Mathematical modelling of upflow anaerobic sludge bed (UASB) systems treating carbohydrate waste waters

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Abstract

A mathematical model is presented describing product formation and product utilisation along the line of flow in a pelletised sludge bed of a single UASB reactor system with soluble carbohydrate as influent substrate. The model proposes 12 essential processes incorporating 16 essential compounds, and includes product (compound) utilisation/formation by interaction between four groups of organisms, viz. (1) acidogens, (2) acetogens, (3) acetoclastic methanogens, and (4) H_2-utilising methanogens. Product (compound) formation and utilisation associated with the growth of these organism groups are modelled using Monod kinetics. The crucial effect of the hydrogen concentration, or equivalently the hydrogen partial pressure, on the growth/no growth of acetogens and the associated conversion/non-conversion of propionate to acetate are modelled using switching functions. The model assumes biofilm diffusion is negligible and that pH in the profile does not decline below 6,6. The model adequately predicts the concentration profiles of total soluble COD, acetate, propionate, organic nitrogen and free and saline ammonia in the pelletised bed under different chemical oxygen demand (COD) concentrations and influent flow rates with or without a recycle from the effluent to the influent, provided the substrate loading rate is below the maximum observed experimentally.

Introduction

Mathematical models are widely used in waste-water treatment. The objective of a mathematical model is to give quantitative expression to behavioural patterns of interest in a waste-water treatment system. Two extremes in mathematical models can be identified, empirical and mechanistic. An empirical model is based on recognition of the parameters that appear to be essential to describe the behavioural pattern of interest, and linking these by empirical relationships established by observation — the mechanisms and/or processes operating in the system are not known or are ignored.

In contrast, a mechanistic model is based on some conceptualisation of the biological/physical mechanisms operating in the system, i.e. it is based on some conceptual model. The complexity of this conceptual model will depend on the degree of understanding extent on the phenomena occurring in the system. To set up the conceptual model, the processes operating in the system and the compounds on which these act are identified, and the various interactions between the processes, and the processes and compounds are delineated descriptively. From the conceptual model, the process rates and their stoichiometric interactions with the compounds are formulated mathematically, to develop the mechanistic model. The conceptual, and its mathematical equivalent the mechanistic model, very likely will not include all the processes and compounds that are present in the system, only those conceived to be of significance for fulfilling the objectives set for the model need be included. The art of constructing the conceptual and mechanistic models is in eliminating those processes and compounds which contribute little or nothing to fulfilling the objectives set for the model; it is a waste of time and effort to develop a complicated model where a simpler one is adequate. A model can be deemed successful if it fulfills the expectations from it. Eventually, models are only our rationalisation of behavioural patterns of parameters we conceive to be of interest. Due to this rationalisation, the model needs to be adequately verified by appropriate tests and the conditions within which the model is expected to operate successfully need to be firmly delineated.

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The various uses of mathematical models in waste-water treatment can be summarised as follows: A model

- gives expression to conceptual ideas, to account for major events of interest occurring within a system, and allows evaluation of these; by comparing the simulated and the observed response, attention may be drawn to deficiencies in the conceptual structure;
- provides information not apparent from pilot-scale studies; this can be particularly useful if the system being modelled is a complex one;
- allows potentially feasible solutions to be explored that are not covered by the pilot-scale and other studies, thereby giving guidance for selecting the more promising ones for testing;
- assists in identifying the parameters that significantly influence the system response and thereby gives guidance for the establishment of design criteria; and
- assists in identifying possible causes for system malfunction or failure, and in devising remedial measures.

It is unlikely that any particular model will fulfill all of these uses. Simpler models may be developed to satisfy specific uses in the list above; these will have limited use but also usually require less input than the more complex models, with their greater range.

Research into upflow anaerobic sludge bed (UASB) reactor systems developing pelletised sludge beds has now progressed to the extent that development of a relatively complex mechanistically based kinetic model is feasible, to describe their behaviour. It is the objective of this paper to develop such a model.

Modelling tasks

To set up a model for the UASB system a number of tasks need to be completed:

- Describe the conditions within which the model is to operate.
- Identify the essential compounds utilised and formed.
- Identify the processes acting on these compounds.
- Conceptualise a mechanistic model that qualitatively describes the kinetic and stoichiometric behaviour of the processes and compounds.

- Formulate mathematically the process rates, stoichiometry and transport relationships.
- Calibrate the model and test its response against that observed experimentally.

Model conditions

The kinetic model presented here is restricted to a UASB system producing a pelletised sludge bed. (The hypothesised conceptual model for pelletisation is described later). Sam-Soon *et al.* (1987, 1990a, 1990b, 1991a, 1991b, 1991c) have described the conditions necessary for a UASB system to develop a pelletised sludge bed. Briefly they are the following:

- Influent substrate must give rise to a high hydrogen partial pressure ($\bar{p}H_2$) zone in the bed. Substrates that comply are of carbohydrate or proteinaceous nature; during the acidogenesis of these substrates hydrogen is generated at a high rate, to give rise to a high $\bar{p}H_2$ zone. Substrates that do not comply are (i) the short-chain fatty acid (SCFA) acetate; during conversion to methane (by acetoclastic methanogens) no hydrogen is generated, (ii) SCFAs propionate and butyrate; during conversion to acetate (by acetogens) hydrogen is generated but this conversion only takes place under low $\bar{p}H_2$, (iii) long-chain fatty acids; during breakdown to acetate, or acetate and propionate, (via β-oxidation by acetogens) hydrogen is generated, but the breakdown only takes place under low $\bar{p}H_2$, and (iv) lipids; these are broken down to long-chain fatty acids and (iii) applies.
- Ammonia nitrogen must be present in excess in the influent (or developed in excess in the fermentation of proteinaceous wastes). The influent nitrogen/COD ratio should exceed 0,017 to 0,02 mgN/mgCOD to obtain the maximum pellet formation. When the influent nitrogen/COD ratio declines below this limit, there is an associated reduction in pellet formation until at a lower ratio limit (0,0086 mgN/mgCOD) pellet formation effectively ceases.
- The influent alkalinity/COD ratio must be high enough [> 1,2 mg alkalinity (as $CaCO_3$)/mg influent COD] to ensure that the minimum pH in the bed does not fall below about 6,6 otherwise methanogenesis will be inhibited. The influent alkalinity/COD ratio can be reduced by recycling from the effluent to the influent.
- No oxidising agents (e.g. sulphate) must be present in the influent. These will result in a reduction in the H_2 substrate available to the pellet forming *Methanobacterium* Strain *AZ (M.* Strain *AZ)* (e.g. H_2-utilising sulphidogens compete with *M.* Strain *AZ* for the H_2 in order to reduce sulphate and form hydrogen sulphide).
- Not even a trace of cysteine must be available. If cysteine is more readily available the pelletisation process is reduced or ceases.

The conditions for pelletisation above restrict the kinetic model to a UASB system treating a soluble carbohydrate or proteinaceous waste, with adequate influent nitrogen and alkalinity, and no oxidising agent or cysteine in the influent. In this paper the model will be restricted to deal with soluble carbohydrate waste only, e.g. apple juice, glucose. Other restrictions set on the model are the following system and operating conditions:

- Sludge bed volume is fixed.
- Temperature is fixed at 30°C.
- The liquid passes in a plug flow fashion through the bed; no vertical mixing between sludge bed layers (Sam-Soon *et al.*, 1987, 1990a).
- Loading rate is less than the maximum rate determined by experiment (Sam-Soon *et al.*, 1991c).

Compounds

There appear to be 16 essential compounds directly involved in a UASB system treating a carbohydrate substrate. Some of these compounds are directly observable. With others the means for measuring these were not available in the laboratory; their existence has to be inferred, either from the hypothesised biochemical behaviour, or from the requirement of mass balances. Six compounds are directly observable, viz. concentrations of:

- soluble unbiodegradable COD;
- acetic acid (HAc);
- propionic acid (HPr);
- ammonium nitrogen (NH_3-N);
- soluble organic nitrogen (orgN); and
- methane (CH_4).

Ten compounds are inferred, viz. concentrations of:

- molecular hydrogen (H_2);
- glucose;
- polymer mass;
- nitrogen in polymer;
- nitrogen in biomass;
- unbiodegradable particulate COD;
- acidogens;
- acetogens;
- acetoclastic methanogens; and
- H_2-utilising methanogens.

In modelling the behaviour in the compounds identified above, only changes of the compounds in the bulk liquid are described. The compound concentrations within the pellet may differ from the bulk liquid, but modelling these is not practical; techniques to measure concentrations within the pellet were not available.

Processes

The processes that act on the compounds were identified by observing changes in the compounds under a variety of conditions, e.g. different influent COD concentrations, flow rates and NH_3-N concentrations. Twelve essential processes are identified:

Growth:
- Acidogens on glucose under high $\bar{p}H_2$
- Acidogens on glucose under low $\bar{p}H_2$
- H_2-utilising methanogens on hydrogen
- Acetoclastic methanogens on acetic acid
- Acetogens on propionic acid

Death:
- Acidogens
- H_2-utilising methanogens
- Acetoclastic methanogens
- Acetogens

Other processes:
- Ammonification of soluble organic nitrogen
- Pellet break-up
- Adsorption/enmeshment of soluble organic nitrogen.

Conceptual model

The conceptual model is based on the biochemical model for pelletisation of Sam-Soon *et al.* (1987). However, the conceptual model (and the mathematical model developed from this) takes a more macroscopic approach than the microscopic approach used for the biochemical model. A microscopic approach would require modelling each biochemical reaction and the mechanisms controlling it; there is no experimental data for structuring a model to incorporate these. Accordingly, the conceptual model will be structured considering only the net effects as present in the bulk liquid.

Microbial population

In conceptualising the behaviour of the UASB system it is necessary to identify the biological agents that mediate the processes and utilise or generate the compounds. Four microbial populations are involved in the fermentation of soluble carbohydrates (e.g. glucose): Acidogens; acetogens; acetoclastic methanogens; and H_2-utilising methanogens.

- ***Acidogens:*** The acidogens convert glucose to SCFA (acetic, propionic and butyric acids), carbon dioxide and hydrogen. The SCFA generated will depend on the hydrogen partial pressure, $\bar{p}H_2$ (Sam-Soon *et al.*, 1990a). Under lower $\bar{p}H_2$ ($\bar{p}H_2 < \pm 10^{-3,7}$atm), acetic and butyric acids are generated together with hydrogen and carbon dioxide. Under higher $\bar{p}H_2$ ($\bar{p}H_2 > \pm 10^{-3,7}$atm), acetic, propionic and butyric acids are generated together with hydrogen and carbon dioxide. However, butyric acid was not observed in any of the high/low $\bar{p}H_2$ single reactor UASB systems when apple juice waste water or glucose served as substrates. An hypothesis for the non-appearance of butyrate in high/low $\bar{p}H_2$ reactor systems has been put forward by Sam-Soon *et al.* (1990a). As butyrate is not expected to be present in a real system, this compound is not included in the model.

- ***Acetogens:*** The acetogens convert propionic acid to acetic acid, hydrogen and carbon dioxide. Propionic acid conversion becomes significant only when $\bar{p}H_2$ declines to less than $10^{-4,1}$atm; at higher $\bar{p}H_2$ propionic acid conversion becomes negligible or does not take place, that is, conversion of propionic acid to acetic acid is a function of the $\bar{p}H_2$ or equivalently, the hydrogen concentration. Propionate conversion is used to define the $\bar{p}H_2$ zones in the UASB system. In the lower active (high $\bar{p}H_2$) zone no apparent propionate conversion takes place; in the upper active (low $\bar{p}H_2$) zone propionate conversion takes place (Sam-Soon *et al.*, 1987; 1990a).

- ***Acetoclastic methanogens:*** Acetoclastic methanogens convert acetic acid to methane and carbon dioxide; this conversion is independent of $\bar{p}H_2$. Dubourguier *et al.* (1985, 1988) concluded that the dominant acetoclastic methanogen in granular anaerobic sludges is *Methanothrix soehngenii.*

- ***H_2-utilising methanogens:*** H_2-utilising (hydrogenotrophic) methanogens utilise hydrogen as sole energy source, and CO_2 as carbon source, to produce methane. It is assumed that *M.* Strain *AZ* (now known as *Methanobrevibacter aboriphilus*), is the main H_2-utilising methanogen present in a UASB system treating a carbohydrate substrate; Dubourguier *et al.* (1985, 1988) concluded that *M.* Strain *AZ* is the dominant H_2-utilising species present in granular anaerobic sludges. This species is the principal organism mediating pelletisation (Sam-Soon *et al.*, 1987, 1990a).

Pellet formation

The characteristics of *M.* Strain *AZ* are central to describing the pelletisation phenomena (Sam-Soon *et al.*, 1987, 1990a). This organism has the unusual characteristic that it cannot manufacture the amino acid cysteine and depends on external sources, such as cysteine in the influent or that liberated from death of other organisms, for its cysteine supply.

Under high $\bar{p}H_2$ conditions (i.e. high H_2 substrate concentration), in the presence of excess of free and saline ammonia, a high production of all the amino acids (except cysteine) is stimulated. If the cysteine supply is limited, *M.*Strain *AZ* cannot utilise the amino acids for cell synthesis. The excess amino acids are released to the surrounding medium, and/or are linked in polypeptide chains which are extruded from active sites. These polypeptide chains bind the *M.* Strain *AZ* species and other microorganisms into pellets. Thus, H_2 oxidised by *M.* Strain *AZ* reappears in the compounds methane, organism mass, polypeptide polymer and/or free amino acids, the relative magnitudes of the fractions produced depending on the cysteine availability. If, for example, the feed is supplemented with cysteine, theoretically this should result in an increase in the *M.* Strain *AZ* species and a reduction in both volatile polypeptide solids yield and free amino acids released to the surrounding medium, the net effect being a reduction in volatile solids (Sam-Soon *et al.*, 1987).

Other factors limiting the generation of polypeptide/free amino acids are as follows:

- ***Ammonia (NH_3-N) concentration:*** If the influent NH_3-N/COD ratio is below some upper value (0,017 to 0,02 mgN/mgCOD), a reduction in polypeptide yield and soluble free amino acids is to be expected (Sam-Soon *et al.*, 1990b) and H_2 generated in the system is not fully utilised by *M.* Strain *AZ* due to a lack of NH_3-N for the formation of the polypeptide or amino acids. Sam-Soon *et al.* (1990b) have shown that with limited NH_3-N the H_2 that cannot be utilised is lost from the system as H_2 gas.

- ***Secondary reactions:*** Even though the substrate has the potential to give rise to a high $\bar{p}H_2$, if secondary reactions abstract H_2 (e.g. for sulphate reduction), this will reduce the H_2 substrate available to *M.* Strain *AZ*, and hence reduce polypeptide generation (Sam-Soon *et al.*, 1991a).

- ***Influent substrate:*** Generation of polypeptide/free amino acids will be limited if the influent substrate itself does not yield hydrogen (e.g. acetate) or can be broken down only under low $\bar{p}H_2$ (e.g. lipids or long-chain fatty acids). In the first case no H_2 substrate will be available to *M.* Strain *AZ;* in the second because the $\bar{p}H_2$ is low the rate of substrate diffusion (H_2) into *M.* Strain *AZ* cells will be slow so that sufficient cysteine will be available from the influent or from cell death for the H_2 to be used for cell production. In both instances excess amino acid production will be limited — polypeptide generation is not to be expected (Sam-Soon *et al.*, 1991b).

In the conditions for the model set out earlier it was assumed that (1) the influent substrate is soluble carbohydrate, i.e. can generate a high $\bar{p}H_2$; (2) influent NH_3-N is present in excess; (3) no oxidising agents, e.g. sulphate, are present in influent; and (4) no cysteine is added in the influent. Therefore, none of the limitations for pelletisation described above will apply.

Substrate transfer

The model assumes no diffusion limitation on substrate transfer in

the pellets. The pellets are hypothesised to behave as "gas pumps". Gases (methane and CO_2) produced inside the pellets are released via gas channels to the surrounding medium; as the gas escapes from the pellets, a pressure drop is generated in the channels causing liquid (substrate) to be drawn into the pellets. In such a situation very likely mass transfer resistance, due to diffusion limitations, becomes negligible and should not be a factor influencing the kinetics of the processes in the pelletised sludge bed. The assumption that the pellets behave as "gas pumps" is supported by observations of Robinson *et al.* (1984); they produced scanning electron micrographs of biofilms from anaerobic fixed-bed reactors, which clearly show the presence of an extensive network of channels and openings. They concluded that these channels may facilitate gas and nutrient exchange. Wiegant and De Man (1986) also demonstrated a similar network of channels and openings in granular methanogenic sludge.

Soluble organic nitrogen

In the aqueous phase in a pelletised sludge bed, soluble organic nitrogen is present in substantial concentrations (Sam-Soon *et al.*, 1987, 1990a). This fraction can be conceptualised to arise from the following sources: death of organisms (acidogens, acetogens, H_2-utilising methanogens and acetoclastic methanogens); pellet break-up; and release of free amino acids by *M.*Strain *AZ.* Sinks for the organic nitrogen can be conceptualised to be adsorption/enmeshment of soluble organic nitrogen, probably of free polypeptide chains (from pellet break-up); and ammonification of soluble organic nitrogen.

With regard to the sources of soluble organic nitrogen, in "normal" anaerobic methane fermentation systems the presence of soluble organic nitrogen is ascribed to the endogenous mass loss (or death) of the anaerobic microorganisms. Generation of organic nitrogen due to organism death is included in the model. However, experimentally in a UASB pelletised sludge system the concentration of soluble organic nitrogen in the bed liquid is much higher than can be attributed to death of microorganisms. The sources for this high soluble organic nitrogen are conceptualised to be due to (1) generation of free amino acids by *M.* Strain *AZ,* and (2) polypeptide polymer release due to break-up of pellets (Sam-Soon *et al.,* 1987). With the experimental set-ups in the studies of Sam-Soon *et al.,* it is not possible to differentiate between these two processes. For the purpose of modelling, the two processes are lumped together and it is assumed that the **excess** soluble organic nitrogen is derived only from break-up of the polypeptide chains of the pellet. The rate of polypeptide break-up is linked to the polymer mass.

The conceptualised sinks for soluble organic nitrogen are ammonification and adsorption/enmeshment; in the model these are treated as separate processes. With regard to ammonification, in UASB concentration profiles Sam-Soon *et al.* (1990a) observed that the ammonia concentration first decreases due to uptake for polymer formation and cell synthesis, thereafter it increases and then remains virtually constant; in the model this increase is conceptualised to be due to ammonification of soluble organic nitrogen. With regard to adsorption/enmeshment of the soluble organic nitrogen, the existence of this process cannot be clearly identified from the experimental profiles; very likely it occurs. In the model it is included as a function of soluble organic nitrogen, but this is more for the sake of completeness than quantitative estimation.

Model presentation

In the mathematical model, the process rates and the stoichiometric relationships between the processes and compounds are formulated mathematically. The large number of complex interactions between compounds and processes necessitates that these be clearly presented. Following the proposals of the IAWPRC Task Goup (1987) on "Mathematical Modelling of Waste-water Treatment", the processes and compounds are set out in a compound-process matrix (Table 1). This format facilitates clear and unambiguous presentation of the compounds and processes and their interaction. The setting up of such a matrix, how to interpret it and how it is incorporated in the mathematical solution procedures are described briefly in **Appendix 1.** For greater detail on solution procedures for the matrix, see Billing (1987) and Billing and Dold (1988a, 1988b, 1988c).

Model description

The matrix of compounds and processes is set out in Table 1. The compounds, "i" in number, are listed in symbol form across the top of the matrix, one compound per matrix column; a more complete description of each compound is given at the base of the respective column. The processes, "j" in number are listed down the left hand side of the matix, one process per matrix row. The kinetic rate expression, "ρ", for each process is listed on the right hand of the compound-process matrix, as a **column matrix,** the rate expression being in the same row as the process. The stoichiometric conversion factors from one compound to another are listed horizontally for each process below the affected compounds. Details of the derivation of the stoichiometric conversion factors are given in **Appendix 2.**

Following the IAWPRC recommendation, volatile suspended solids (VSS) specific yields and other associated parameters are expressed in COD units. Nitrogenous compounds are expressed in terms of the element nitrogen (N).

To facilitate the discussion, the processes in the matrix are categorised into:

- Growth of organisms (j = 1 to 5)
- Death of organisms (j = 6 to 9)
- Ammonification (j = 10)
- Physical effects (j = 11 to 13).

Growth of organisms (j = 1 to 5)

The microbial growth rate and substrate utilisation rate expressions for the 4 groups of organisms present in the UASB systems are based on the Monod's formulation. Monod's formulation is used because in the model the substrates utilised by the organism groups (glucose by acidogens; propionate by acetogens; acetate by acetoclastic methanogens; CO_2 and H_2 by hydrogenotrophic methanogens) are all soluble and can be taken up directly without extracellular enzymatic breakdown - experience has shown that Monod's formulation provides a very useful mathematical description for soluble substrate utilisation and for growth on these substrates. [For more complex substrates that require extracellular breakdown (e.g. lipids), alternative formulations may be required]. The growth of each group of organisms is discussed below.

Acidogen growth (j = 1 to 2): From the conceptual model two processes are needed to describe acidogen growth. The first process (j = 1) takes place under high $\bar{p}\,H_2$ conditions and the second process (j = 2) under low $\bar{p}\,H_2$ conditions. The two processes have a number of factors in common: For every 1 COD unit of active mass (i = 1) appearing, $(1+Y_A)/Y_A$ COD units of glucose (i = 9) are consumed, where Y_A is the specific yield constant in COD units

TABLE 1
MATRIX FOR UASB REACTOR SYSTEM WITH SOLUBLE CARBOHYDRATE AS INFLUENT

COMPONENT → i	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	PROCESS RATE, ρ_j
j PROCESS ↓	$X_{B,A}$	$X_{B,MH}$	$X_{B,AM}$	$X_{B,AP}$	$X_{B,P}$	$X_{N,H}$	$X_{N,B}$	$S_{I,D}$	S_G	S_A	S_P	$S_{I,P}$	S_{NH}	S_{ND}	S_H	S_{CH_4}	M L^{-3} T^{-1}
1 Acidogen growth on S_G (at high pH_2)	1						$+i_{XBN}$		$-\frac{(1+Y_A)}{Y_A}$	$1/3 \cdot 1/Y_A$	$7/12 \cdot 1/Y_A$		$-i_{XBN}$		$1/12 \cdot 1/Y_A$		$\hat{\mu}_A \frac{S_G}{K_A+S_G} \frac{S_H}{(K_H+S_H)} X_{B,A}$
2 Acidogen growth on S_G (at low pH_2)	1						$+i_{XBN}$		$-\frac{(1+Y_A)}{Y_A}$	$2/3 \cdot 1/Y_A$			$-i_{XBN}$		$1/3 \cdot 1/Y_A$		$\hat{\mu}_A \frac{S_G}{K_A+S_G}\left(1-\frac{S_H}{(K_H+S_H)}\right) X_{B,A}$
3 H_2-utilizing methanogen growth		1			Y_P/Y_{MH}	$\frac{Y_P \cdot i_{XPN}}{Y_{MH}}$	$+i_{XBN}$						$\frac{-i_{XBN}}{-Y_P \cdot i_{XPN}}$ / Y_{MH}		$-1/Y_{MH}$	$\frac{(1-Y_P-Y_{MH})}{Y_{MH}}$	$\hat{\mu}_{MH} \frac{S_H}{(K_{MH}+S_H)} X_{B,MH}$
4 Acetoclastic methanogen growth			1				$+i_{XBN}$			$-\frac{(1+Y_{MA})}{Y_{MA}}$			$-i_{XBN}$			$\frac{(1-Y_{MA})}{Y_{MA}}$	$\hat{\mu}_{MA} \frac{S_A}{(K_{MA}+S_A)} X_{B,AM}$
5 Acetogen growth on HPr				1			$+i_{XBN}$			$4/7 \cdot 1/Y_{AP}$	$-\frac{(1+Y_{AP})}{Y_{AP}}$		$-i_{XBN}$		$3/7 \cdot 1/Y_{AP}$		$\hat{\mu}_{AP} \frac{S_P}{K_{AP}+S_P}\left(1-\frac{S_H}{(K_H+S_H)}\right) X_{B,AP}$
6 Death acidogens	-1						$-i_{XBN}$	1						i_{XBN}			$b_A \cdot X_{B,A}$
7 Death H_2-utilizing methanogens		-1					$-i_{XBN}$	1						i_{XBN}			$b_{MH} \cdot X_{B,MH}$
8 Death acetoclastic methanogens			-1				$-i_{XBN}$	1						i_{XBN}			$b_{MA} \cdot X_{B,AM}$
9 Death acetogens				-1			$-i_{XBN}$	1						i_{XBN}			$b_{AP} \cdot X_{B,AP}$
10 Ammonification													+1	-1			$K_{ND}\left(\sum X_B \text{ except } X_{B,P}\right)$
11 Pellet Break up					-1	$-i_{XPN}$						+1		$+i_{XPN}$			$K_{BP}\,(0{,}1\rho_1+0{,}1\rho_2+0{,}1\rho_3+0{,}7\rho_4)$
12 Adsorption/Enmeshment of soluble orgN					+1	i_{XPN}						-1.		$-i_{XPN}$			$K_{EP} \cdot S_{ND}$
	Biological active acidogen mass -M(COD)L^{-3}	Biological active H_2-utilizing methanogen mass -M(COD)L^{-3}	Biological active acetoclastic methanogen mass -M(COD)L^{-3}	Biological active acetogen mass -M(COD)L^{-3}	Polymer mass -M(COD)L^{-3}	Nitrogen content of polymer -M(N)L^{-3}	Nitrogen content of biomass -M(N)L^{-3}	Inert mass (organism death) -M(COD)L^{-3}	Soluble glucose substrate -M(COD)L^{-3}	Soluble acetic acid substrate -M(COD)L^{-3}	Soluble propionic acid substrate -M(COD)L^{-3}	Soluble inert polymer mass -M(COD)L^{-3}	Soluble ammonia nitrogen -M(N)L^{-3}	Soluble organic nitrogen -M(N)L^{-3}	Soluble hydrogen -M(COD)L^{-3}	Methane -M(COD)L^{-3}	

for the acidogens. With acidogen growth nitrogen is incorporated in cell mass giving rise to a reduction in ammonia concentration (i=13) and an increase in the nitrogen content of biomass (i=7).

However, acidogen growth under high ($\bar{p}H_2 > \pm 10^{-3,7}$atm) and low $\bar{p}H_2$ ($\bar{p}H_2 < \pm 10^{-3,7}$atm) differs in the stoichiometric production of acetic and propionic acids and hydrogen.

Under high $\bar{p}H_2$: For every $(1+Y_A)/Y_A$ units of glucose (i=9) consumed, $1/3 \times 1/Y_A$ units of acetic acid (i=10), $7/12 \times 1/Y_A$ units of propionic acid (i=11) and $1/12 \times 1/Y_A$ units of hydrogen (i=15), are generated, all in COD units.

Under low $\bar{p}H_2$: For every $(1+Y_A)/Y_A$ units of glucose (i=9) consumed, $2/3 \times 1/Y_A$ units of acetic acid (i=10), 0 units propionic acid (i=11) and $1/3 \times 1/Y_A$ units of hydrogen (i=15) are generated, all in COD units.

Derivations of these stoichiometric ratios are given in **Appendix 2.**

The process rate of utilisation of glucose by the acidogens (in the process rate column) is modelled using Monod's equation with maximum specific growth rate $\hat{\mu}_A$ and half saturation coefficient K_A with respect to the glucose concentration. The process rate also is modelled as first order with respect to the acidogen concentration.

The extent to which process j=1 or 2 predominates depends on the hydrogen concentration. A switching function is utilised to switch from one process to the other based on the hydrogen concentration. The Monod rate expression is multiplied by the switching function $S_H/(K_H+S_H)$, where S_H is the hydrogen concentration and K_H is the switching constant. Consider acidogen growth on glucose when S_H is high, $S_H/(K_H+S_H)$ approaches unity and process j=1 is the predominant reaction; when S_H decreases below K_H then $S_H/(K_H+S_H)$ decreases eventually to near zero, process j=2 becomes the predominant reaction and process j=1 becomes inoperative. [It should be noted that the terms "high" and "low" $\bar{p}H_2$ used here to differentiate acidogen growth do not correspond to the high and low $\bar{p}H_2$ zones in the UASB system sludge bed. For acidogen growth $\bar{p}H_2 = \pm 10^{-3,7}$ atm defines the division between high and low $\bar{p}H_2$ whereas for the sludge bed $\bar{p}H_2 = \pm 10^{-4,1}$atm (which is the $\bar{p}H_2$ below which propionate conversion by acetogens takes place) defines the division between high and low $\bar{p}H_2$ zones. However, for the purpose of modelling, distinguishing between the acidogen and acetogen $\bar{p}H_2$s is not justified from the experimental data available. Accordingly, the same half-saturation constant for hydrogen (K_H) is used in the switching functions for acidogen growth and for acetogen growth].

H_2-utilising methanogen growth (j=3): In H_2-utilising methanogenic growth both active organism and polymer masses are being formed simultaneously. The substrate source for both organism and polymer is hydrogen. Stoichiometrically, for every one unit of active mass (i=2) formed, Y_P/Y_{MH} units of polymer (i=5) and $(1-Y_P-Y_{MH})/Y_{MH}$ units of methane (i=16) are generated and $1/Y_{MH}$ units of hydrogen (i=15) are utilised, all in COD units **(Appendix 2),** where Y_P is the specific yield constant for polymer mass and Y_{MH} is the specific yield constant for H_2-utilising methanogens, both also in COD units. With H_2-utilising methanogen growth, nitrogen is incorporated both in cell mass and in polymer mass giving rise to a reduction in ammonia concentration (i=13) and an increase in the nitrogen content of biomass (i=7) and polymer mass (i=6).

The Monod kinetic growth constants are $\hat{\mu}_{MH}$ (maximum specific growth rate) and K_{MH} (half-saturation constant) with respect to the hydrogen concentration. The process rate is modelled as first order with respect to the H_2-utilising methanogen concentration.

Acetoclastic methanogen growth (j=4): In acetoclastic methanogen growth on acetic acid, for every one COD unit of active mass (i=3) formed, $(1-Y_{MA})/Y_{MA}$ COD units of methane (i=16) are generated and $(1+Y_{MA})/Y_{MA}$ COD units of acetic acid (i=10) are utilised, where Y_{MA} is the specific yield constant in COD units for the acetoclastic methanogens (see **Appendix 2).** For acetoclastic methanogen growth, nitrogen is incorporated in cell mass giving rise to a reduction in ammonia concentration (i=13) and an increase in the nitrogen content of biomass (i=7).

The growth rate is modelled using Monod kinetics with kinetic growth rate constants $\hat{\mu}_{MA}$ (maximum specific growth rate) and K_{MA} (half-saturation constant) with respect to the acetic acid concentration. The growth rate also is modelled as first order with respect to the acetoclastic methanogen concentration.

Acetogen growth (j=5): From the conceptual model, acetogen growth on propionic acid is a function of the hydrogen concentration surrounding the organisms. As $\bar{p}H_2$ increases (or equivalently as hydrogen concentration increases), acetogen growth decreases until the growth reaction thermodynamically is not feasible; i.e. growth rate becomes zero. Mathematically this is achieved by multiplying the Monod rate expression by a switching function of the form $[1-S_H/(K_H+S_H)]$ which is similar to the one used for acidogen growth at low $\bar{p}H_2$. When $S_H >> K_H$, $S_H/(K_H+S_H)$ tends to unity, the switching function tends to zero and process rate tends to zero. When $S_H << K_H$ then the value of the switching function approaches unity and the process rate will be given by the relevant Monod equation.

For every 1 unit of active mass (i=4) appearing $4/7 \times 1/Y_{AP}$ units of acetic acid (i=10) and $3/7 \times 1/Y_{AP}$ units of hydrogen (i=15) are produced and $(1+Y_{AP})/Y_{AP}$ units of propionic acid (i=11) are consumed, all in COD units, where Y_{AP} is the specific yield constant in COD units for the acetogens (see **Appendix 2).** With acetogen growth, nitrogen is incorporated in cell mass resulting in a reduction in ammonia concentration (i=13) and an increase in the nitrogen content of biomass (i=7).

The Monod kinetic constants are $\hat{\mu}_{AP}$ (maximum specific growth rate) and K_{AP} (half-saturation coefficient) with respect to the propionic acid concentration. The process rate also is modelled as first order with respect to the acetogen concentration.

Death of organisms (j = 6 to 9)

The rate of death of organisms is modelled as a first order reaction with respect to the relevant active mass. For every COD unit of organism disappearing (i=1 to 4), one COD unit of "dead" volatile material is generated (i=8). From the experimental data it is not possible to subdivide this material into, say, inert and biodegradable fractions. However, the mass released to the surrounding medium is small relative to the active mass so that for the purpose of modelling it is sufficient to ascribe the products of death to an inert soluble mass — i.e. a soluble "unbiodegradable" COD. Associated with death of organisms is the loss of nitrogen associated with the active mass (i=7); this nitrogen reappears as soluble organic nitrogen (i=14). The specific kinetic decay or death rate constants for acidogens, H_2-utilising methanogens, acetoclastic methanogens and acetogens are b_A, b_{MH}, b_{MA} and b_{AP} respectively, units (d^{-1}).

Ammonification of soluble organic nitrogen (j = 10)

From the conceptual model, in line with experimental observations of Sam-Soon *et al.* (1987, 1990a) that in the upper regions of the sludge bed the ammonia concentration increases, conversion

(ammonification) of soluble organic nitrogen to ammonia is incorporated in the kinetic model (j = 10). The rate of ammonification is modelled as a first order reaction with respect to the sum of all active masses with a specific rate constant K_{ND}. For every one N unit of ammonia generated (i = 11), one N unit of soluble organic nitrogen is consumed (i = 12).

Physical processes (j = 11 to 12)

From the conceptual model, two physical processes, namely pellet break-up and adsorption/enmeshment of soluble organic nitrogen, have been identified as taking place in the pelletised sludge bed.

Pellet break-up (j = 11): The rate of pellet break-up is modelled as a first order reaction (kinetic rate constant K_{BP}) with respect to the **growth rates** of the 4 groups of organisms - gas production is related to growth, and break-up of the pellets is assumed to be due to disruption by the gas. During organism growth gaseous products always are released. However, hydrogen gas released during acidogenic growth on glucose and during acetogenic growth on propionic acid, is removed virtually instantaneously by the H_2-utilising methanogens so that the gases released to the surrounding medium are methane and carbon dioxide. Since it is estimated that approximately 70 per cent of the methane generated comes from acetic acid fermentation (Jeris and McCarty, 1965; Smith and Mah, 1966) the stoichiometric coefficient is taken as 0,7 for process rate ρ_4 (acetoclastic methanogen growth rate) and as 0,1 for each of the three process rates ρ_1 (acidogen growth rate at high $\bar{p}\,H_2$), ρ_2 (acidogen growth rate at low $\bar{p}\,H_2$) and ρ_3 (H_2-utilising methanogen growth rate).

Experimentally, it was not possible to obtain quantitative measures of this process. It is assumed that the material from pellet break-up is released as soluble inert polymer mass to the surrounding liquid and eventually discharges in the effluent. From the matrix, for every one COD unit of polymer mass (i = 5) disappearing, one COD unit of soluble inert polymer mass (i = 12) is generated. Associated with the disappearance of polymer mass is the loss of nitrogen incorporated in the polymer (i = 6); this nitrogen reappears as soluble organic nitrogen (i = 14).

Adsorption/enmeshment of soluble organic nitrogen (j = 12): The rate of adsorption/enmeshment of soluble organic nitrogen is modelled as first order with respect to soluble organic nitrogen and the first order kinetic rate constant is K_{EP}.

From the matrix, for every one nitrogen unit of soluble organic nitrogen (i = 14) enmeshed, one nitrogen unit is added to the nitrogen content of polymer (i = 6). Associated with the enmeshment of organic nitrogen is the removal of soluble inert polymer mass (i = 12) from solution; this mass reappears as enmeshed polymer mass (i = 5).

Matrix solution

The matrix presentation of the compounds, processes and rates defines the behaviour at a single point in the system. To obtain the response of the system, the following need to be incorporated: System configuration (single or multiple reactors), reactor type (continuously fed, batch etc.), hydraulic mixing regime in the reactor (plug flow or completely mixed), solids regime (suspended or fixed), recycle flows between reactors, and mass transport of compounds in and out of each reactor.

Within the requirements stated above, the UASB system configuration is a single reactor, the reactor is continuously fed, the hydraulic mixing regime (i.e. mixing regime of the aquous phase) is of the plug flow type (Sam-Soon *et al.* 1987), the pelletised solids are assumed to be fixed and there is an option for a recycle from the effluent to the influent point of the reactor. Of these the distribution of the solids within the reactor needs to be described in greater detail.

Pelletised bed VSS concentration

In the UASB reactor it was observed that pellet size varied from the bottom to the top of the pelletised bed, with maximum size at the bottom of the bed. One may expect, therefore, that the VSS concentration would vary up the sludge bed. In the laboratory studies it was not possible to obtain a profile of the VSS concentration. In attempting to obtain a profile of VSS concentration on the laboratory-scale reactors, sampling disturbed the *in situ* concentration at the sampling point because the diameter of the reactor was small; only the average concentration could be obtained by draining the entire pelletised bed and sampling the bed after mixing to obtain a uniform concentration. However, profiles obtained on laboratory-scale studies have been reported in the literature. Hamoda and Van den Berg (1984) measured the distribution of VSS up a UASB reactor and found that the VSS concentration profile exhibited three zones:

- a lower zone, at the bottom of the bed, in which the VSS concentration was at a maximum and constant;
- a transitional zone in the upper part of the bed in which the VSS concentration decreased linearly with height to a minimum at the top of the bed; and
- a suspended blanket zone above the bed, in which the VSS concentration was low and constant. Sam-Soon *et al.* (1987, 1990a) found that the suspended blanket zone above the sludge bed exhibited no biological activity and therefore is omitted from the mathematical model.

Hamoda and Van den Berg (1984) observed that within the bed VSS concentration zones, the solid concentration profile was a function of organic loading - the VSS concentrations increased, and each zone extended further up the reactor, with increase in the organic loading. In the profiles to be simulated a similar dependency was noted; the average VSS concentration increased with the organic loadings - average VSS ranged from about 29 gVSS/ℓ at a loading rate of 25,5 kgCOD/m³ sludge bed volume.d to about 35 gVSS/ℓ at a loading rate of 80,1 kgCOD/m³ sludge bed volume.d.

For modelling purposes a linear dependency between the **average** bed VSS concentration and organic loading is accepted. The sludge bed VSS profile for any particular average VSS (obtained from the associated organic loading) is constructed as follows:

> The depth of the pelletised bed is taken as the depth observed in the experimental study being simulated. For all organic loadings the VSS concentration at the top of the bed is fixed between 15 and 35 gVSS/ℓ. The zone of constant concentration in the bottom zone of the bed is assumed to extend from the bottom of the reactor up to ¼ of the bed depth; thereafter the concentration is assumed to decrease linearly to the selected minimum at the top of the bed. The VSS concentration at the bottom of the bed is found by trial and error so that the average VSS concentration for the profile is equal to that estimated from the loading/average bed VSS concentration relationship.

With the information supplied above, a solution procedure for the system is structured as follows:

> The plug flow reactor is divided into a set of elements, the product output of the preceding element forming the input to the

succeeding element. The influent compound concentrations and flows are used to obtain the initial concentrations and flows at the reactor base. Concentration profiles in the reactor of the various compounds in the matrix are obtained by integrating forward (using a predictor/corrector method) from the initial concentrations, up the bed. For the integration, the rate equations are obtained from the matrix and the VSS concentrations from the hypothesised VSS profile (as described above).

Further details of solution techniques for the matrix are given in **Appendix 1.**

Model constants

Kinetic and stoichiometric constants were obtained from the literature or from trial curve fitting of simulated data to experimental observations; only three constants were obtained by curve fitting, K_{BP}, K_{EP} and K_{ND}.

Polymer and organism mass fractions

Sam-Soon *et al.* (1987) found the ratio polymer mass: organism mass to be approximately 0,9:0,1; this ratio is accepted in the model. The organism mass consists of different organism mass fractions; for modelling the subdivision into the different organism types is assumed to be the same as that reported by Dolfing (1987) for a granular methanogenic sludge grown on a waste water from a sugar factory, i.e. acidogens: H_2-utilising methanogens: acetoclastic methanogens: acetogens = 0,9:0,08:0,01:0,01.

Kinetic and stoichiometric constants for organisms

A search of the literature for kinetic and stoichiometric constants for the four groups of microorganisms (viz. acidogens, acetogens, acetoclastic methanogens and H_2-utilising methanogens) indicated considerable variation for each, up to an order of magnitude; these are shown in Table 2. For example, the maximum specific growth rate ($\hat{\mu}_{AP}$) and half saturation (K_{AP}) constants for the acetogens (propionate utilisers) range from 0,16 to 1,4/d and 48 to 330 mgCOD/ℓ respectively. The values of the constants selected for use in the model are those that have shown consistent grouping in the literature. For anaerobic organism specific decay rate and specific yield values there is a consistency in the reported values for each of the four groups of organisms. The kinetic and stoichiometric values used in the model are given in Table 3.

The **gross** specific yield for H_2-utilising methanogens of 0,56 mgVSS/mgCOD(H_2) utilised, as calculated by Sam-Soon *et al.* (1990a), includes polymer/free amino acids generated and organism masses. Accepting a specific organism yield of 0,03 mgVSS/mgCOD(H_2) utilised [0,043 mgCOD/mgCOD (H_2)] for H_2-utilising methanogens (Shea *et al.*, 1968, Table 2), then the specific yield for polymer plus free amino acids is 0,53 mgVSS/mgCOD(H_2) utilised. The nitrogen content of the

TABLE 2
KINETIC AND STOICHIOMETRIC CONSTANTS REPORTED IN THE LITERATURE

	$\hat{\mu}_{max}$ d^{-1}	K_s mgCOD/ℓ	b d^{-1}	Y mgCOD/mgCOD
Acidogens				
Hill and Barth (1977)	0,4	150	0,04	0,14
Denac *et al.* (1988)	1,2	140	0,04	0,03
Zoetemeyer *et al.* (1982)	7,2	22	-	0,10
Acetogens				
Lawrence and McCarty (1969)	0,31	48	0,01	0,042
Heyes and Hall (1983)	1,4	250	0,015	-
Heyes and Hall (1983)	1,2	330	-	-
Gujer and Zehnder (1983)	0,155	246	-	0,036
Acetoclastic methanogens				
Hill and Barth (1977)	0,4	25	0,04	0,04
Denac *et al.* (1988)	0,34	237	0,015	0,03
Ten Brummeler *et al.* (1985)	0,48-0,72	320	-	0,031-0,034
Lawrence and McCarty (1969)	0,24	356	0,037	0,038
Smith and Mah (1978)	0,60	320	-	0,04
Gujer and Zehnder (1983)	0,34	165	0,015	0,04
Lawrence and McCarty (1969)	0,39	180	0,02	0,04
H_2-utilising methanogens				
Shea *et al.* (1968)	1,06	9	0,009	0,043
Denac *et al.* (1988)	1,40	0,6	0,09	0,029
Gujer and Zehnder (1983)	1,40	0,6	-	0,04
Kaspar and Wuhrmann (1978)	-	1,26	-	-

b = decay (death) rate
K_s = half saturation constant
Y = yield
$\hat{\mu}_{max}$ = maximum specific growth rate

polymer was calculated to have a value of 0,113 mgN/mgCOD by Sam-Soon *et al.* (1987); this value is accepted in the model.

The COD/VSS and TKN/COD ratios for organisms are determined from the stoichiometric formula $C_5H_7O_2N$ for biosolids (McCarty, 1972), giving COD/VSS = 1,42 mgCOD/mgVSS and N/COD = 0,086 mgN/mgCOD respectively.

Model verification

The predictive capability of the UASB model was tested against experimental responses observed by Sam-Soon *et al.* (1990a, 1991b) on laboratory-scale flow-through systems with glucose and apple juice waste as influent and systems with a recycle from the unsettled effluent to the influent with apple juice as influent. The experimental systems were operated over a range of loading rates.

The same set of kinetic and stoichiometric constants, as listed in Table 3, was used in all the simulations reported in this paper, except in one instance (see below).

Flow-through systems

Responses were simulated for the flow-through experiments listed in Table 4.

Figs. 1 to 4 show the response profiles in the sludge bed, predicted and observed, for the following parameters: Total COD, SCFA (acetic and propionic acids), free and saline ammonia and organic nitrogen.

Comparison of the experimental observed and simulated responses indicates a most satisfactory correlation. The following two comments need to be made:

- The same set of constants was used in all cases except in one instance, at the loading of 14 kgCOD/m³ reactor volume.d (Exp. 3, Table 4). In this particular case the half saturation constant of the acetogens (K_{AP}) had to be increased from 250 to 330 mgCOD/ℓ to obtain satisfactory correlation between observation and prediction. However, the K_{AP} value of 330 mgCOD/ℓ,

TABLE 3
KINETIC PARAMETERS AND STOICHIOMETRIC CONSTANTS USED IN THE MATRIX

Symbol	Constant description	Range of values	Units
	Acidogens		
$\hat{\mu}_A$	Maximum specific growth rate	0,7-1,0	d^{-1}
K_A	Half saturation constant	150	mgCOD/ℓ
b_A	Decay (death) rate	0,041	d^{-1}
Y_A	Yield	0,1	mgCOD volatile mass/mgCOD
	Acetogens		
$\hat{\mu}_{AP}$	Maximum specific growth rate	1,1-1,2	d^{-1}
K_{AP}	Half saturation constant	250-330	mgCOD/ℓ
b_{AP}	Decay (death) rate	0,015	d^{-1}
Y_{AP}	Yield	0,042	mgCOD volatile mass/mgCOD
	H_2-utilising methanogens		
$\hat{\mu}_{MH}$	Maximum specific growth rate	0,3-0,5	d^{-1}
K_{MH}	Half saturation constant	2,5	mgCOD/ℓ
b_{MH}	Decay (death) rate	0,010	d^{-1}
Y_{MH}	Yield	0,041	mgCOD volatile mass/mgCOD
	Acetoclastic methanogens		
$\hat{\mu}_{MA}$	Maximum specific growth rate	0,35-0,40	d^{-1}
K_{MA}	Half saturation constant	350	mgCOD/ℓ
b_{MA}	Decay (death) rate	0,037	d^{-1}
Y_{MA}	Yield	0,041	mgCOD volatile mass/mgCOD
	Other constants		
i_{XBN}	Nitrogen content of organism	0,086	mgN/mgCOD
i_{XPN}	Nitrogen content of polymer	0,113	mgN/mgCOD
Y_P	Polymer yield	0,63	mgCOD volatile mass/mgCOD
K_H	Half saturation constant, switching function	10	mgCOD/ℓ
K_{BP}	Pellet break-up rate	4-8	d^{-1}
K_{EP}	Enmeshment rate	10-15	d^{-1}
K_{ND}	Ammonification rate	0,010-0,018	d^{-1}

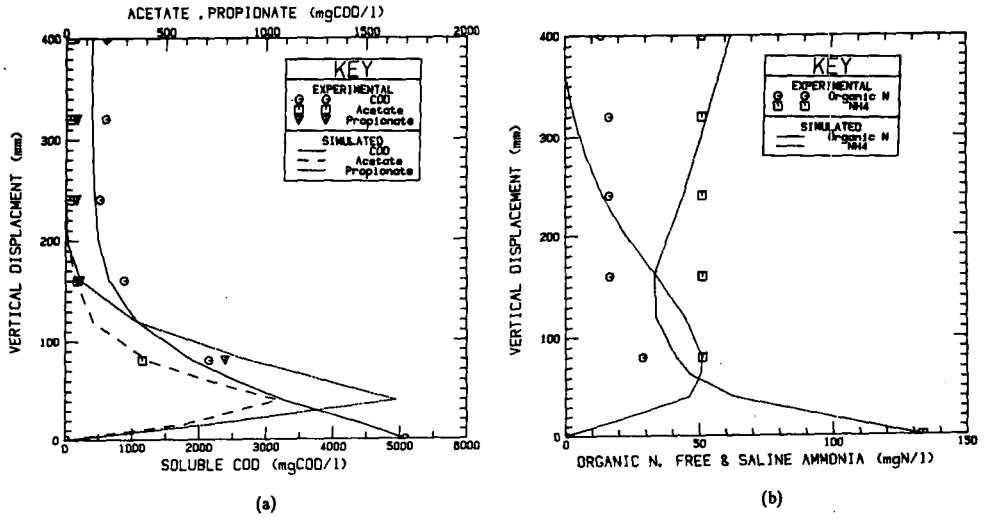

Figure 1

Experimentally observed and simulated concentration profiles in the pelletised sludge bed of a single high/low pH_2 UASB system (substrate glucose, influent COD = 5 079 mg/ℓ, flow rate = 15 ℓ/d, recycle ratio = 0:1; Table 4, Exp. 1).

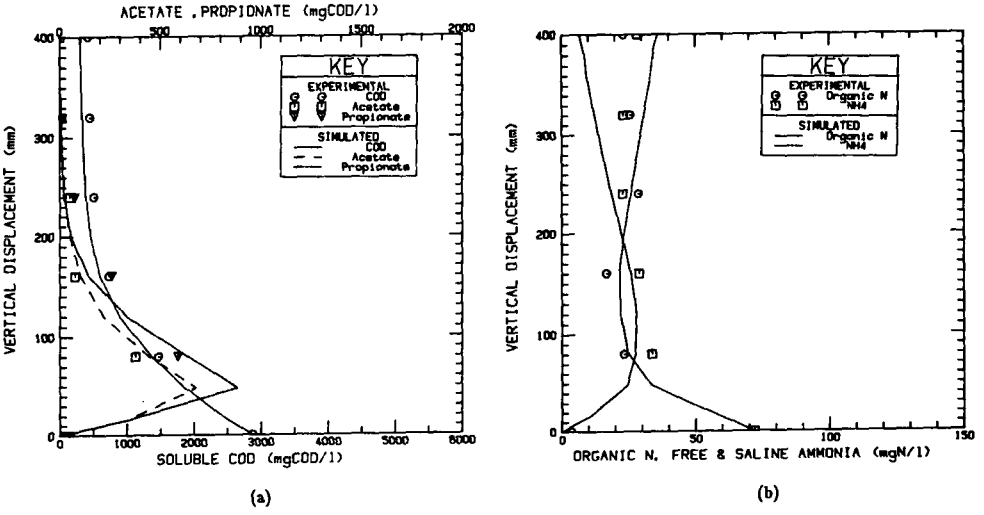

Figure 2

Experimentally observed and simulated concentration profiles in the pelletised sludge bed of a single high/low $\bar{p}\,H_2$ UASB system (substrate apple juice, influent COD = 2 872 mg/ℓ, flow rate = 30 ℓ/d, recycle ratio = 0:1; Table 4, Exp. 2).

lies within the range of reported half saturation constant values for acetogens (Heyes and Hall, 1983).

- In Table 3 the value of the half saturation constant (K_H), in the switching function for the process (ρ_1, ρ_2 and ρ_5), was taken as 10 mgCOD/ℓ. Usually for switching functions the half saturation constant values are selected to be small so that switching from one process to another takes place at a very low concentration. In this study the effect of the magnitude of the selected value of K_H on process behaviour could not be evaluated — the rate of utilisation of glucose was very rapid so that glucose concentration reduced to zero before the first sampling port at the bottom of the reactor. Reducing the value of K_H to 5 did not appear to have an observable influence on the simulated response.

System with recycle

Two experiments on UASB systems with recycles were simulated (see Table 5).

The observed and simulated responses are shown in Figs. 5 and 6. Clearly the simulated responses show significant deviations from the experimentally observed responses. In general, the experimental data indicate that the process rates of the different compounds were more rapid than the simulated rates. The following

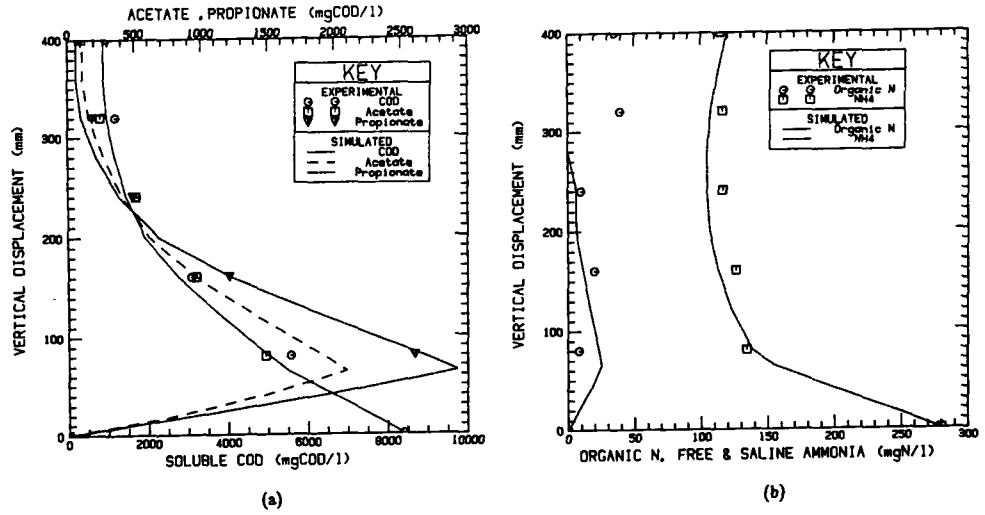

Figure 3

Experimentally observed and simulated concentration profiles in the pelletised sludge sludge bed of a singly high/low pH_2 UASB system (substrate apple juice, influent COD = 8 397 mg/ℓ, flow rate = 15 ℓ/d, recycle ratio = 0:1; Table 4, Exp. 3).

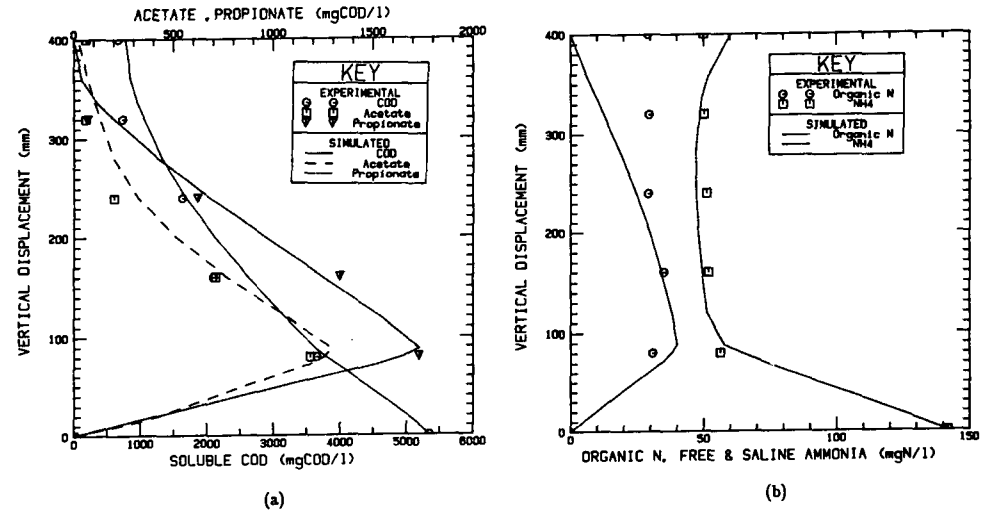

Figure 4

Experimentally observed and simulated concentration profiles in the pelletised sludge bed of a single high/low pH_2 UASB system (substrate glucose, influent COD = 5 345 mg/ℓ, flow rate = 45 ℓ/d, recycle ratio = 0:1; Table 4, Exp. 4).

factors probably contributed to these deviations: In the region above the sludge bed a certain degree of settlement of the debris, discharged from the bed, took place, to form a suspended solids blanket. This suspended solids material was discharged via the recycle to the influent. Although the model assumes that the suspended solids material discharged is inert, very likely this is not true and recycling of this material could have contributed in increasing the process rates in the sludge bed. Recent investigations in the laboratory at the University of Cape Town on the biological activity of the suspended solids material have indicated that biological activity occurs when substrate is added to this material. In future investigations, to test the model when a recycle is imposed on the system, it will be necessary either to induce sufficient turbulence in the suspended solids blanket so that there is no increase in solid concentration (due to settlement) or the effluent particulate material must be separated and the clarified liquid recycled.

Discussion

A significant feature in this model is that it required virtually no calibration. The stoichiometric conversion constants were obtained from established biochemical pathways, and yield values from studies reported in the literature on pure cultures; likewise

TABLE 4
DATA FOR FLOW-THROUGH UASB SYSTEMS

Experiment No.	Influent COD mg/ℓ	Flow rate ℓ/d	Depth of sludge bed mm	Mean sludge bed density gVSS/ℓ	Loadings kgCOD/m³.d Reactor volume	Loadings kgCOD/m³.d Sludge bed volume
1	5 079	15	400	29	8,5	25,5
2	2 872	30	400	29	9,6	28,8
3	8 397	15	400	20	14,0	42,0
4	5 345	45	400	35	26,7	80,1

Diameter of reactor 100 mm
Effective reactor volume 9 ℓ, bed volume 3 ℓ.

TABLE 5
DATA FOR UASB SYSTEMS WITH RECYCLE

Experiment No.	Influent COD mg/ℓ	Flow rate ℓ/d	Recycle ratio	Depth of sludge bed mm	Mean sludge bed density gVSS/ℓ	Loadings kgCOD/m³.d Reactor volume	Loadings kgCOD/m³.d Sludge bed volume
1	5 481	15	1:1	400	29	9,1	27,3
2	2 848	30	1:1	400	31,9	9,5	28,5

Diameter of reactor 100 mm
Effective reactor volume 9 ℓ, bed volume 3 ℓ.

for the maximum specific growth rates and half saturation constants (in the Monod formulation). Other input data such as the mass fractions of the different microorganisms in the pellets and the distribution of VSS concentration up the reactor also were obtained from reported data in the literature. Indeed the only constants that were obtained by trial and error curve fitting were:

- the specific rate for pellet break-up (K_{BP});
- the specific rate for adsorption/enmeshment of soluble organic nitrogen (K_{EP}); and
- the specific rate for ammonification of soluble organic nitrogen (K_{ND}).

The model therefore is much broader based, on fundamental aspects or independently obtained data, than it would have been if the constants were all derived by curve fitting.

One omission in the model is that it does not simulate pH and alkalinity changes in the sludge bed. It assumes in fact that the alkalinity provision in the influent is sufficient to prevent pH decline below 6,6 at any point in the bed. Because of the rapid changes in SCFA concentrations in the lower part of the bed, it is likely that regions might develop where the pH decline is such that inhibition of methanogenesis could take place - both acetoclastic and H_2-utilising methanogens are reported to be inhibited by low pH. The model should be capable of predicting such a situation and hence should include the parameters pH and alkalinity and the inhibitory effect of pH on the methanogens. Any such extension would necessarily require additional experimental information. In the present study the orientation was towards determining "normal" behaviour of the UASB system; the situation at or near failure due to pH effects was not pursued and consequently the factors giving rise to such failure were not investigated in detail.

A second omission in the model is that pellet generation is not simulated, so that it is not possible to calculate the pellet production for a fixed bed volume, or, the depth (or equivalently volume) to which the bed would rise if there was not artificial wastage of pellets. Furthermore, the concentration ratios of the four organism groups up the bed are accepted to remain constant and form part of the input to the model. In a future extension of the model, the steady state VSS concentration profile should be found in the solution, also the respective concentrations of the organism groups.

Accepting the omissions set out above, by simulating the behaviour under various reactor loading conditions the following information can be abstracted:

- For the same mass of sludge the cross-sectional area of the reactor does not appear to have an influence on process kinetics. If the cross-sectional area is doubled, the depth of the sludge will be reduced to half. Theoretically the effluent products and their concentrations will remain the same in both situations. The profiles will retain the same shape with respect to relative depths of the sludge bed. The maximum cross-sectional surface loading rate very likely will be determined from practical considerations, such as limiting disturbance of the sludge bed by limiting the gas evolution rate per unit cross-sectional area of reactor.
- Theoretically the imposition of a recycle reduces the concentration of products in the reactor in the ratio flow/(flow + recycle flow). (Experimentally the reduction was slightly greater). This, Sam-Soon *et al.* (1991c) have shown, leads to an associated reduction in the alkalinity supplementation. Such alkalinity reduction is of particular importance in the treatment of high strength wastes of say > 5 000 mgCOD/ℓ. By reducing the waste strength (by imposing a recycle) of an influent of 20 000 mgCOD/ℓ to say 1 000 to 5 000 mgCOD/ℓ, the alkalinity requirement is reduced to approximately 0,05 to 0,25 of that needed in a flow-through system; SCFA concentrations inside

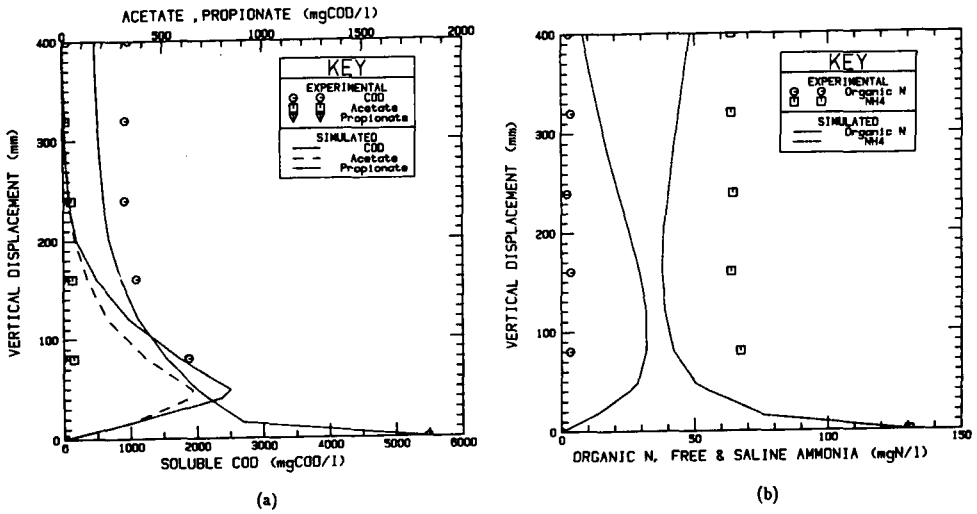

Figure 5

Experimentally observed and simulated concentration profiles in the pelletised sludge bed of a single high/low pH_2 UASB system with recycle (substrate apple juice, influent COD = 5 481 mg/ℓ, flow rate = 15 ℓ/d, recycle ratio = 1:1; Table 5, Exp. 1).

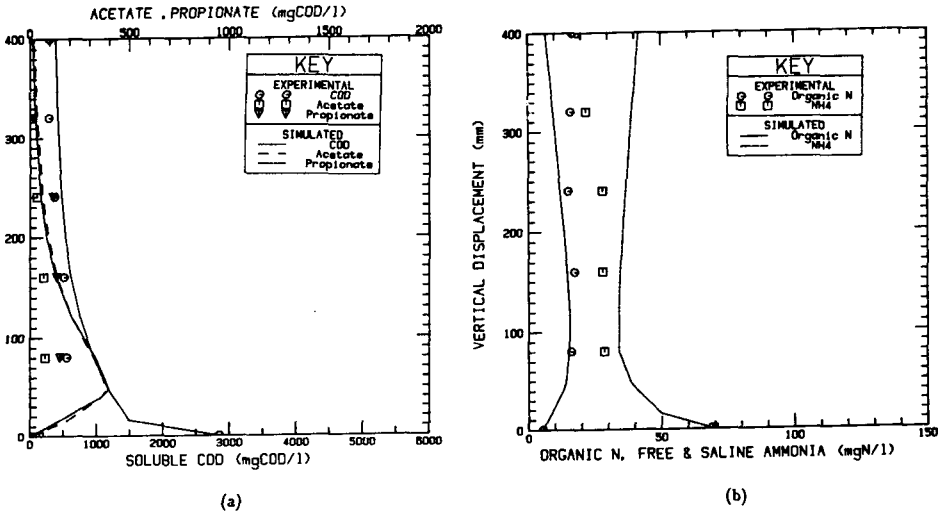

Figure 6

Experimentally observed and simulated concentration profiles in the pelletised sludge bed of a single high/low pH_2 UASB system with recycle (substrate apple juice, influent COD = 2 848 mg/ℓ, flow rate = 30 ℓ/d, recycle ratio = 1:1; Table 5, Exp. 2).

the sludge bed likewise are reduced into a range where the system appears to operate efficiently.

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Appendix 1

Matrix method for model presentation

To fully understand the mathematical model (Table 1) it is useful to gain an insight into the representation and workings of the matrix as described briefly below.

Representation

The matrix is represented by a number of columns and rows; one column for each compound and one row for each process. The symbols for the compounds are listed at the head of the appropriate column and the compounds are defined at the bottom of the corresponding column. The index "i" is assigned to identify a compound in the totality of compounds. The processes are itemised one below the other down the left-hand side of the matrix. The index "j" is assigned to identify the process. The process rates are formulated mathematically and listed down the right-hand side of the matrix, in line with the respective process row. These process rates are given the symbol "ρ_j", where j identifies the process.

Along each process row the stoichiometric coefficient for conversion from one compound to another is inserted so that each column lists the processes that influence that compound. The stoichiometric coefficients are given the symbol "$\nu_{i,j}$" where i denotes the index of the compound and j the index of the process. The stoichiometric coefficients $\nu_{i,j}$ are greatly simplified by working in consistent units; in this case concentrations are expressed in COD or nitrogen (N) units. Sign convention in the matrix for the stoichiometric coefficients is "negative for consumption" and "positive for production".

The matrix forms a succinct summary of the complex interactions between compounds and processes. The matrix in effect constitutes a fingerprint uniquely characterising the phenomenon. It allows alterations in processes, compounds, stoichiometry and kinetics to be readily incorporated.

The matrix representation method has two main benefits:

- It allows the effect of a particular process on the compounds to be easily determined, as follows: The reader moves along a particular row, i.e. process, and multiplies the stoichiometric coefficient ($\nu_{i,j}$) by the process rate (ρ_j). This gives the reaction rate ($r_{i,j}$) for the particular compound being affected by the single process, i.e.

$$r_{i,j} = \nu_{i,j}\rho_j \qquad (1.1)$$

  In the matrix, by adding up the reaction rates for a particular process, a mass balance must be obtained, i.e. $\sum_i r_{i,j} = 0$.

- It allows rapid and easy recognition of the fate of each compound, as follows: The reader moves down the column representing the compound of interest, and multiplies the stoichiometric coefficient ($\nu_{i,j}$) by the process rate (ρ_j). The summation of these multiplications gives the overall reaction rate (r_i) for the compound, i.e.

$$r_i = \sum_j \nu_{i,j}\rho_j \qquad (1.2)$$

Switching function

Under certain conditions the process rate equations are not

operative, e.g. propionic acid degradation is not operative under high $\bar{p}H_2$. Mathematically, switching the process rate "on" and "off" can be achieved by multiplying the appropriate rate by a "switching" factor, which is zero when the process rate is inoperative, or unity when the process rate is operate. The general expression used for the switching function is:

$$\frac{C}{K + C} \qquad (1.3)$$

where C = concentration of compound effecting the switch
K = constant

This is a Monod-type expression. By selecting very small values for K, the function is close to unity when C is present. The function decreases to zero only at very low concentrations of C. A Monod-type expression is utilised as it provides continuity between the "off" and the "on" situation which helps to eliminate problems of numerical instability in computer calculations.

Matrix solution

Solution of the matrix can be in time (e.g. plug flow reactor, batch reactor), space (e.g. steady state multiple reactor system), or time and space (e.g. multiple reactor system with time varying flow). For detailed solution procedures the reader is referred to Billing, 1987.

Appendix 2

Derivation of stoichiometric ratios for the matrix

The stoichiometric relationships in the production of various compounds during anaerobic fermentation of glucose are derived below.

Glucose to short-chain fatty acids

As no butyrate was observed in the single UASB system under varying loadings, butyrate generation is not considered.

Under "high" $\bar{p}H_2$ ($\bar{p}H_2 > 10^{-3,7}$ atm):

From Sam-Soon *et al.* (1990a, Eq. 3), under high $\bar{p}H_2$, 1 mol glucose (24 electron equivalents, e^-) produces 1 mol propionic acid, HPr (14 e^-), 1 mol acetic acid, HAc (8 e^-), 1 mol hydrogen, H_2 (2 e^-) and 1 mol carbon dioxide, CO_2. In terms of COD units, 1 COD unit of glucose gives:

$$1 = \frac{8}{24}\ HAc + \frac{14}{24}\ HPr + \frac{2}{24}\ H_2 \qquad (2.1)$$

The energy derived from catabolism of glucose is used to incorporate Y_A COD units glucose into organism mass, i.e.

$$Y_A = (Y_A)\ \text{organisms} \qquad (2.2)$$

Adding Eqs. (2.1) and (2.2) gives:

$$1 + Y_A = (Y_A)\ \text{organisms} + \frac{8}{24}\ HAc + \frac{14}{24}\ HPr + \frac{2}{24}\ H_2 \qquad (2.3)$$

Since the rate equations in the matrix (Table 1) are expressed in terms of rate of organism growth, the stoichiometric equation is expressed as unity with respect to organism mass. Therefore, dividing Eq. (2.3) by Y_A:

$$\frac{1+Y_A}{Y_A} = (1)\ \text{organisms} + \left(\frac{8}{24} \times \frac{1}{Y_A}\ HAc\right) + \left(\frac{14}{24} \times \frac{1}{Y_A}\ HPr\right) + \left(\frac{2}{24} \times \frac{1}{Y_A}\ H_2\right) \qquad (2.4)$$

Equation (2.4) can be interpreted as follows: For every one COD r unit of organism mass formed, $\frac{(1+Y_A)}{Y_A}$ COD units of glucose are utilised, and $\frac{8}{24} \times \frac{1}{Y_A}$ COD units of HAc, $\frac{14}{24} \times \frac{1}{Y_A}$ of HPr and $\frac{2}{24} \times \frac{1}{Y_A}$ of H_2 are produced.

Similar derivations are made for other stoichiometric equations below.

Under "low" $\bar{p}H_2$ ($\bar{p}H_2 < \pm\ 10^{-3,7}$ atm):

Under low $\bar{p}H_2$, 1 mol glucose produces 2 mol HAc and 4 mol H_2 (Sam-Soon *et al.*, 1990a, Eq. 1). The energy derived from catabolism is used to incorporate glucose into organism mass, i.e.

$$1+Y_A = (Y_A)\ \text{organisms} + \frac{16}{24}\ HAc + \frac{8}{24}\ H_2 \qquad (2.5)$$

dividing by Y_A:

$$\frac{1+Y_A}{Y_A} = (1)\ \text{organisms} + \left(\frac{16}{24} \times \frac{1}{Y_A}\ HAc\right) + \left(\frac{8}{24} \times \frac{1}{Y_A}\ H_2\right) \qquad (2.6)$$

Equation (2.6) gives the stoichiometric relationship between glucose and products formed under low $\bar{p}H_2$.

Conversion of HPr to HAc

1 mol HPr propionic acid is converted to 1 mol HAc, 3 mol H_2 and 1 mol CO_2 (Sam-Soon *et al.*, 1990a, Eq. 5). The energy derived from catabolism of propionic acid is used to incorporate Y_{AP} units propionic acid into organism mass. In terms of COD units, the equation is

$$1+Y_{AP}=(Y_{AP})\ \text{organisms}+\frac{8}{14}\ \text{HAc}+\frac{6}{14}\ H_2 \quad (2.7)$$

dividing by Y_{AP}:

$$\frac{1+Y_{AP}}{Y_{AP}}=(1)\ \text{organisms}+\left(\frac{8}{14}\times\frac{1}{Y_{AP}}\ \text{HAc}\right)+\left(\frac{6}{14}\times\frac{1}{Y_{AP}}\ H_2\right) \quad (2.8)$$

i.e. for one unit of acetogenic mass formed, $\frac{1+Y_{AP}}{Y_{AP}}$ units of HPr are utilised, and $\frac{8}{14}\times\frac{1}{Y_{AP}}$ units HAc and $\frac{6}{14}\times\frac{1}{Y_{AP}}$ units of H_2 are produced, all units as COD.

Conversion of HAc to methane

In conversion of HAc to methane (CH_4) by the acetoclastic methanogens 1 mol HAc generates 1 mol CH_4 (Sam-Soon *et al.*, 1990a, Eq. 7), i.e.:

$$1=(Y_{MA})\ \text{organisms}+(1\text{-}Y_{MA})\ CH_4 \quad (2.9)$$

dividing by Y_{MA}:

$$\frac{1}{Y_{MA}}=(1)\ \text{organisms}+\left[\frac{(1\text{-}Y_{MA})}{Y_{MA}}\right]\ CH_4 \quad (2.10)$$

i.e. for one unit of acetoclastic methanogen mass formed, $\frac{1}{Y_{MA}}$ units HAc are utilised, and $(1\text{-}Y_{MA})/Y_{MA}$ units CH_4 produced, all units as COD.

Conversion of H_2 to CH_4

The conversion of H_2 to CH_4 by the hydrogenotrophs is given by Sam-Soon *et al.* (1990a, Eq. 6). Also, from Sam-Soon *et al.* (1990a), it is hypothesised that the energy derived from oxidation of hydrogen to methane is used to generate (1) organism mass and (2) polymer mass, i.e.:

$$1=(Y_{MH})\ \text{organisms}+(Y_p)\ \text{polymer}+(1\text{-}Y_p\text{-}Y_{MH})CH_4 \quad (2.11)$$

dividing by Y_{MH}:

$$\frac{1}{Y_{MH}}=(1)\ \text{organisms}+\left(\frac{Y_P}{Y_{MH}}\right)\text{polymer}+\left[\frac{(1\text{-}Y_P\text{-}Y_{MH})}{Y_{MH}}\right]\ CH_4 \quad (2.12)$$

From Eq. (2.12) one unit mass of hydrogenotrophic mass is generated from $\frac{1}{Y_{MH}}$ units of H_2, with the formation of $\frac{Y_P}{Y_{MH}}$ units of polymer mass and $\frac{(1\text{-}Y_P\text{-}Y_{MH})}{Y_{MH}}$ units of CH_4, all units as COD.