & \frac{X_{DE}^S}{X_{DE}^{OUT}} &= \frac{X_{CE}^S}{X_{CE}^{OUT}} \\
 \frac{X_{ET}^S}{X_{ET}^{OUT}} &= \frac{X_{CE}^S}{X_{CE}^{OUT}} & \frac{X_{AC}^S}{X_{AC}^{OUT}} &= \frac{X_{CE}^S}{X_{CE}^{OUT}} & Q_{CO2}^G &= r_{CO2}^G \\
 Q_{H2}^G &= r_{H2}^G & Q_{CH4}^G &= r_{CH4}^G & &
 \end{aligned}$$

$f (= 0.2)$, $f_R (= 1.5)$, $f_S (= 2.5)$: empirical settling tank coefficients

Table 4: Simulation input parameters

Parameter	90% degrad.	50% degrad.	Parameter	90% degrad.	50% degrad.
$Q_F [L \cdot h^{-1}]$	10	10	$COD_{IN \text{ MAX}} [mg \cdot L^{-1}]$	38000	50000
$COD_F [mg \cdot L^{-1}]$	455300	455300	$X_{CE \text{ OUT}} [mg \cdot L^{-1}]$	5000	5000
$TS_F [\%]$	33	33	$S_{CE \text{ OUT}} [mg \cdot L^{-1}]$	2000	20000
$TS_{IN} [\%]$	6	6			

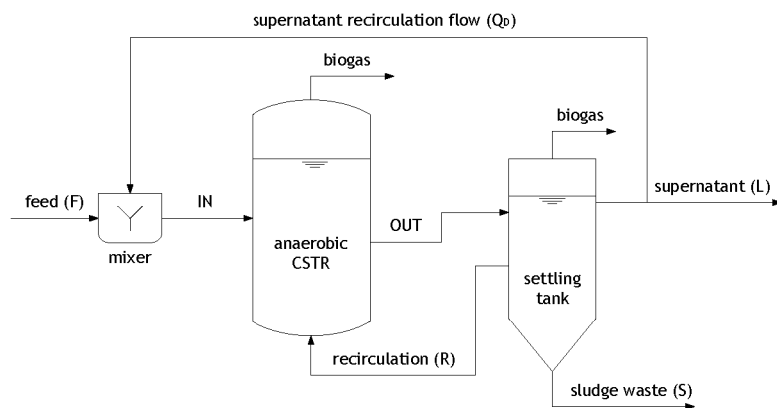


Figure 3: Plant design

Table 5 Simulation results

Parameter	90% degrad	50% degrad	Parameter	90% degrad	50% degrad
Q_D [$L \cdot h^{-1}$]	112.4	83.1	$X_{DE S}$ [$mg \cdot L^{-1}$]	6819	3211
V [L]	187307	77767	$S_{ET OUT}$ [$mg \cdot L^{-1}$]	60.97	83.18
Q_R [$L \cdot h^{-1}$]	127.2	54.3	$S_{AC OUT}$ [$mg \cdot L^{-1}$]	46.70	66.01
$X_{CE R}$ [$mg \cdot L^{-1}$]	8734	12118	$S_{I OUT}$ [$mg \cdot L^{-1}$]	8181	14269
$S_{CE R}$ [$mg \cdot L^{-1}$]	1766	25382	$S_{ET R}$ [$mg \cdot L^{-1}$]	60.97	83.18
$X_{CE S}$ [$mg \cdot L^{-1}$]	5833	2976	$S_{AC R}$ [$mg \cdot L^{-1}$]	46.70	66.01
$S_{CE S}$ [$mg \cdot L^{-1}$]	11667	59524	$S_{I R}$ [$mg \cdot L^{-1}$]	7225	18109
Q_S [$L \cdot h^{-1}$]	23.54	26.35	$S_{ET S}$ [$mg \cdot L^{-1}$]	60.97	83.18
$X_{ET OUT}$ [$mg \cdot L^{-1}$]	1735	2227	$S_{AC S}$ [$mg \cdot L^{-1}$]	46.70	66.01
$X_{AC OUT}$ [$mg \cdot L^{-1}$]	538.1	599.3	$S_{I S}$ [$mg \cdot L^{-1}$]	47720	42467
$X_{DE OUT}$ [$mg \cdot L^{-1}$]	5844	5394	Q_{CH4} [NL·h]	956	580
$X_{ET R}$ [$mg \cdot L^{-1}$]	3031	5397	Q_{CO2} [NL·h]	728.7	380.4
$X_{AC R}$ [$mg \cdot L^{-1}$]	940	1435	Q_{H2} [NL·h]	0.00	0.00
$X_{DE R}$ [$mg \cdot L^{-1}$]	10209	13073	Q_{OUT} [L·h]	250	147
$X_{ET S}$ [$mg \cdot L^{-1}$]	2024	1325	Q_L [L·h]	99	67
$X_{AC S}$ [$mg \cdot L^{-1}$]	628	357			

Table 6: Average distillery production data (2004-2009)

GM = grape marc [q]; WL = wine lees [q]; Feedstock = GM + WL.

Feedstock ratio [GM/WL]	Grappa/Feedstock ratio [L/q]	Diesel oil/Feedstock ratio [L/q]
5.16	3.75	2.86

Table 7: Calculated biogas flowrates

Substrate	Q_{CH4} [NL/h]	Q_{CO2} [NL/h]	Q_{H2} [NL/h]
Exhausted grape marc + wine lees	956	728.7	0.00
Exhausted grape marc	812	766.8	0.00

Energy balances were then calculated in order to assess the self-sustainability of the energy needs of a distillery of Friuli Venezia Giulia region. The data of *grappa* production and the related energy consumption are reported in Table 6. The calculated methane rate production of exhausted grape marc and exhausted grape marc with wine lees (5:1 weight ratio) are stated in table 7.

Neglecting the substrate preheating, because of the usual high temperature of distillation by-products, a simple net energy balance Q_{NE} [$MJ \cdot kg^{-1}$] was calculated:

$$Q_{NE} = Q_{CH_4} - Q_{CO_2} - Q_{diesel} \quad (1)$$

in which: Q_{CH_4} = CH_4 energy contribution, Q_{CO_2} = CO_2 energy losses and Q_{diesel} = energy spent in distillation process. The energy contributions are reported in Table 8.

Table 8: Energy contributions [$MJ \cdot kg^{-1}$] to net energy balance

Substrate	Q_{CH_4}	Q_{CO_2}	Q_{diesel}
Exhausted grape marc + wine lees	3.37	0.020	1.001
Exhausted grape marc	2.92	0.021	1.001

According to equation (1) net energy values of 1.9 [$MJ \cdot kg^{-1}$] for exhausted grape marc and of 2.35 [$MJ \cdot kg^{-1}$] for exhausted grape marc and wine lees mixture were obtained. The significant differences between produced (methane) and consumed (diesel) energy indicate a possible self-sustainability of the distillery.

4. Conclusions

In this paper a simplified version of the IWA ADM1 process design model is proposed to describe an industrial plant producing biogas by anaerobic digestion of winery wastes (exhausted grape mark). The required kinetic parameters have been obtained from preliminary laboratory tests. The model accounts for 9 biological processes and 12 state variables: waste is characterized by cellulose and hydrogenotrophic methanogenesis is considered negligible in respect to acetoclastic methanogenesis. Simulation results have been usefully applied by verifying the possible energy self-sustainability of a distillery of Friuli Venezia Giulia region.

References

- Batstone D.J., Keller J., Angelidaki I., Kalyuzhnyi S.V., Pavlostathis S.G., Rozzi A., Sanders W.T.M., Vavilin V.A., 2002a, The IWA Anaerobic Digestion Model No 1 (ADM1), *Water Science and Technology*, 45(10), 65-73.
- Batstone D.J., Keller J., Angelidaki I., Kalyuzhnyi S.V., Pavlostathis S.G., Rozzi A., Sanders W.T.M., Siegrist H., Vavilin V.A., 2002b, Anaerobic Digestion Model No.1, Scientific and Technical Report (STR) No 13, International Water Association, London, UK.
- Colussi I., Cortesi A., Gallo V., Stefani N., Vitanza R., 2009, Anaerobic Treatment of Winery Wastes in Suspended and Attached Growth Biomass Reactors, *Atti della Conferenza "5th International Specialized Conference on Sustainable Viticulture: Winery Waste and Ecologic Impacts Management"*, Trento e Verona (I), 30 March – 3 April, 325-331.
- Husain A., 1998, Mathematical Models of the Kinetics of Anaerobic Digestion – Selected Review, *Biomass and Bioenergy*, 14(5/6), 561-571.
- ISTAT, 2008, The production of grapes and wine, year 2007 (In Italian), Italian National Institute of Statistics, Rome, Italy.
- Vanrolleghem P.A., Rosen C., Zaher U., Copp J., Benedetti L., Ayasa E., Jeppsson U., 2005, Continuity-Based Interfacing of Models for Wastewater Systems Described by Petersen Matrices, *Water Science & Technology*, 52(1-2), 493–500.