# Le modèle AMOCO

## PARTIE I : Modelling of bioprocesses for environmental purposes

**Jérôme Harmand**

Equipe d'ingénierie des Procédés

Laboratoire de Biotechnologie de l'Environnement - INRA

Projet INRA-INRIA-MERE

Narbonne - France

email : harmand@ensam.inra.fr -
http://www.montpellier.inra.fr/narbonne

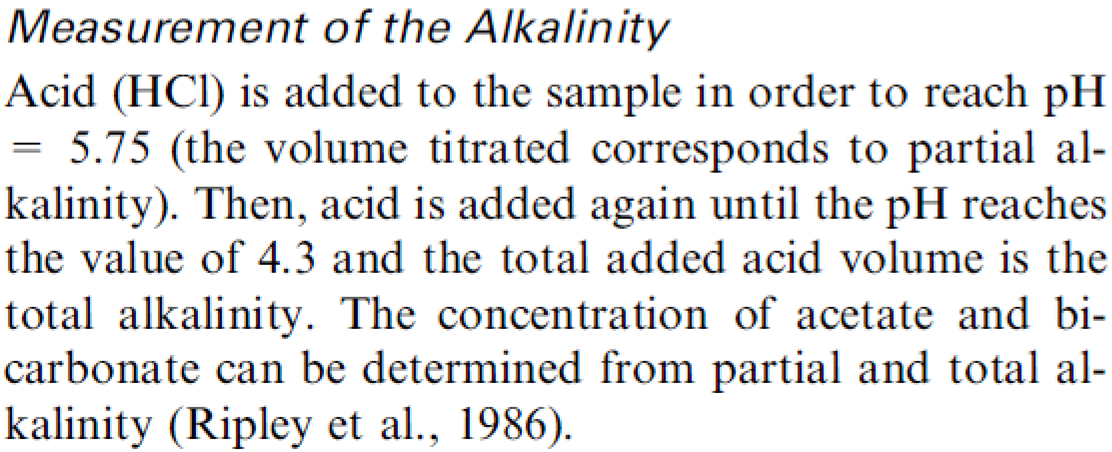
# Le modèle AMOCO

## Dynamical Model Development and Parameter Identification for an Anaerobic Wastewater Treatment Process

**Olivier Bernard,[1] Zakaria Hadj-Sadok,[1] Denis Dochain,[2]**
**Antoine Genovesi,[3] Jean-Philippe Steyer[3]**

*[1]INRIA, COMORE Project, BP93, 06902 Sophia-Antipolis Cedex,*
*France; telephone: +33 492 38 77 85;*
*fax: +33 492 38 78 58; e-mail: obernard@sophia.inria.fr*
*[2]CESAME-UCL, Av G. Lemaître, 4-6, 1348 Louvain-La-Neuve, Belgium*
*[3]LBE-INRA, Av des Etangs, 11100 Narbonne, France*

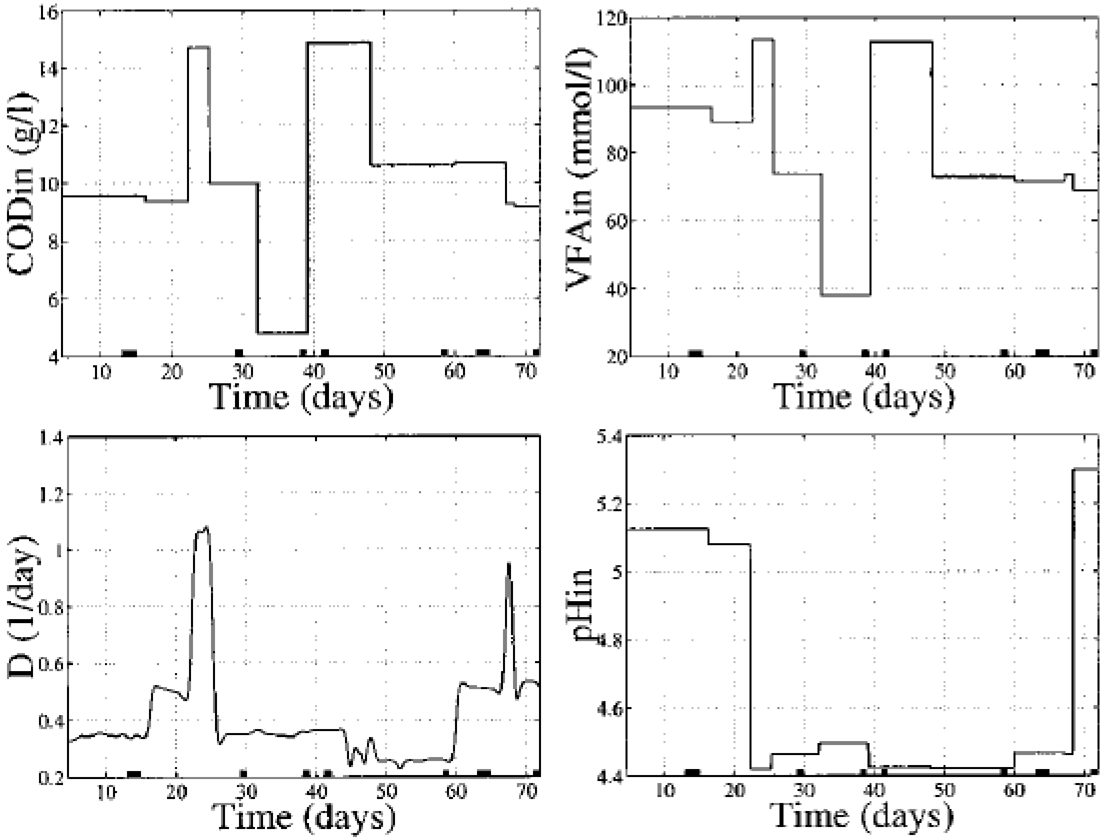
# Les mesures, DCO, AGV et…



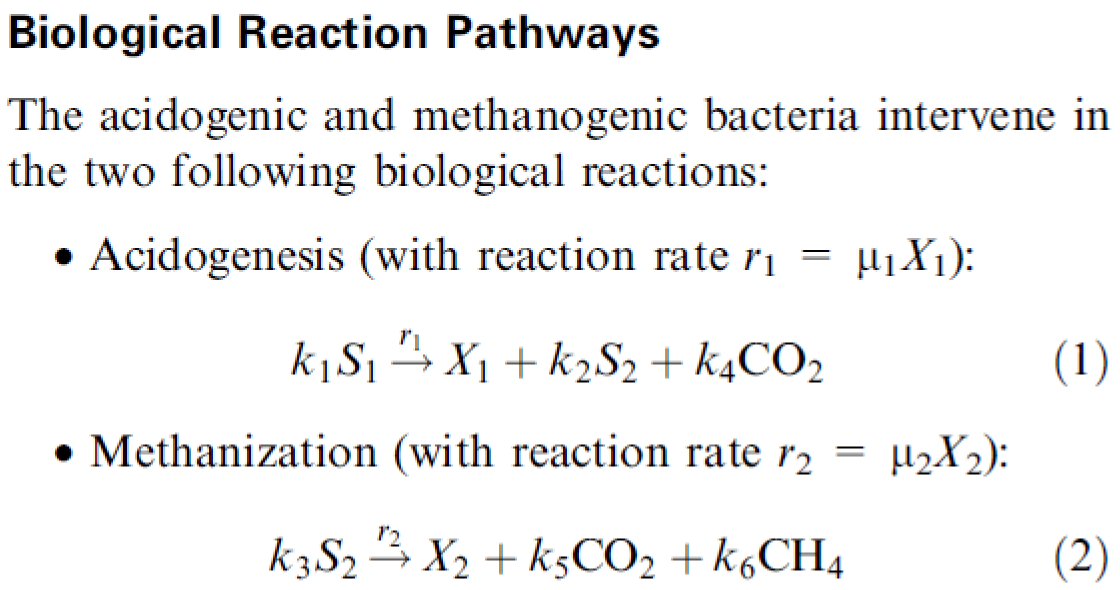
### *Measurement of the Alkalinity*

Acid (HCl) is added to the sample in order to reach pH = 5.75 (the volume titrated corresponds to partial alkalinity). Then, acid is added again until the pH reaches the value of 4.3 and the total added acid volume is the total alkalinity. The concentration of acetate and bicarbonate can be determined from partial and total alkalinity (Ripley et al., 1986).

# Les entrées


CODin (g/l)
16
14
12
10
8
6
4
10
20
30
40
50
60
70
Time (days)
VFAin (mmol/l)
120
100
80
60
40
20
10
20
30
40
50
60
70
Time (days)
D (1/day)
1.4
1.2
1
0.8
0.6
0.4
0.2
10
20
30
40
50
60
70
Time (days)
pHin
5.4
5.2
5
4.8
4.6
4.4
10
20
30
40
50
60
70
Time (days)

# Le système biologique



### Biological Reaction Pathways

The acidogenic and methanogenic bacteria intervene in the two following biological reactions:

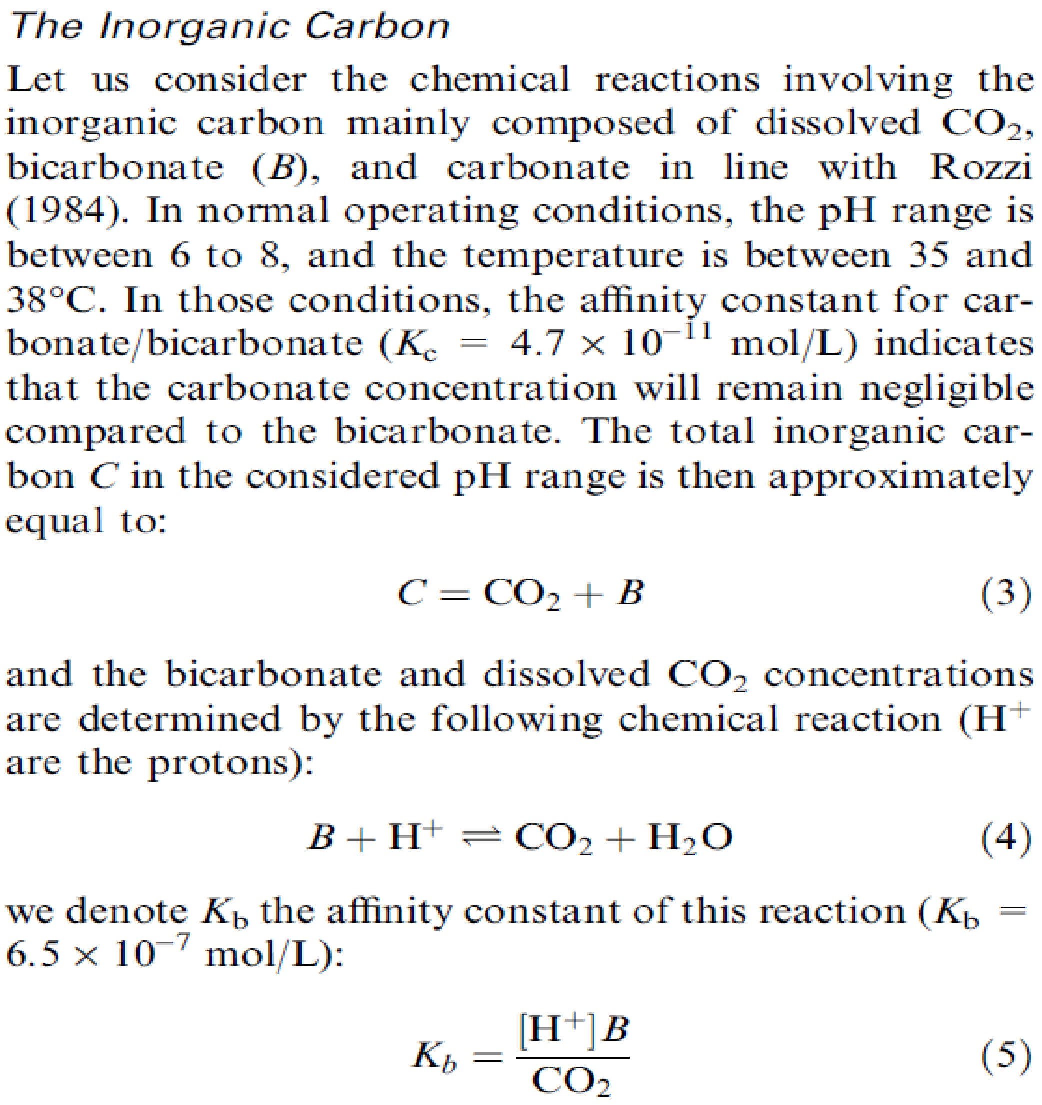
- Acidogenesis (with reaction rate $r_1 = \mu_1 X_1$):

$$k_1 S_1 \xrightarrow{r_1} X_1 + k_2 S_2 + k_4 CO_2 \qquad (1)$$

- Methanization (with reaction rate $r_2 = \mu_2 X_2$):

$$k_3 S_2 \xrightarrow{r_2} X_2 + k_5 CO_2 + k_6 CH_4 \qquad (2)$$

# Les espèces chimiques (pour le lien avec le pH)



*The Inorganic Carbon*

Let us consider the chemical reactions involving the inorganic carbon mainly composed of dissolved $CO_2$, bicarbonate ($B$), and carbonate in line with Rozzi (1984). In normal operating conditions, the pH range is between 6 to 8, and the temperature is between 35 and 38°C. In those conditions, the affinity constant for carbonate/bicarbonate ($K_c = 4.7 \times 10^{-11}$ mol/L) indicates that the carbonate concentration will remain negligible compared to the bicarbonate. The total inorganic carbon $C$ in the considered pH range is then approximately equal to:

$$C = CO_2 + B \tag{3}$$

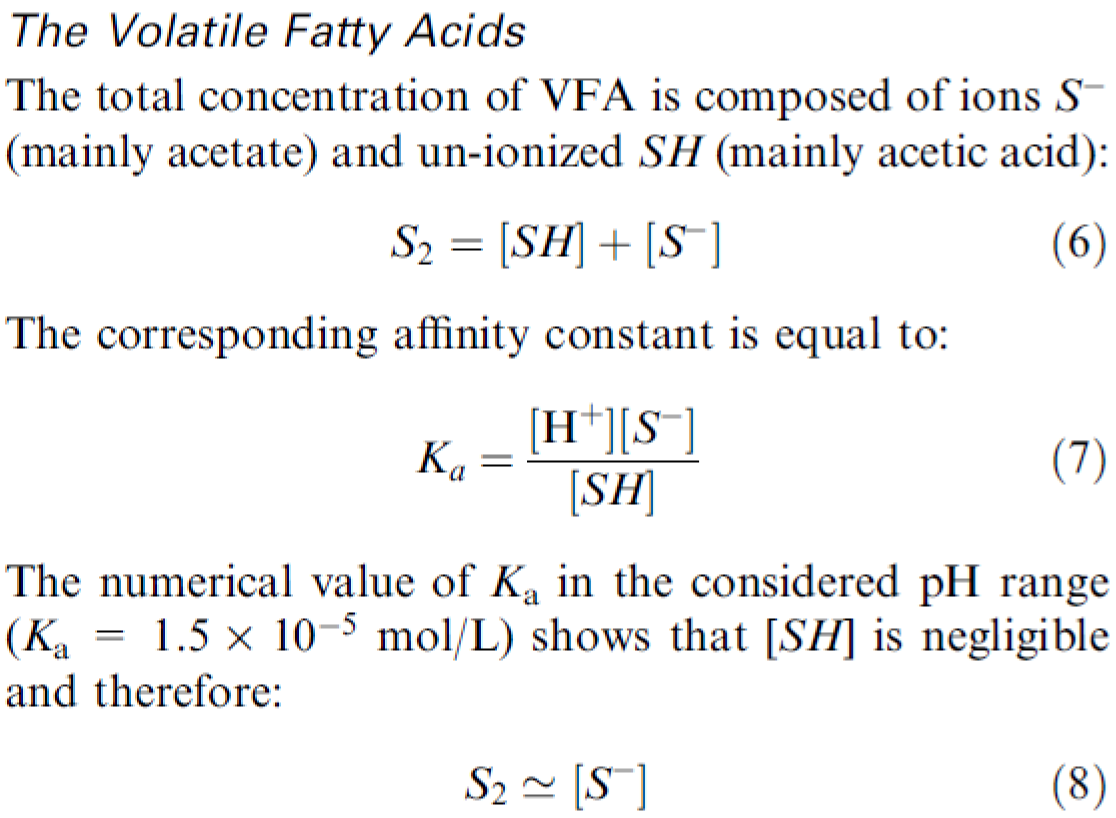
and the bicarbonate and dissolved $CO_2$ concentrations are determined by the following chemical reaction ($H^+$ are the protons):

$$B + H^+ \rightleftharpoons CO_2 + H_2O \tag{4}$$

we denote $K_b$ the affinity constant of this reaction ($K_b = 6.5 \times 10^{-7}$ mol/L):

$$K_b = \frac{[H^+]B}{CO_2} \tag{5}$$

# A propos des acides gras volatils…



*The Volatile Fatty Acids*

The total concentration of VFA is composed of ions $S^-$ (mainly acetate) and un-ionized $SH$ (mainly acetic acid):

$$S_2 = [SH] + [S^-] \tag{6}$$

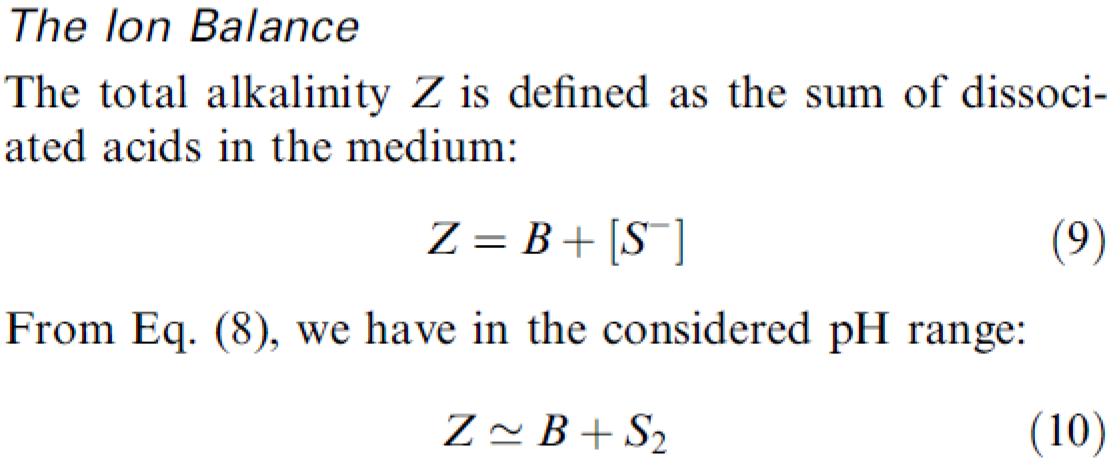
The corresponding affinity constant is equal to:

$$K_a = \frac{[\mathrm{H}^+][S^-]}{[SH]} \tag{7}$$

The numerical value of $K_\mathrm{a}$ in the considered pH range ($K_\mathrm{a} = 1.5 \times 10^{-5}$ mol/L) shows that $[SH]$ is negligible and therefore:

$$S_2 \simeq [S^-] \tag{8}$$

# Les équilibres physico-chimiques



### *The Ion Balance*

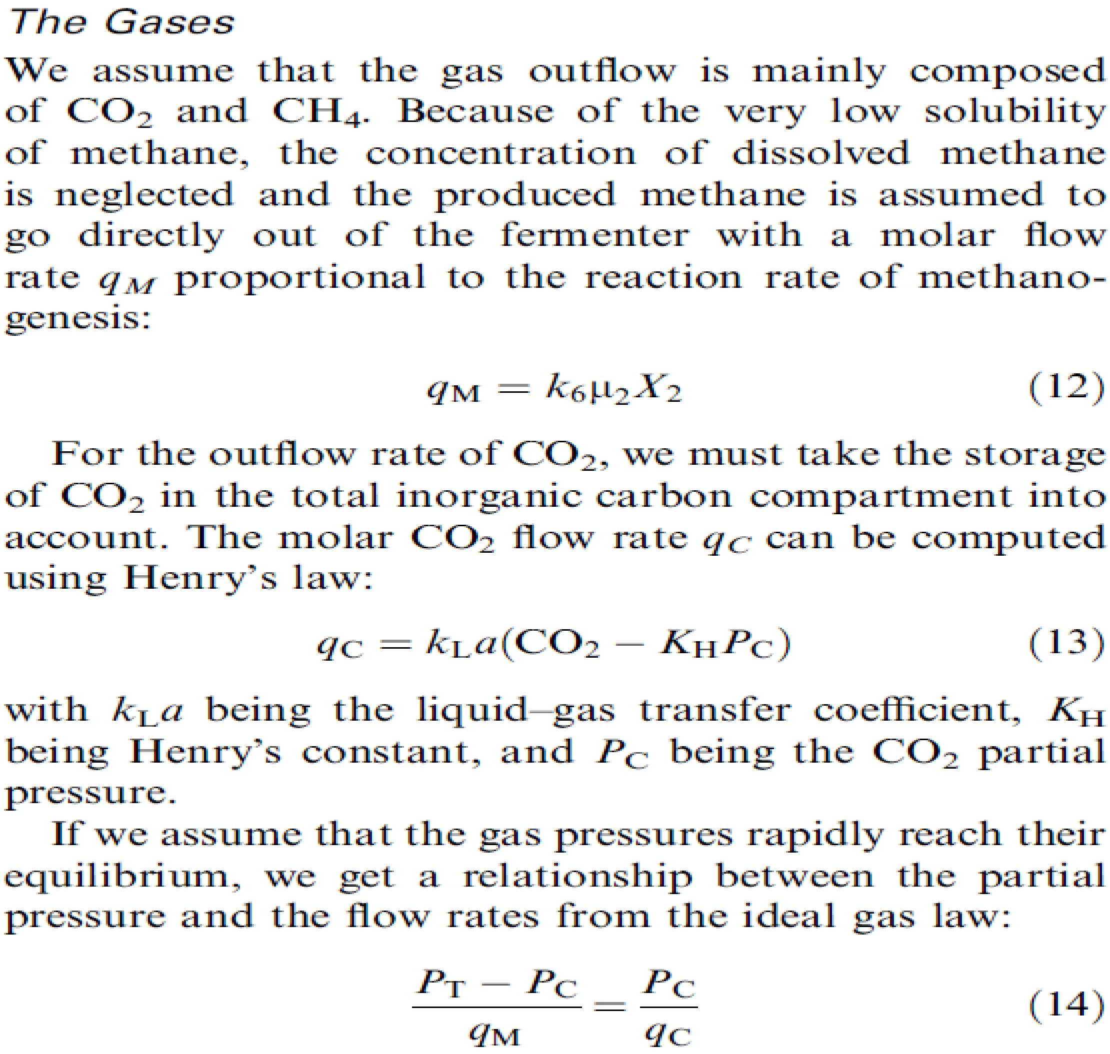
The total alkalinity $Z$ is defined as the sum of dissociated acids in the medium:

$$Z = B + [S^-] \tag{9}$$

From Eq. (8), we have in the considered pH range:

$$Z \simeq B + S_2 \tag{10}$$

# Les gaz



### *The Gases*

We assume that the gas outflow is mainly composed of $CO_2$ and $CH_4$. Because of the very low solubility of methane, the concentration of dissolved methane is neglected and the produced methane is assumed to go directly out of the fermenter with a molar flow rate $q_M$ proportional to the reaction rate of methanogenesis:

$$q_{\mathrm{M}} = k_6 \mu_2 X_2 \qquad (12)$$

For the outflow rate of $CO_2$, we must take the storage of $CO_2$ in the total inorganic carbon compartment into account. The molar $CO_2$ flow rate $q_C$ can be computed using Henry's law:

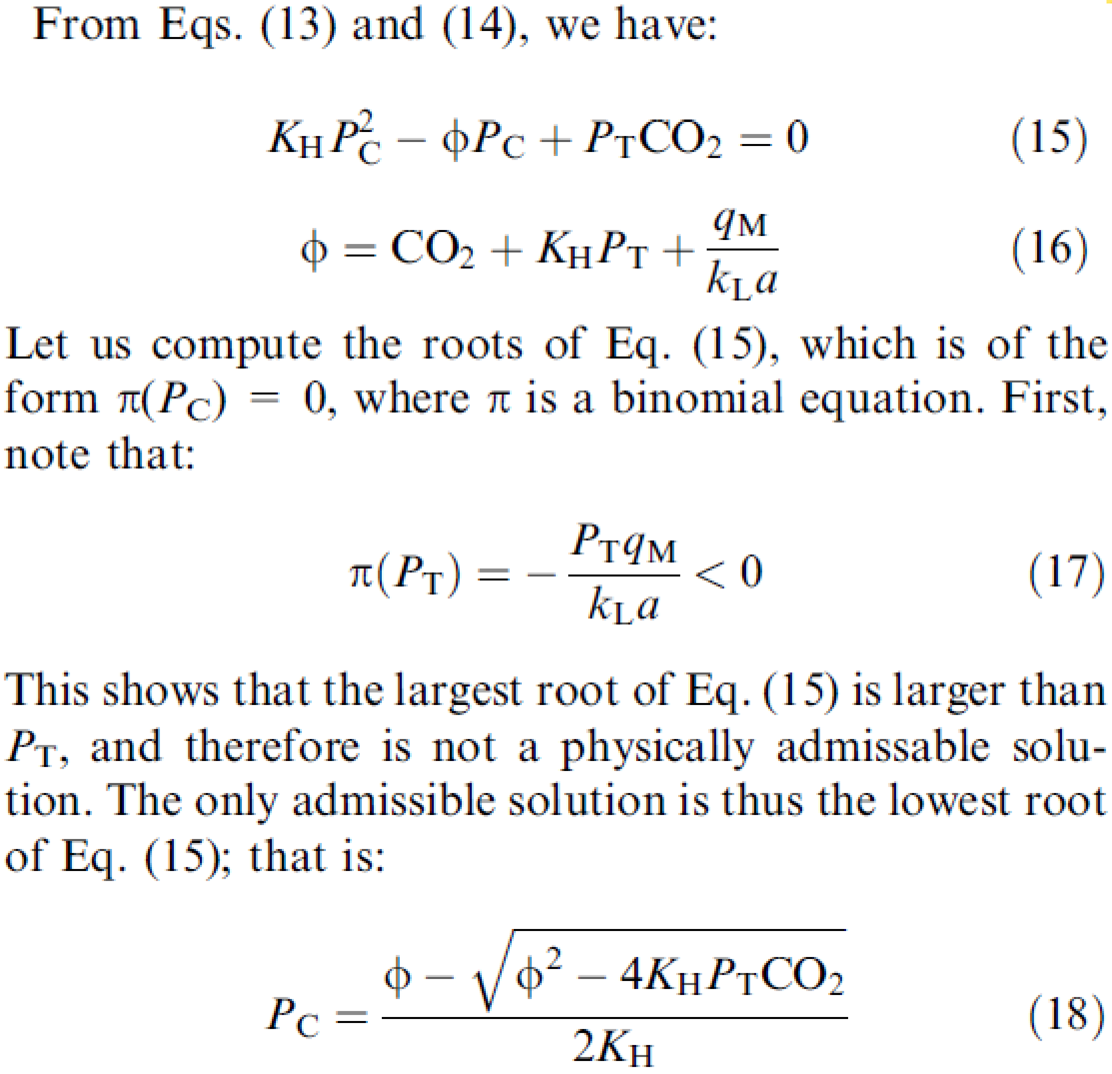
$$q_{\mathrm{C}} = k_{\mathrm{L}}a(\mathrm{CO}_2 - K_{\mathrm{H}} P_{\mathrm{C}}) \qquad (13)$$

with $k_{\mathrm{L}}a$ being the liquid–gas transfer coefficient, $K_{\mathrm{H}}$ being Henry's constant, and $P_{\mathrm{C}}$ being the $CO_2$ partial pressure.

If we assume that the gas pressures rapidly reach their equilibrium, we get a relationship between the partial pressure and the flow rates from the ideal gas law:

$$\frac{P_{\mathrm{T}} - P_{\mathrm{C}}}{q_{\mathrm{M}}} = \frac{P_{\mathrm{C}}}{q_{\mathrm{C}}} \qquad (14)$$

# Les gaz (2)



From Eqs. (13) and (14), we have:

$$K_H P_C^2 - \phi P_C + P_T CO_2 = 0 \qquad (15)$$

$$\phi = CO_2 + K_H P_T + \frac{q_M}{k_L a} \qquad (16)$$

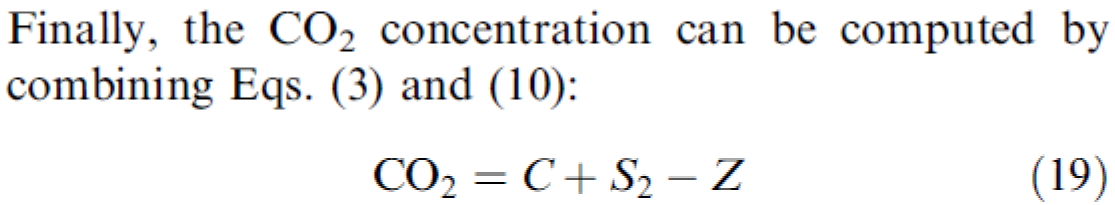
Let us compute the roots of Eq. (15), which is of the form $\pi(P_C) = 0$, where $\pi$ is a binomial equation. First, note that:

$$\pi(P_T) = -\frac{P_T q_M}{k_L a} < 0 \qquad (17)$$

This shows that the largest root of Eq. (15) is larger than $P_T$, and therefore is not a physically admissable solution. The only admissible solution is thus the lowest root of Eq. (15); that is:

$$P_C = \frac{\phi - \sqrt{\phi^2 - 4K_H P_T CO_2}}{2K_H} \qquad (18)$$

# Les gaz (3)



Finally, the $CO_2$ concentration can be computed by combining Eqs. (3) and (10):

$$CO_2 = C + S_2 - Z \qquad (19)$$

# *II. Modelling of an anaerobic continuous process*

2000

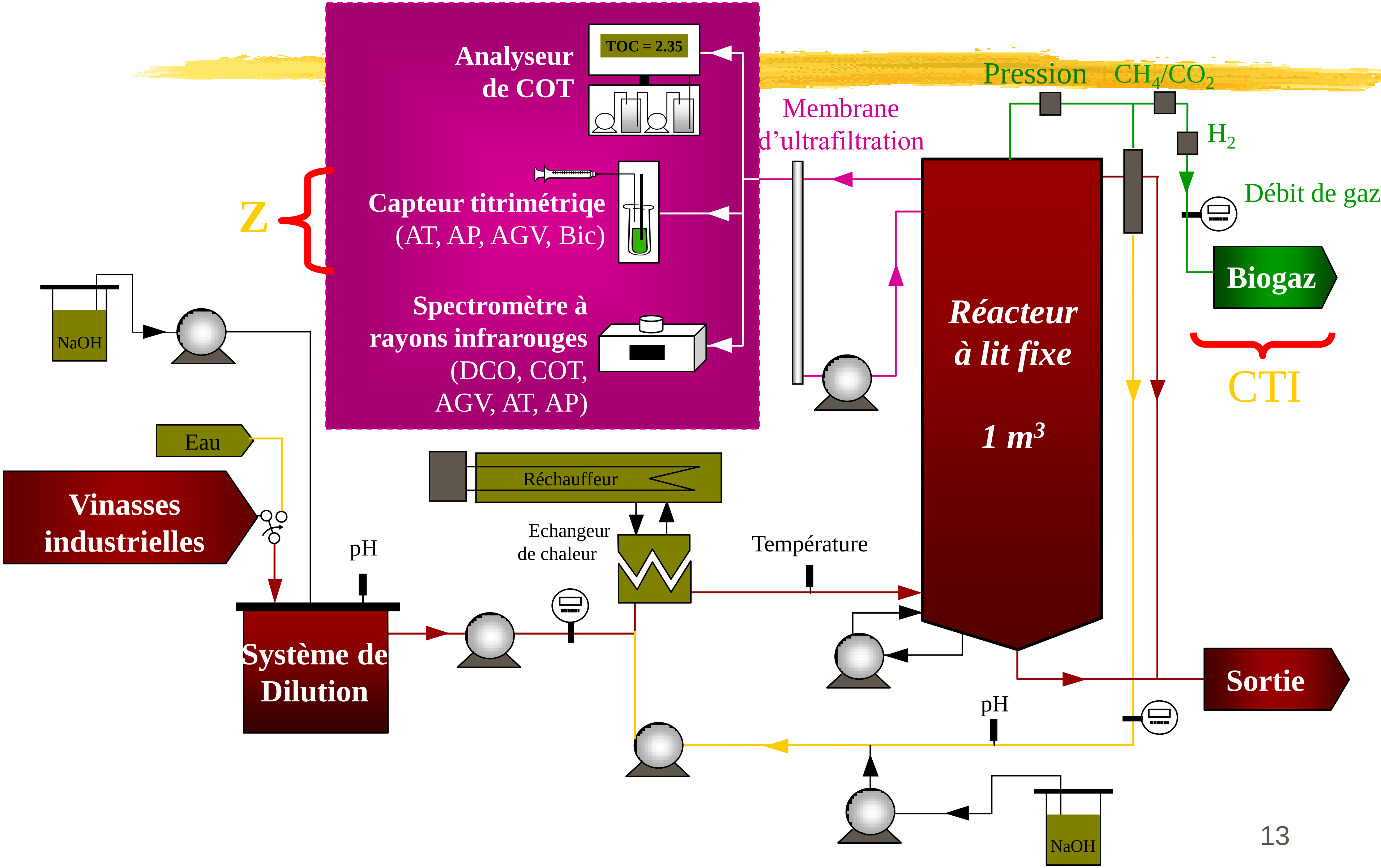
**Effluent : Industrial wine vinasses**

**Reactor : Fixed bed reactors**
**circular column**

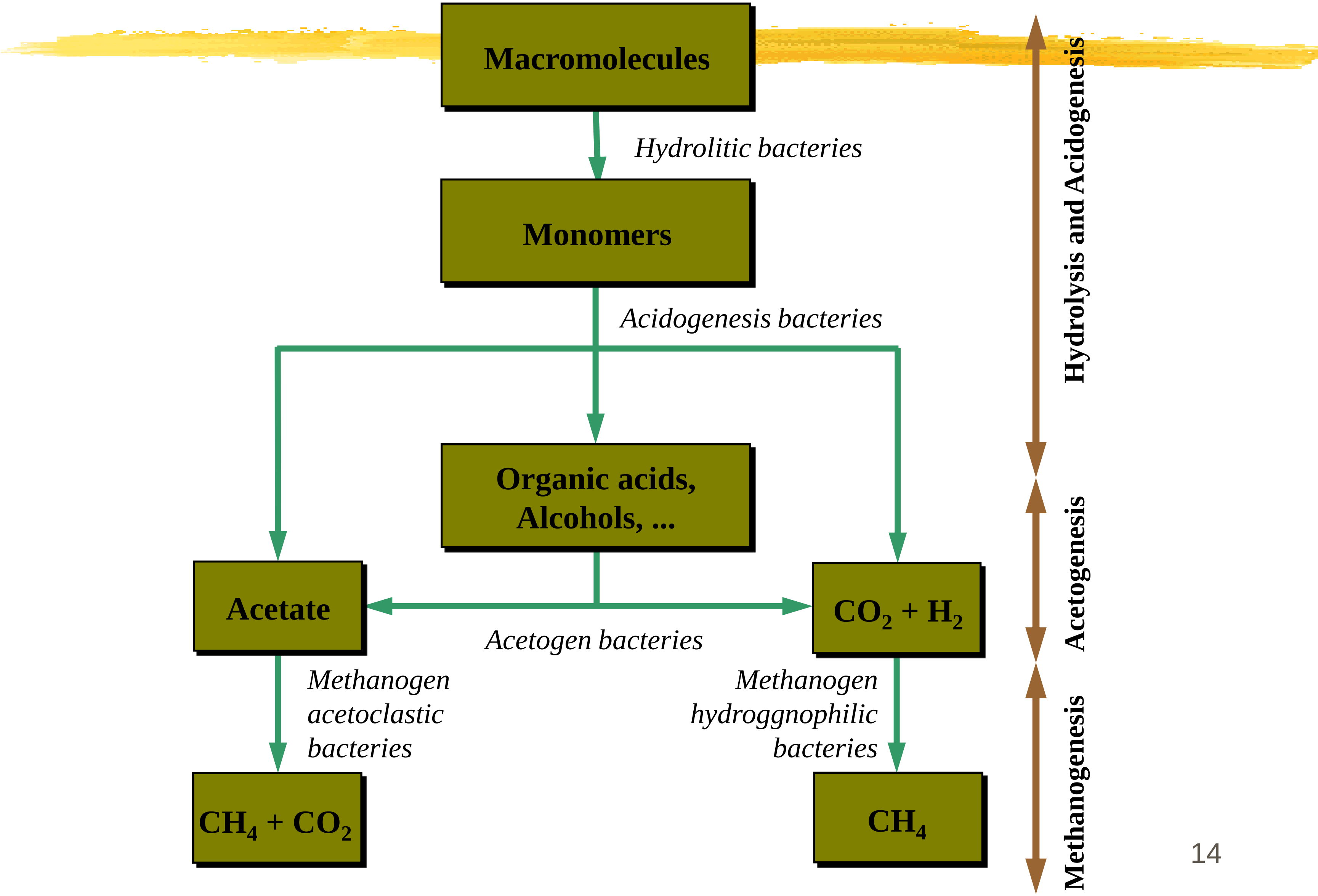
- 3,5 m height,
- 0,6 m diameter,
- 982 liters of total volume.

2006

# Process synoptic



# The anaerobic digestion



**Macromolecules**

*Hydrolitic bacteries*

**Monomers**

*Acidogenesis bacteries*

**Organic acids, Alcohols, ...**

**Acetate**

*Acetogen bacteries*

**$CO_2 + H_2$**

*Methanogen acetoclastic bacteries*

*Methanogen hydroggnophilic bacteries*

**$CH_4 + CO_2$**

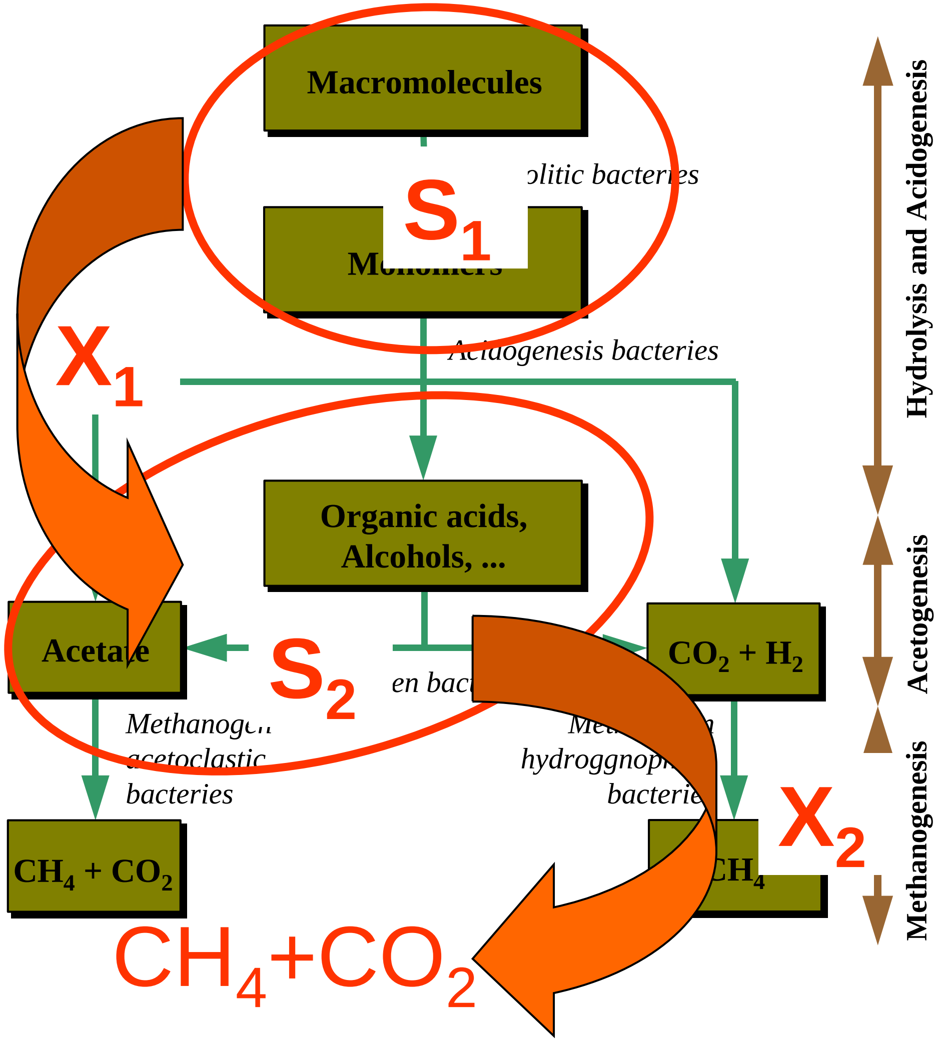
**$CH_4$**

**Hydrolysis and Acidogenesis**

**Acetogenesis**

**Methanogenesis**

# The anaerobic digestion



$$\begin{cases} S_1 \xrightarrow{\mu_1} X_1 + S_2 \\ S_2 \xrightarrow{\mu_2} X_2 + P_i \end{cases}$$

$$\mu_1(S_1) = \mu_{\max 1} \frac{S_1}{K_{S1} + S_1}$$

$$\mu_2(S_2) = \mu_{\max 2} \frac{S_2}{K_{S2} + S_2 + \left(\frac{S_2}{K_I}\right)^2}$$

# The "AMOCO" model

*(Bernard, et coll., 1997)*

Hypotheses :

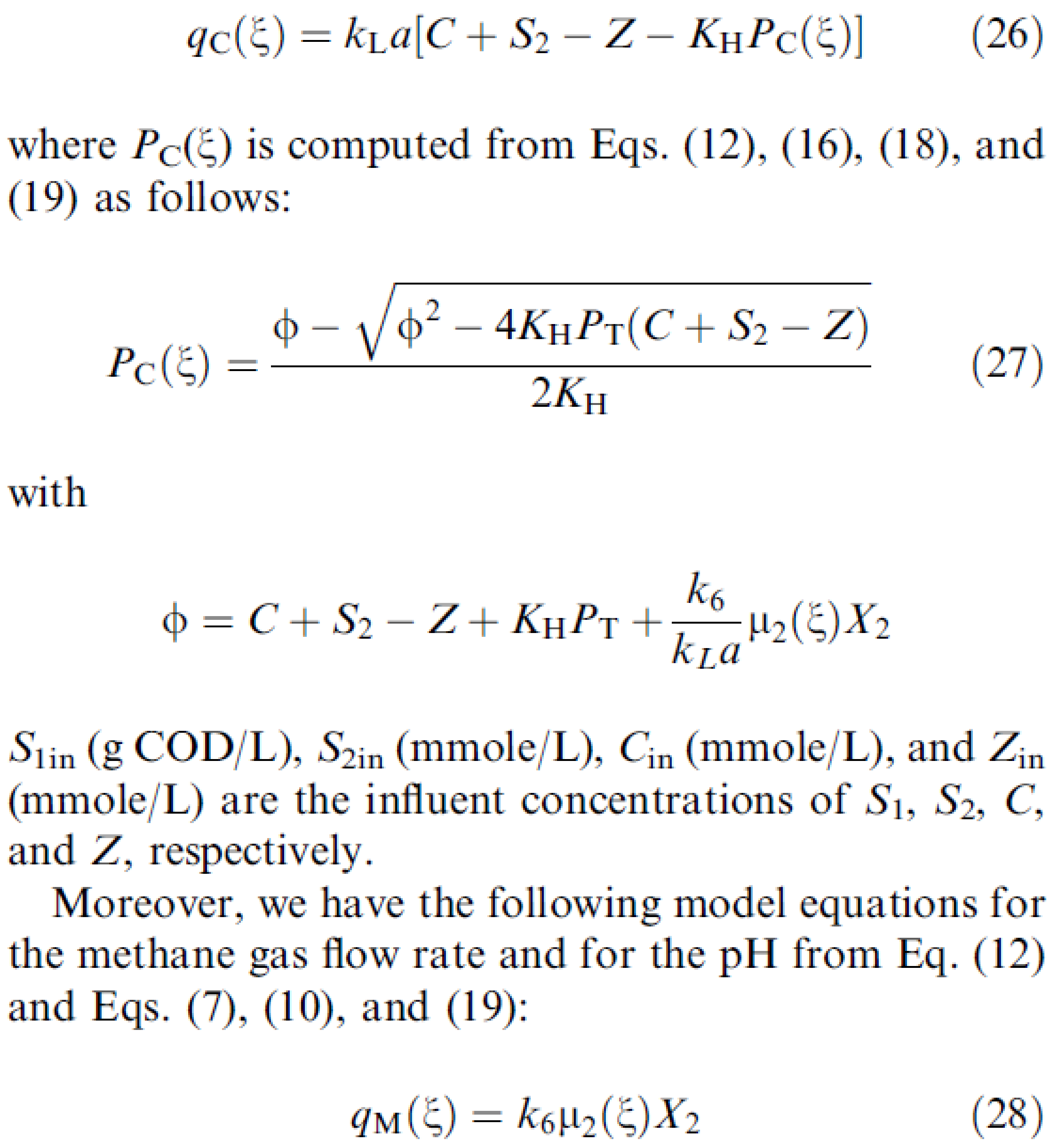
a) $6 \leq pH \leq 8$

b) Acetic acid is the dominant acid

c) $P_{CO_2}$ is always at equilibrium

$$
\begin{cases}
\dot{X}_1 = (\mu_1 - \alpha D) X_1 \\
\dot{X}_2 = (\mu_2 - \alpha D) X_2 \\
\dot{C}_{TI} = D(C_{TI}^i - C_{TI}) + k_7 (k_8 P_{CO_2} + Z - C_{TI} - S_2) + k_4 \mu_1 X_1 + k_5 \mu_2 X_2 \\
\dot{Z} = D(Z^i - Z) \\
\dot{S}_1 = D(S_1^i - S_1) - k_1 \mu_1 X_1 \\
\dot{S}_2 = D(S_2^i - S_2) + k_2 \mu_1 X_1 - k_3 \mu_2 X_2
\end{cases}
$$

# The "AMOCO" model



$$q_C(\xi) = k_L a[C + S_2 - Z - K_H P_C(\xi)] \qquad (26)$$

where $P_C(\xi)$ is computed from Eqs. (12), (16), (18), and (19) as follows:

$$P_C(\xi) = \frac{\phi - \sqrt{\phi^2 - 4K_H P_T(C + S_2 - Z)}}{2K_H} \qquad (27)$$

with

$$\phi = C + S_2 - Z + K_H P_T + \frac{k_6}{k_L a}\mu_2(\xi)X_2$$

$S_{1\text{in}}$ (g COD/L), $S_{2\text{in}}$ (mmole/L), $C_{\text{in}}$ (mmole/L), and $Z_{\text{in}}$ (mmole/L) are the influent concentrations of $S_1$, $S_2$, $C$, and $Z$, respectively.

Moreover, we have the following model equations for the methane gas flow rate and for the pH from Eq. (12) and Eqs. (7), (10), and (19):

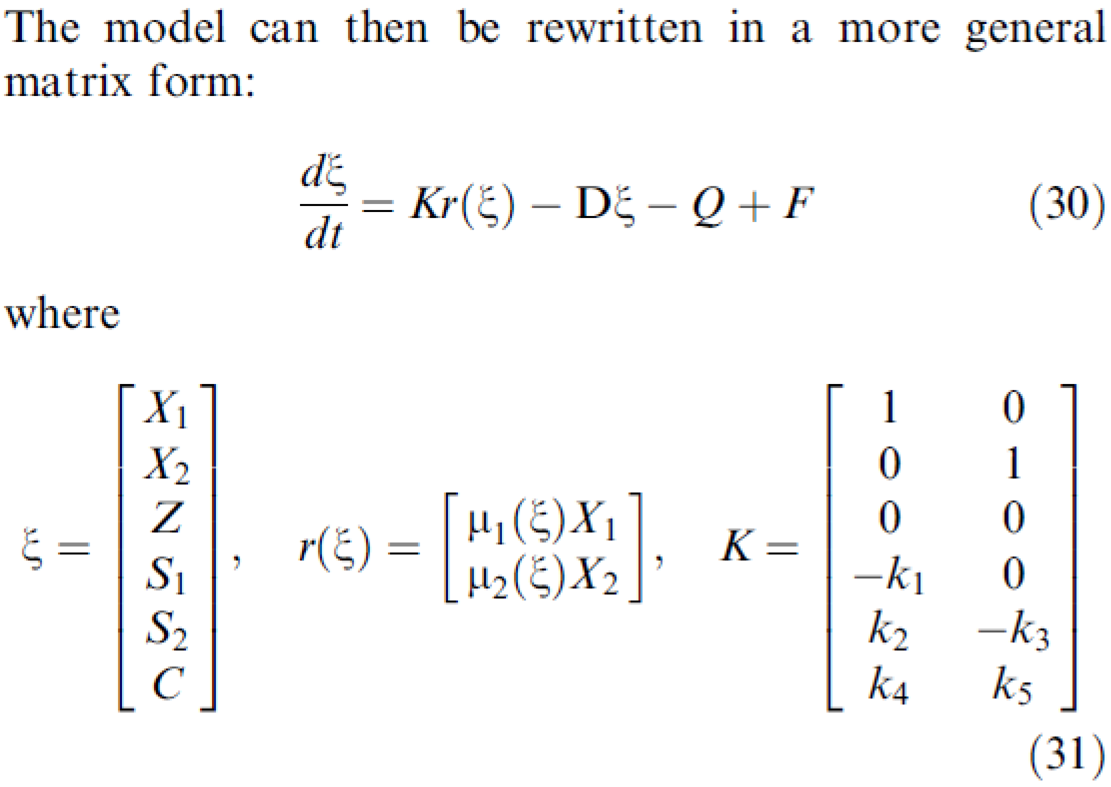
$$q_M(\xi) = k_6\mu_2(\xi)X_2 \qquad (28)$$

# The "AMOCO" model

$$K_b = \frac{[\mathrm{H}^+]B}{\mathrm{CO}_2} \qquad (5)$$

$$\mathrm{pH}(\xi) = -\log_{10}\left(K_\mathrm{b}\frac{C - Z + S_2}{Z - S_2}\right) \qquad (29)$$

# The "AMOCO" model



The model can then be rewritten in a more general matrix form:

$$\frac{d\xi}{dt} = Kr(\xi) - \mathrm{D}\xi - Q + F \tag{30}$$

where

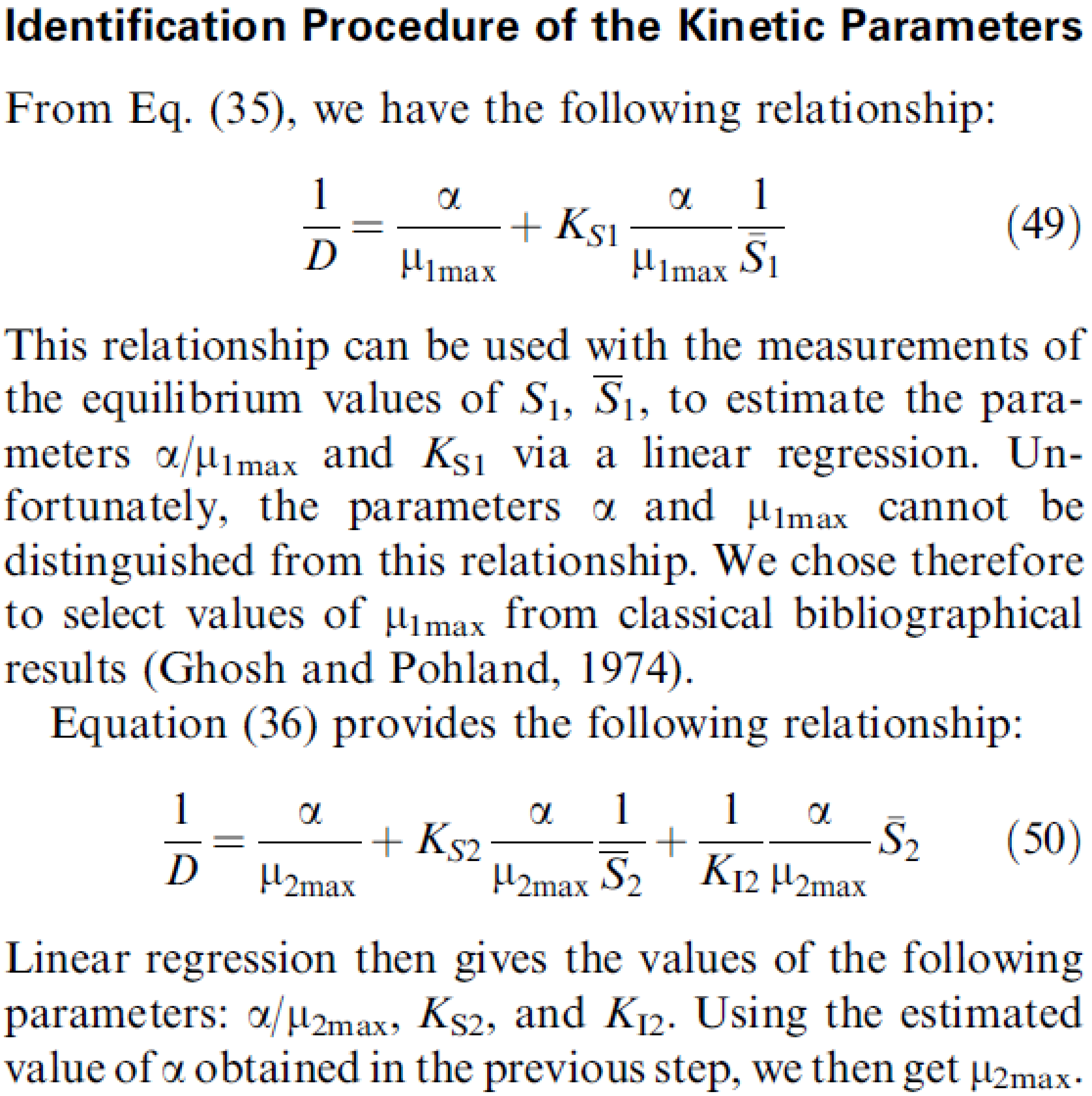
$$\xi = \begin{bmatrix} X_1 \\ X_2 \\ Z \\ S_1 \\ S_2 \\ C \end{bmatrix}, \quad r(\xi) = \begin{bmatrix} \mu_1(\xi)X_1 \\ \mu_2(\xi)X_2 \end{bmatrix}, \quad K = \begin{bmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \\ -k_1 & 0 \\ k_2 & -k_3 \\ k_4 & k_5 \end{bmatrix} \tag{31}$$

# The "AMOCO" model

$$F = \begin{bmatrix} 0 \\ 0 \\ DZ_{\text{in}} \\ DS_{1\text{in}} \\ DS_{2\text{in}} \\ DC_{\text{in}} \end{bmatrix}, \quad Q = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ q_{\text{C}}(\xi) \end{bmatrix},$$

$$D = \begin{bmatrix} \alpha D & 0 & 0 & 0 & 0 & 0 \\ 0 & \alpha D & 0 & 0 & 0 & 0 \\ 0 & 0 & D & 0 & 0 & 0 \\ 0 & 0 & 0 & D & 0 & 0 \\ 0 & 0 & 0 & 0 & D & 0 \\ 0 & 0 & 0 & 0 & 0 & D \end{bmatrix} \qquad (32)$$

# The "AMOCO" model



### Identification Procedure of the Kinetic Parameters

From Eq. (35), we have the following relationship:

$$\frac{1}{D} = \frac{\alpha}{\mu_{1\max}} + K_{S1}\frac{\alpha}{\mu_{1\max}}\frac{1}{\bar{S}_1} \tag{49}$$

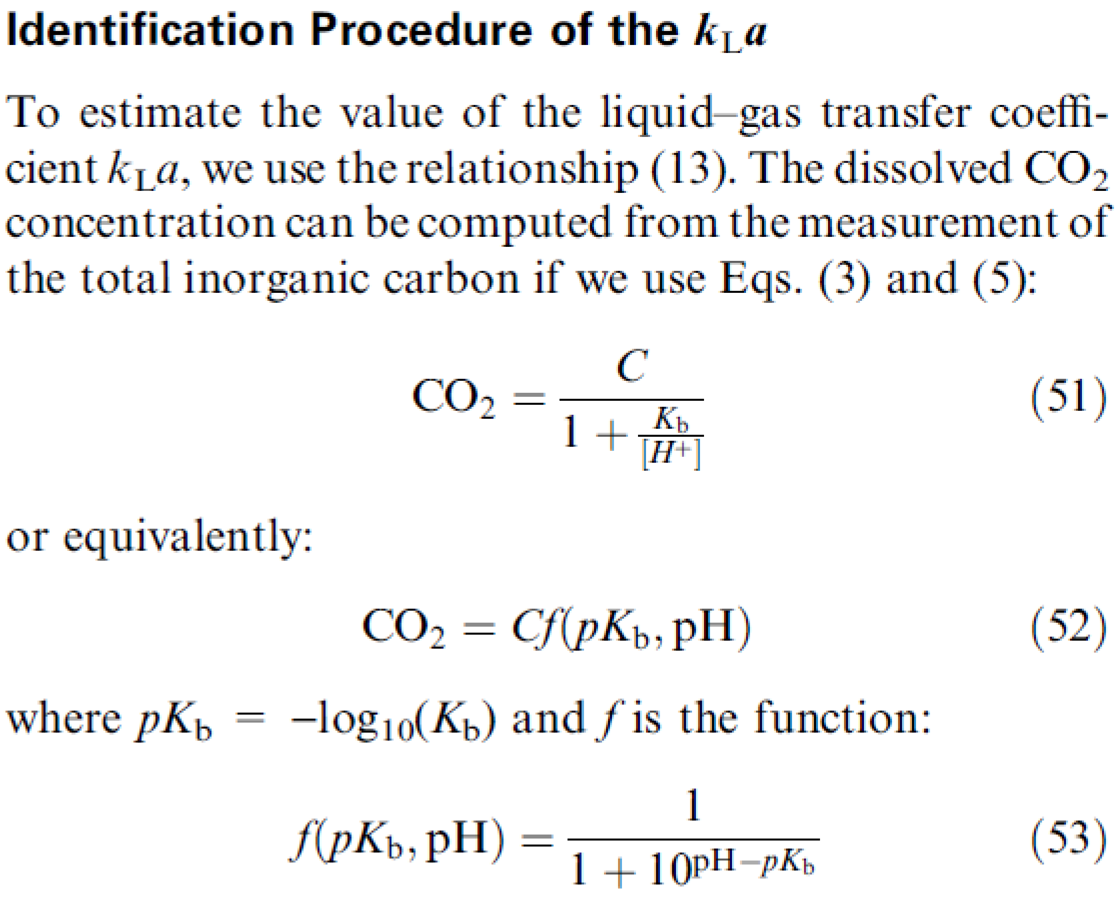
This relationship can be used with the measurements of the equilibrium values of $S_1$, $\overline{S}_1$, to estimate the parameters $\alpha/\mu_{1\max}$ and $K_{S1}$ via a linear regression. Unfortunately, the parameters $\alpha$ and $\mu_{1\max}$ cannot be distinguished from this relationship. We chose therefore to select values of $\mu_{1\max}$ from classical bibliographical results (Ghosh and Pohland, 1974).

Equation (36) provides the following relationship:

$$\frac{1}{D} = \frac{\alpha}{\mu_{2\max}} + K_{S2}\frac{\alpha}{\mu_{2\max}}\frac{1}{\bar{S}_2} + \frac{1}{K_{I2}}\frac{\alpha}{\mu_{2\max}}\bar{S}_2 \tag{50}$$

Linear regression then gives the values of the following parameters: $\alpha/\mu_{2\max}$, $K_{S2}$, and $K_{I2}$. Using the estimated value of $\alpha$ obtained in the previous step, we then get $\mu_{2\max}$.

# The "AMOCO" model



### Identification Procedure of the $k_L a$

To estimate the value of the liquid–gas transfer coefficient $k_L a$, we use the relationship (13). The dissolved $CO_2$ concentration can be computed from the measurement of the total inorganic carbon if we use Eqs. (3) and (5):

$$CO_2 = \frac{C}{1 + \frac{K_b}{[H^+]}} \qquad (51)$$

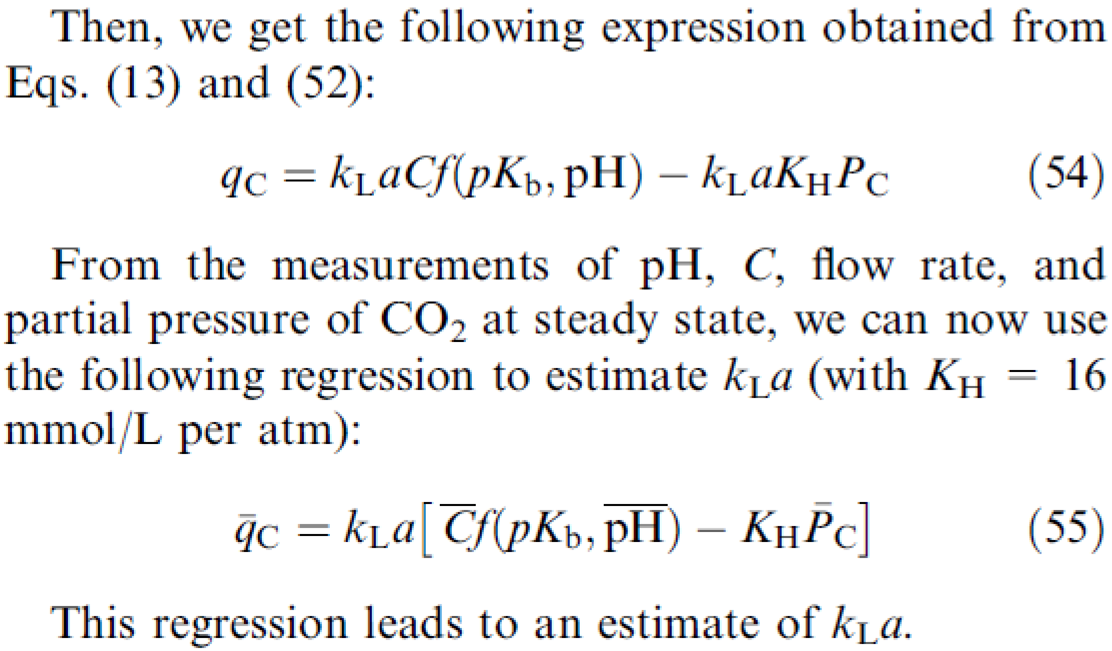
or equivalently:

$$CO_2 = Cf(pK_b, \mathrm{pH}) \qquad (52)$$

where $pK_b = -\log_{10}(K_b)$ and $f$ is the function:

$$f(pK_b, \mathrm{pH}) = \frac{1}{1 + 10^{\mathrm{pH} - pK_b}} \qquad (53)$$

# The "AMOCO" model



Then, we get the following expression obtained from Eqs. (13) and (52):

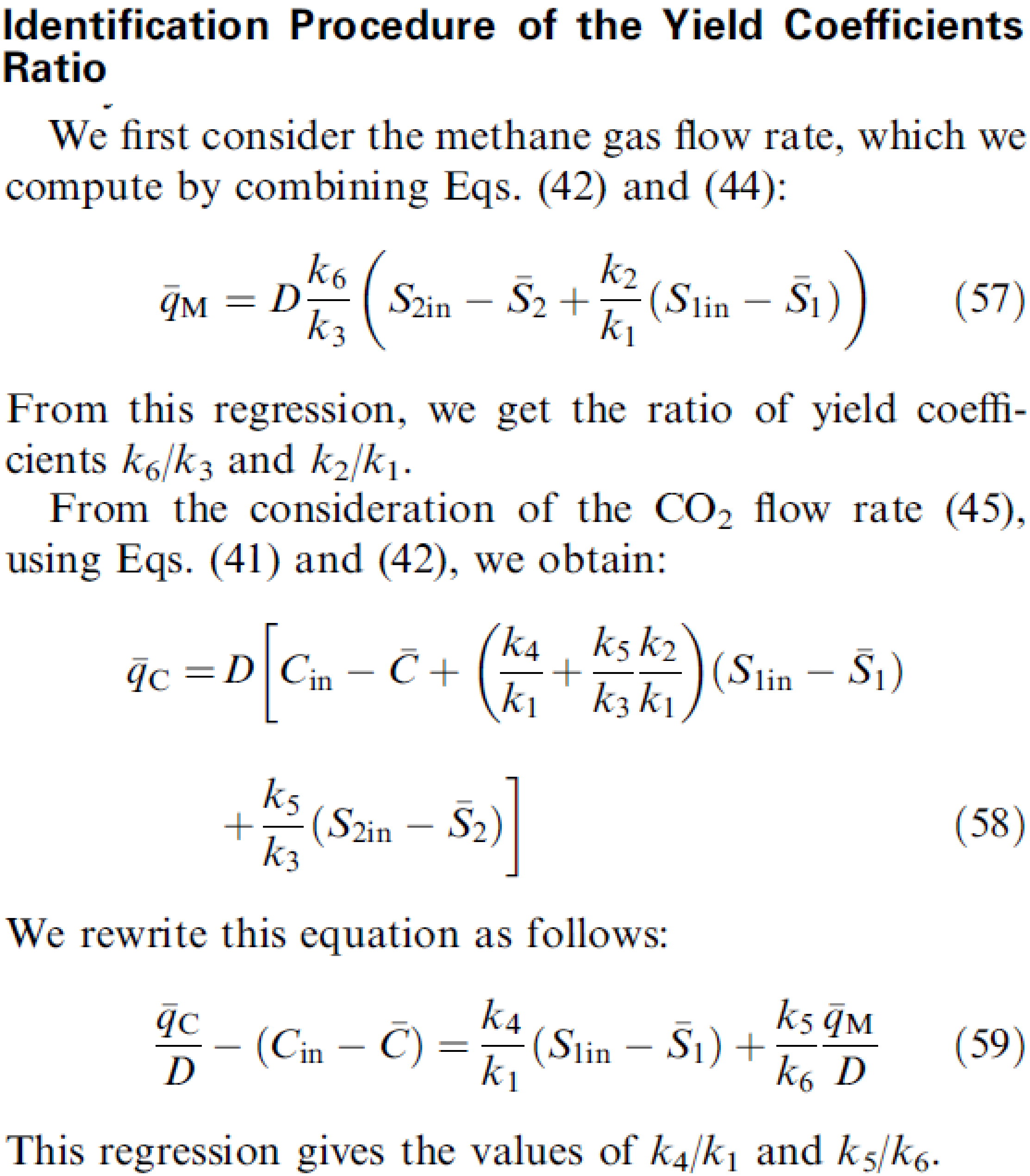
$$q_{\mathrm{C}} = k_{\mathrm{L}}aCf(pK_{\mathrm{b}}, \mathrm{pH}) - k_{\mathrm{L}}aK_{\mathrm{H}}P_{\mathrm{C}} \qquad (54)$$

From the measurements of pH, $C$, flow rate, and partial pressure of $CO_2$ at steady state, we can now use the following regression to estimate $k_{\mathrm{L}}a$ (with $K_{\mathrm{H}} = 16$ mmol/L per atm):

$$\bar{q}_{\mathrm{C}} = k_{\mathrm{L}}a\left[\bar{C}f(pK_{\mathrm{b}}, \overline{\mathrm{pH}}) - K_{\mathrm{H}}\bar{P}_{\mathrm{C}}\right] \qquad (55)$$

This regression leads to an estimate of $k_{\mathrm{L}}a$.

# The "AMOCO" model



### Identification Procedure of the Yield Coefficients Ratio

We first consider the methane gas flow rate, which we compute by combining Eqs. (42) and (44):

$$\bar{q}_M = D\frac{k_6}{k_3}\left(S_{2\mathrm{in}} - \bar{S}_2 + \frac{k_2}{k_1}(S_{1\mathrm{in}} - \bar{S}_1)\right) \tag{57}$$

From this regression, we get the ratio of yield coefficients $k_6/k_3$ and $k_2/k_1$.

From the consideration of the $CO_2$ flow rate (45), using Eqs. (41) and (42), we obtain:

$$\bar{q}_C = D\left[C_{\mathrm{in}} - \bar{C} + \left(\frac{k_4}{k_1} + \frac{k_5}{k_3}\frac{k_2}{k_1}\right)(S_{1\mathrm{in}} - \bar{S}_1) + \frac{k_5}{k_3}(S_{2\mathrm{in}} - \bar{S}_2)\right] \tag{58}$$

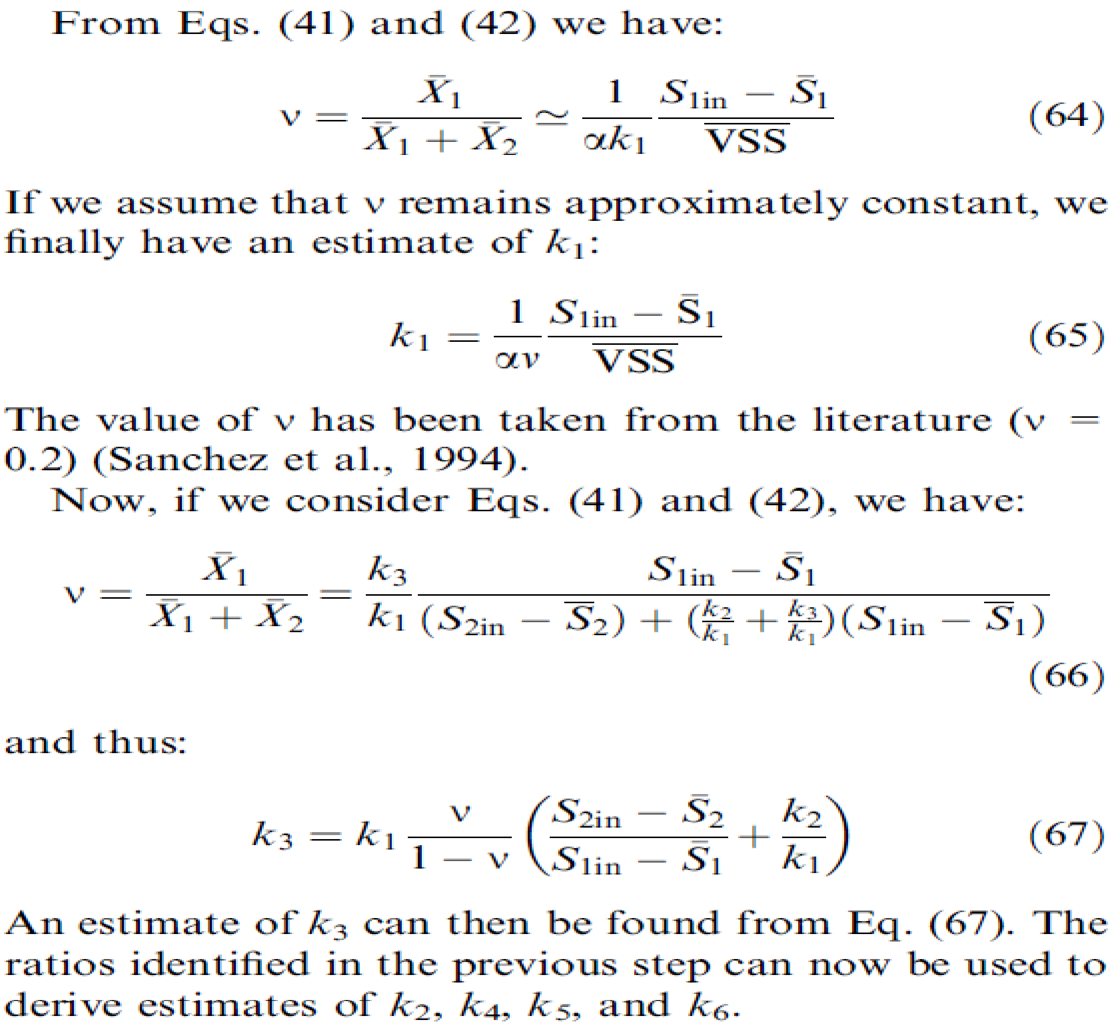
We rewrite this equation as follows:

$$\frac{\bar{q}_C}{D} - (C_{\mathrm{in}} - \bar{C}) = \frac{k_4}{k_1}(S_{1\mathrm{in}} - \bar{S}_1) + \frac{k_5}{k_6}\frac{\bar{q}_M}{D} \tag{59}$$

This regression gives the values of $k_4/k_1$ and $k_5/k_6$.

# The "AMOCO" model

## Determination of the Yield Coefficients



From Eqs. (41) and (42) we have:

$$\nu = \frac{\bar{X}_1}{\bar{X}_1 + \bar{X}_2} \simeq \frac{1}{\alpha k_1} \frac{S_{1\text{in}} - \bar{S}_1}{\overline{\text{VSS}}} \qquad (64)$$

If we assume that $\nu$ remains approximately constant, we finally have an estimate of $k_1$:

$$k_1 = \frac{1}{\alpha \nu} \frac{S_{1\text{in}} - \bar{S}_1}{\overline{\text{VSS}}} \qquad (65)$$

The value of $\nu$ has been taken from the literature ($\nu = 0.2$) (Sanchez et al., 1994).

Now, if we consider Eqs. (41) and (42), we have:

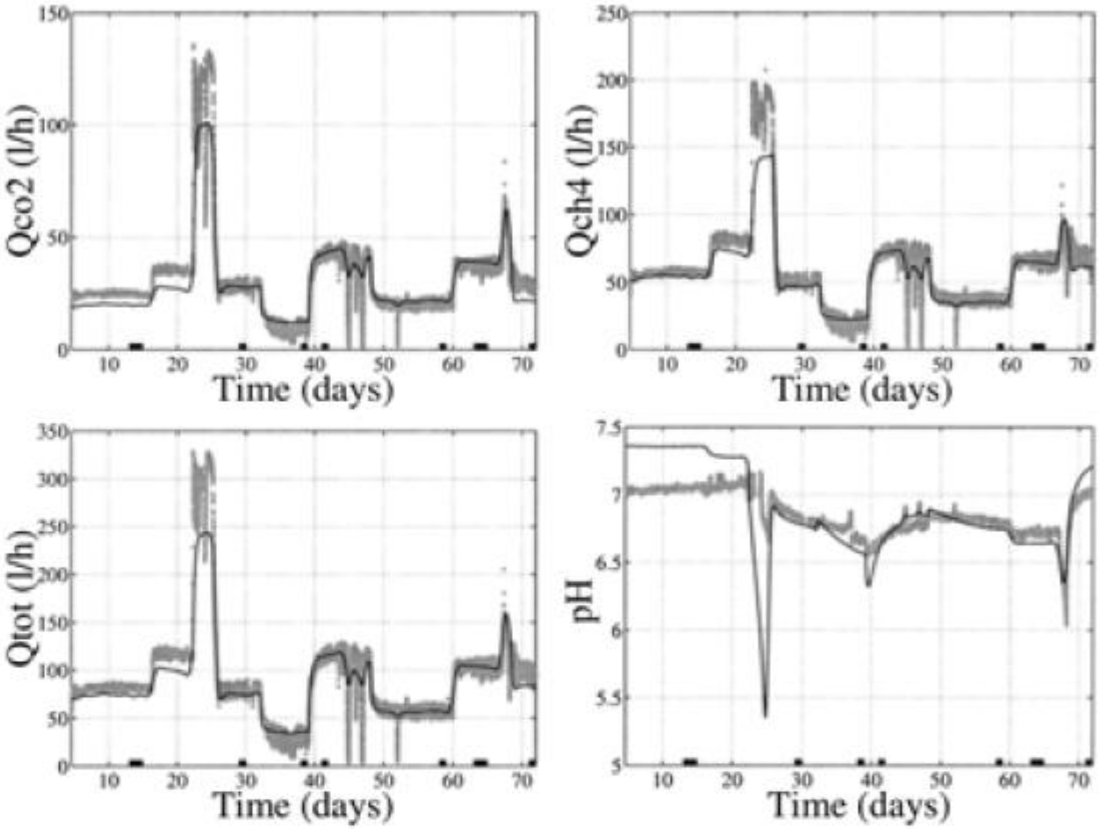
$$\nu = \frac{\bar{X}_1}{\bar{X}_1 + \bar{X}_2} = \frac{k_3}{k_1} \frac{S_{1\text{in}} - \bar{S}_1}{(S_{2\text{in}} - \bar{S}_2) + (\frac{k_2}{k_1} + \frac{k_3}{k_1})(S_{1\text{in}} - \bar{S}_1)} \qquad (66)$$

and thus:

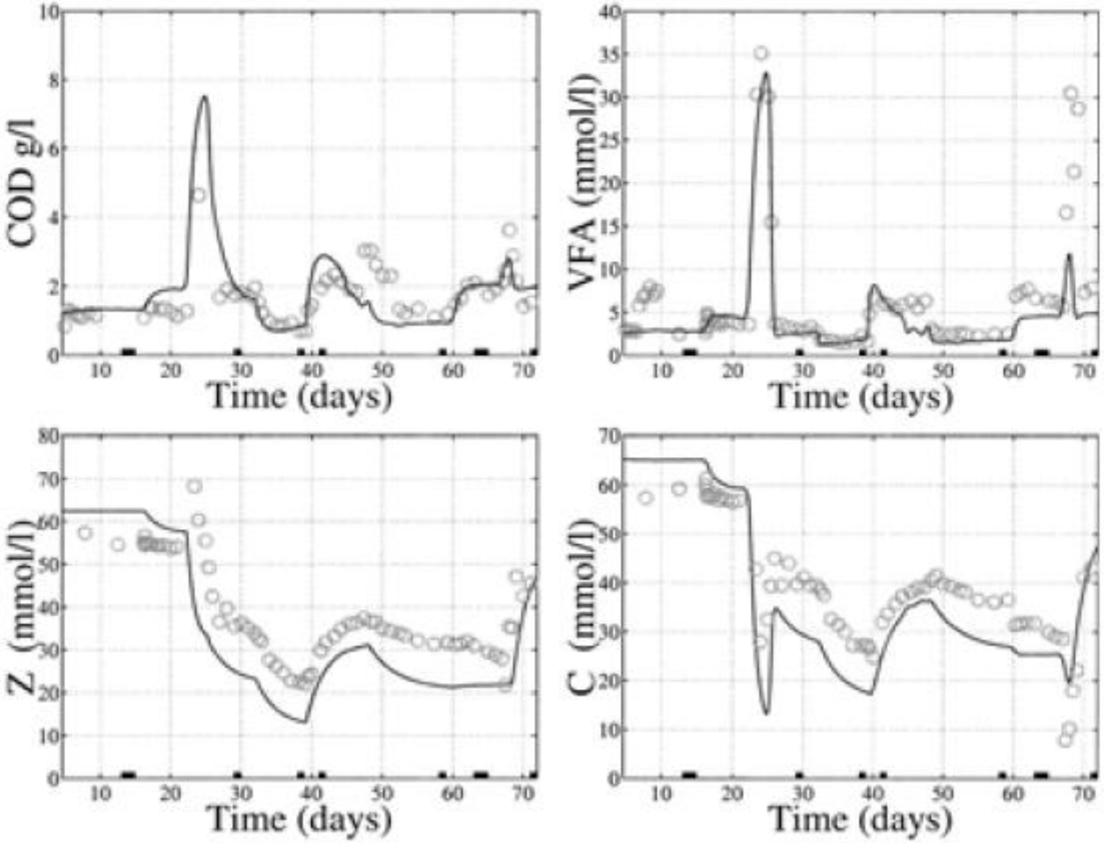
$$k_3 = k_1 \frac{\nu}{1 - \nu} \left( \frac{S_{2\text{in}} - \bar{S}_2}{S_{1\text{in}} - \bar{S}_1} + \frac{k_2}{k_1} \right) \qquad (67)$$

An estimate of $k_3$ can then be found from Eq. (67). The ratios identified in the previous step can now be used to derive estimates of $k_2$, $k_4$, $k_5$, and $k_6$.

# The "AMOCO" model



# The "AMOCO" model



# *Experimental avaluation of the model (2001)*