

PIPE REACTOR BALANCE.

B. Tal-Figiel* , M. Kryłów**

* Institute of Chemical and Process Engineering, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland

** Institute of Water Supply and Environmental Protection, Cracow University of Technology, ul. Warszawska 24, Kraków
(E-mail: malkryl@vistula.wis.pk.edu.pl)

ABSTRACT

In the report, a mathematical model describing the kinetics of biochemical reactions in a pipe reactor was formulated. The experimental results were compared with the theoretical models. In isothermal conditions, the pipe reactor process design and modelling can be based on the microorganism growth vs. biomass concentration relationship.

KEYWORDS

Kinetic, biochemical reaction, pipe reactor,

INTRODUCTION

About 95% of digestion processes proceeds in batch reactors or pipe reactors. The model of ideal reactor is the basic model describing the phenomenas taking place in such reactors. The mass balance equation in the isothermal conditions can be written as:

$$\begin{array}{cccc}
 \left(\begin{array}{c} \text{Change of} \\ \text{mass in time,} \\ \text{in balanced} \\ \text{space} \\ \text{(acumulation)} \end{array} \right) & = & \left(\begin{array}{c} \text{Inflow-outflow} \\ \text{of mass stream} \\ \text{through} \\ \text{conversion} \end{array} \right) & + & \left(\begin{array}{c} \text{Inflow-outflow} \\ \text{of mass stream} \\ \text{through} \\ \text{diffusion} \end{array} \right) & + & \left(\begin{array}{c} \text{mass} \\ \text{production} \\ \text{or loss} \end{array} \right) \\
 \mathbf{1} & & \mathbf{2} & & \mathbf{3} & & \mathbf{4}
 \end{array}$$

For the ideal pipe reaktor the mass balance can be described by the following equation:

$$\frac{dc_i}{dt} = \frac{c_{i,0} \cdot v^*_0 - c_i \cdot v^*_i}{V_R} + \frac{D_i \cdot A \cdot dc_i / dx}{V_R} + \sum_i v_{i,j} \cdot r_j$$

where: index 0 marks inflow values.

In the ideal pipe reactor the diffusion term is equal zero and the inflow and outflow mass volume streams are constant. Hence, the mass balance equation is:

$$\frac{dc_i}{dt} = \frac{v^*}{V_R} \cdot (c_{i,0} - c_i) + \sum_i v_{i,j} \cdot r_j = \frac{v^*}{V_R} \cdot (c_{i,0} - c_i) + R_i$$

In aerobic processes, the pipe reactor are aerated either with air or pure oxygen. Dissolved oxygen concentrations in a solution are defined by the mass transport from the gas phase (air bubble) through a boundary layer to a liquid phase. Therefore, the mass balance equations comprises a convection term, apart from a reaction term:

$$r_{\text{wnikanie masy}} = \beta_o \cdot (S_G)_{V_R} \cdot (c_o^* - c_o)$$

where:

$(S_G)_{V_R}$ = specific boundary surface in $(m^2/m^3 + m^{-1})$,

$\beta_o = \frac{D_o}{\delta}$ = degree of penetration,

c_o^* = oxygen saturation concentration in solution,

c_o = oxygen concentration in solution

Substituting to the mass balance equation we get the following solution.

$$\frac{dc_i}{dt} = \frac{v^*}{V_R} \cdot (c_{i,0} - c_i) + R_i + \beta_o \cdot (S_G)_{V_R} \cdot (c_o^* - c_o)$$

Depending on the pipe reactor process regime (batch, continuous, aerobic, anaerobic) different terms of the mass balance equation will dominate

Process regime		Unsteady term (state) $\frac{dc}{dt}$	Convection term $\frac{v^*}{V_R} \cdot (c_{i,0} - c_i)$	Reaction term R_i	Penetration term $\beta_o = (S_G)_{V_R} \cdot (c_o^* - c_o)$
continuously	Aerobic	0	x	x	x
	Anaerobic	0	x	x	0
batch	Aerobic	x	0	x	z
	Anaerobic	x	0	x	0
Semi-continuous (semi-batch)	Aerobic	x	x	x	x
	Anaerobic	x	x	x	0

Most reactors employ biomass recycle (without catalyst). A layout of a single pipe reactor with recycle is shown in Figure 1.

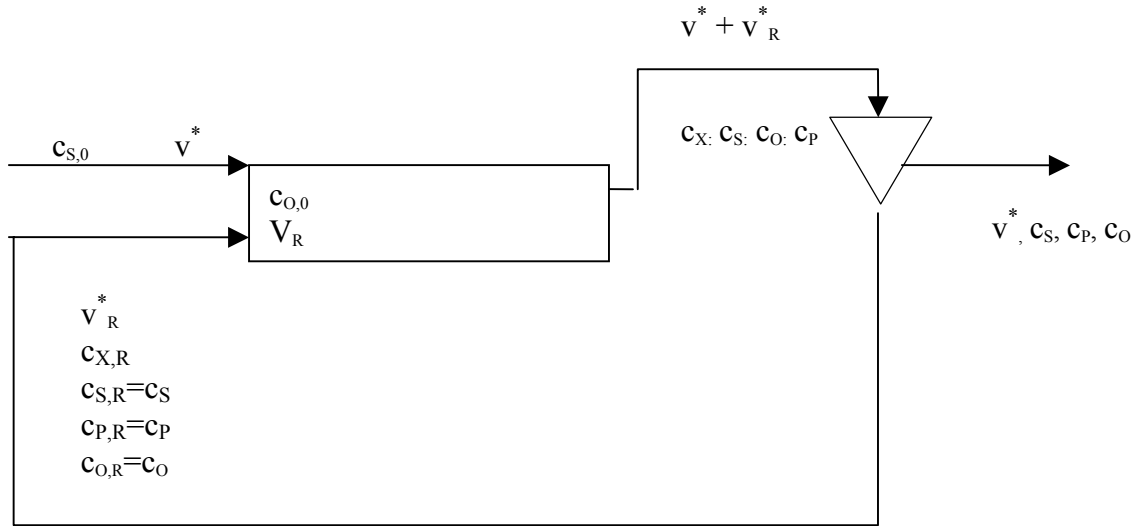


Figure 1. A layout of a single pipe reactor with recycle .

PROCESS KINETIC MODEL

Using a general mass balance equation, mass balance formulas for different system elements can be developed.

1. biomass concentration c_X :

$$\frac{dc_X}{dt} = \frac{1}{V_R} \cdot (v_R^* \cdot c_{X,R} - (v^* + v_R^*) \cdot c_X) + R_X$$

or

$$\frac{dc_X}{dt} = \frac{1}{V_R} \cdot (v_R^* \cdot c_{X,R} - v^* \cdot c_X - v_R^* \cdot c_X) + R_X$$

$$\frac{dc_X}{dt} = \frac{1}{V_R} \cdot (v_R^* \cdot c_{X,R} - v^* \cdot c_X - v_R^* \cdot c_X) + R_X$$

Having assumed the following coefficients:

α , defined as:

$$\alpha = \frac{v_R^*}{v^*}$$

biomass β , defined as:

$$\beta = \frac{c_{X,R}}{c_X}$$

and dilution rate D , defined as:

$$D = \frac{1}{\tau} = \frac{v^*}{V_R}$$

the formula has form:

$$\frac{dc_X}{dt} = -D \cdot c_X \cdot [1 + \alpha \cdot (1 - \beta)] + R_X$$

dimensionless term $[1 + \alpha \cdot (1 - \beta)]$ can be considered for three cases:

a) continuous pipe reactor $[1 + \alpha \cdot (1 - \beta)] = 0$

$$\frac{dc_X}{dt} = R_X$$

b) continuous pipe reactor without recycle $[1 + \alpha \cdot (1 - \beta)] = 1$

$$0 = -D \cdot c_X + R_X$$

c) continuous pipe reactor with recycle $[1 + \alpha \cdot (1 - \beta)] < 1$

$$0 = -D \cdot c_X \cdot [1 + \alpha \cdot (1 - \beta)] + R_X$$

The biomass return rate is usually defined as:

$$R = \frac{v_R^*}{v^* + v_R^*} \cdot \frac{c_{X,R}}{c_X} \quad \text{where} \quad v_R^* = \alpha \cdot v^*$$

$$R = \frac{\alpha}{\alpha + 1} \cdot \beta$$

2. Substrate concentration c_S :

$$\frac{dc_S}{dt} = \frac{1}{V_R} \cdot (v^* \cdot c_{S,0} + v_R^* \cdot c_{S,R} - v_R^* \cdot c_{S,R} - v^* \cdot c_S) + R_S$$

after transformation can be written as:

$$\frac{dc_S}{dt} = \frac{v^*}{V_R} \cdot (c_{S,0} - c_S) + R_S$$

introducing a dilution coefficient:

$$\frac{dc_S}{dt} = D \cdot (c_{S,0} - c_S) + R_S$$

If the loss of substrate R_S is expressed as a biomass growth rate R_X derived from the stoichiometric relationship and a biomass yield constant Y :

$$R_S = -\frac{1}{Y_{X/S}} \cdot R_X$$

the formula can be written as:

$$\frac{dc_S}{dt} = D \cdot (c_{S,0} - c_S) - \frac{1}{Y_{X/S}} \cdot R_X$$

Substrate loss R_S can also be defined as:

$$R_S = -\frac{1}{Y_{X/S}} \cdot R_X - \frac{1}{Y_{P/S}} \cdot R_P$$

and then the mass balance equation is:

$$\frac{dc_S}{dt} = D \cdot (c_{S,0} - c_S) - \frac{1}{Y_{X/S}} \cdot R_X - \frac{1}{Y_{P/S}} \cdot R_P$$

A correlation between production rate and biomass growth rate can be determined using the following equation;

$$R_p = \frac{1}{Y_{X/P}} \cdot R_X$$

Substituting the above formulas in the mass balance equation we get:

$$\frac{dc_S}{dt} = D \cdot (c_{S,0} - c_S) - \frac{1}{Y_{X/P}} \cdot R_X - \frac{1}{Y_{P/S}} \cdot \frac{1}{Y_{X/P}} \cdot R_X$$

3. Product concentration c_p is:

$$\frac{dc_p}{dt} = \frac{1}{V_R} \cdot (v_R^* \cdot c_{p,R} - (v^* + v_R^*) \cdot c_p) + R_p$$

Introducing to the above equation the coefficients α, β and D :

$$\frac{dc_p}{dt} = -D \cdot c_p \cdot [1 + \alpha \cdot (1 - \beta)] + R_p$$

Substituting R_X for R_p using formula:

$$R_p = \frac{1}{Y_{X/P}} \cdot R_X$$

the equation $\frac{dc_p}{dt}$ can be written as:

$$\frac{dc_p}{dt} = -D \cdot c_p \cdot [1 + \alpha \cdot (1 - \beta)] + \frac{1}{Y_{X/P}} \cdot R_X$$

4. Oxygen concentration

The mass balance equation can be presented as:

$$\frac{dc_O}{dt} = \frac{1}{V_R} \cdot (v^* \cdot c_{O,0} + v_R^* \cdot c_{O,R} - v_R^* \cdot c_{O,R} - v^* \cdot c_O) + R_O + \beta_O \cdot S_{V_R} \cdot (c_O^* - c_O)$$

Using $\frac{dc_O}{dt}$ the substrate depletion rate can be written as:

$$\frac{dc_O}{dt} = D \cdot (c_{O,0} - c_O) + R_O + \beta_O \cdot S_{V_R} \cdot (c_O^* - c_O)$$

Defining the oxygen depletion rate R_O with the biomass growth rate R_X , where R_X is defined as:

$$R_O = -\frac{1}{Y_{X/O}} \cdot R_X,$$

the following relationship is obtained:

$$\frac{dc_O}{dt} = D \cdot (c_{O,0} - c_O) - \frac{1}{Y_{X/O}} \cdot R_X + \beta_O \cdot S_{V_R} \cdot (c_O^* - c_O).$$

The oxygen depletion rate is described with the biomass growth rate R_X and the product yield:

$$R_O = -\frac{1}{Y_{X/O}} \cdot R_X - \frac{1}{Y_{P/O}} \cdot R_P$$

Substituting it to the equation describing the product concentration changes in time, the following relationship is obtained:

$$\frac{dc_O}{dt} = D \cdot (c_{O,0} - c_O) - \frac{1}{Y_{X/O}} \cdot R_X - \frac{1}{Y_{P/O}} \cdot R_P + \beta_O \cdot S_{V_R} \cdot (c_O^* - c_O)$$

In the next step, the product yield is defined using the micriorganism growth rate:

$$R_P = -\frac{1}{Y_{X/P}} \cdot R_X$$

and the equation takes form:

$$\frac{dc_O}{dt} = D \cdot (c_{O,0} - c_O) - \frac{1}{Y_{X/O}} \cdot R_X - \frac{1}{Y_{P/O}} \cdot \frac{1}{Y_{X/P}} R_X + \beta_O \cdot S_{V_R} \cdot (c_O^* - c_O)$$

Summarising , we obtain the set of differential equations:

$$\begin{aligned} \frac{dc_X}{dt} &= -D \cdot c_X \cdot [1 + \alpha \cdot (1 - \beta)] + R_X \\ \frac{dc_S}{dt} &= D \cdot (c_{S,0} - c_S) - \frac{1}{Y_{X/P}} \cdot R_X - \frac{1}{Y_{P/S}} \cdot \frac{1}{Y_{X/P}} \cdot R_X \\ \frac{dc_P}{dt} &= -D \cdot c_P \cdot [1 + \alpha \cdot (1 - \beta)] + \frac{1}{Y_{X/P}} \cdot R_X \\ \frac{dc_O}{dt} &= D \cdot (c_{O,0} - c_O) - \frac{1}{Y_{X/O}} \cdot R_X - \frac{1}{Y_{P/O}} \cdot \frac{1}{Y_{X/P}} \cdot R_X + \beta_O \cdot S_{V_R} \cdot (c_O^* - c_O) \end{aligned}$$

The above equations include a reaction term, which can be described with a basic biokinetical equation:

$$R_X = \mu \cdot c_X$$

where:

$$\mu = f(T, \text{pH}, c_S, c_P, c_X)$$

There are different functional relationships describing the above variables, for example:

Table 1. Kinetic relationships for $\mu=f(C_S)$ e.g. $q_P=f(C_S)$ [Birjukow and Knaterie 1986]

No.	Equation	Author
1.	$\mu = \text{const}$	
2.	$\mu = K \cdot C_S$	
3.	$\mu = K \cdot C_S^n$	
4.	$\mu = \mu_{\max} \cdot \frac{C_S}{K_S + C_S}$	Monod
5.	$\mu = \mu_{\max} \cdot \frac{C_S^n}{(K_S + C_S^n)}$	Moser
6.	$\mu = \mu_{\max} \cdot \frac{1 + \frac{C_S}{K_I}}{1 + \frac{C_S}{K_{II}}}$	
7.	$\mu = \mu_{\max} \cdot \frac{C_S}{K_S + C_S + \frac{C_S^2}{K_I}}$	Andrews
8.	$\mu = \mu_{\max} \cdot \frac{C_S}{(K_S + C_S) \cdot \left(1 + \frac{C_S}{K_I}\right)}$	Edwards
9.	$\mu = \mu_{\max} \cdot \frac{C_S}{K_S + C_S + \left(1 + \frac{C_S}{K}\right) \cdot \frac{C_S^2}{K_I}}$	
10.	$\mu = \mu_{\max} \cdot \frac{C_S}{K_S + C_S} \cdot \exp\left(-\frac{C_S}{K_S}\right)$	Aiba
11.	$\mu = \mu_{\max} \cdot \left[\exp\left(-\frac{C_S}{K_I}\right) - \exp\left(-\frac{C_S}{K_S}\right) \right]$	

Table 2 Kinetic relationships for $\mu=f(C_P)$ e.g. $q_P=f(C_P)$ [Birjukow and Kanterie, 1988]

No.	Equation
1.	$\mu = \mu_{\max} - k \cdot C_P$
2.	$\mu = \mu_{\max} \cdot \frac{k_P}{k_P + C_P}$
3.	$\mu = \mu_{\max} \cdot \exp\left(-\frac{K}{C_P}\right)$
4.	$\mu = \mu_{\max} \cdot (1 - K \cdot C_P)^n$
5.	$\mu = \mu_{\max} \cdot \frac{C_P^n}{(K_P + C_P^n)}$
6.	$\mu = \begin{cases} \mu_{\max} & \text{dla } C_P \leq C_{P,KR} \\ \mu_{\max} \cdot \frac{\left(1 + \frac{C_{P,KR}}{K_P}\right)}{1 + \frac{C_P}{K_P}} & \text{dla } C_P > C_{P,KR} \end{cases}$
7.	$\mu = \mu_0 + \mu_1 \cdot \frac{K_P}{K_P + C_P}$

Table 3. Kinetic relationships for $\mu = f(T)$ e.g. $q_p = f(T)$ [Birjukow and Knaterie, 1986]

No.	Equation
1.	$\mu = \mu_0 + K \cdot T$
2.	$\mu = \mu_{\max} - K \cdot \left(\frac{T}{T_0} - 1 \right)^2$
3.	$\mu = \mu_0 \cdot e^{-\frac{K}{T}}$
4.	$\mu = \mu_1 \cdot e^{\frac{K_1}{T}} - \mu_2 \cdot e^{\frac{K_2}{T}}$ $\mu = \mu' \cdot e^{\frac{K}{T}}$

Table 4. Kinetic relationships for $\mu = f(\text{pH})$ e.g. $q_p = f(\text{pH})$, [Birjukow and Kanterie, 1986]

No.	Equation
1.	$\mu = K_0 - K_1 \cdot \text{pH} + K_2 \cdot (\text{pH})^2$
2.	$\mu = \mu_{\max} \cdot \frac{K_H}{K_H + [H]}$
3.	$\mu = \mu_{\max} \cdot \frac{K_{OH}}{K_{OH} + [OH]}$
4.	$\mu = \mu + \frac{\mu_{\max}}{\left(1 + \frac{[OH]}{K_H}\right) \cdot \left(1 + \frac{[OH]}{K_{OH}}\right)}$

$\mu = f(c_X)$

$$\mu = \mu_{\max} \cdot \left(1 - \frac{c_X}{c_{X \max}} \right)$$

EXAMPLE:

The process was carried out in isothermal conditions, in a pipe reactor; the biomass concentrations were measured every hour.

Table 6. Measurement results

time [h]	Biomass concentration g dry solids/dm ³	
	25°C	35°C
0	0,200	0,164
1	0,203	0,165
2	0,210	0,166
3	0,228	0,172
4	0,261	0,195
5	0,314	0,279
6	0,397	0,448
7	0,503	0,682
8	0,621	1,052
9	0,738	1,458
10	0,888	1,618
11	1,137	1,694
12	1,409	1,749
13	1,57	1,784
14	1,649	1,838
15	1,702	1,859
16	1,747	1,885
17	1,776	1,897
18	1,804	1,889
19	1,824	1,885
20	1,847	1,889

If a substrate concentration c_S or a product concentration c_P cannot be determined experimentally then a model can be developed based on the microorganism growth rate and a biomass concentration relationship $\mu = f(c_X)$. In this particular case two models were compared:

Model 1:

$$\mu = \mu_{\max} \cdot \left(1 - \frac{c_X}{c_{X \max}}\right)$$

and model 2

$$\mu = \mu_{\max} \cdot \left(1 - \frac{c_X}{c_{X \max}}\right) \cdot \left(1 - e^{-\frac{t}{t_i}}\right)$$

In both models concentration variations in time, $c_X = f(t)$, were considered:

From model 1,

$$\mu = \frac{1}{c_X} \cdot \frac{dc_X}{dt} = \mu_{\max} \cdot \left(1 - \frac{c_X}{c_{X \max}}\right)$$

after rearranging variables and integration, the model equation can be developed:

$$\int_{c_{X,0}}^{c_X} \frac{dc_X}{c_X \cdot \left(1 - \frac{c_X}{c_{X,max}}\right)} = \mu_{max} \cdot \int_0^t dt$$

with parameters, which can be determined after fitting the curve to the experimental values.

$$c_X = \frac{c_{X,0} \cdot e^{\mu_{max} \cdot t}}{1 - \left(\frac{c_{X,0}}{c_{X,max}}\right) \cdot (1 - e^{\mu_{max} \cdot t})}$$

The same procedure can be applied to the model 2:

$$\mu = \frac{1}{c_X} \cdot \frac{dc_X}{dt} = \mu_{max} \cdot \left(1 - \frac{c_X}{c_{X,max}}\right) \cdot \left(1 - e^{-\frac{t}{t_i}}\right)$$

after rearranging variables and integration, the model equation can be developed:

$$\int_{c_{X,0}}^{c_X} \frac{dc_X}{c_X \cdot \left(1 - \frac{c_X}{c_{X,0}}\right)} = \mu_{max} \cdot \int_0^t \left(1 - e^{-\frac{t}{t_i}}\right)$$

$$c_X = \frac{c_{X,max}}{1 + \left(\frac{c_{X,max}}{c_{X,0}} - 1\right) \cdot e^{\left\{-\mu_{max} \left\{t+t_i \left\{e^{-\frac{t}{t_i}}\right\}\right\}\right\}}}$$

The models describe a log growth phase.

Model parameters $c_{X,0}$, $c_{X,max}$, μ_{max} , t_i were summarized in Table 6 (25 °C).

Tabela 7 . Kinetic parameters (25°C).

Parameters	Model 1	Model 2
$c_{X,0}$ [g/dm ³]	1,95	1,86
$c_{X,max}$ [g/dm ³]	0,063	0,00089
μ_{max} [h ⁻¹]	0,346	0,63
t_i [h]		9,49
r^2	0,9885	0,9960

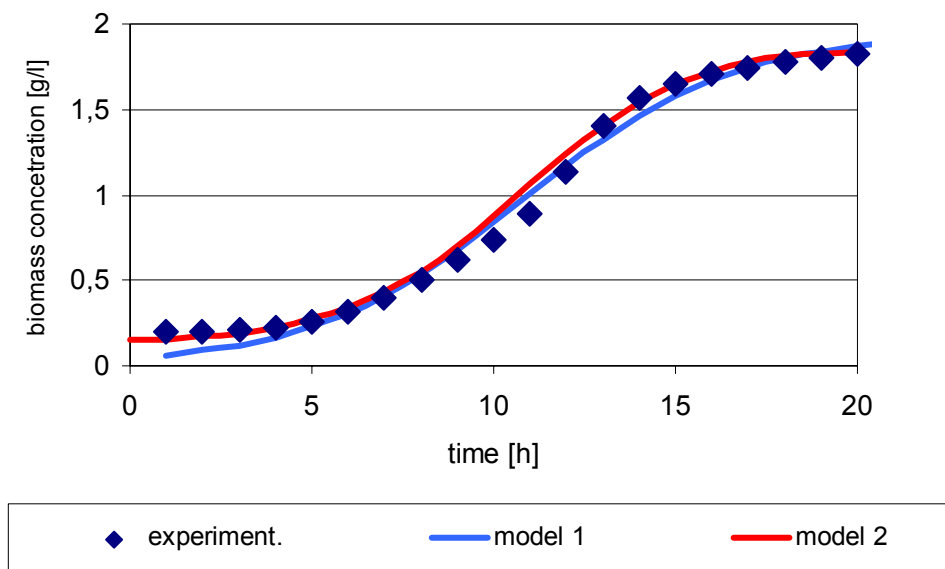


Figure 2. Biomass growth in time.

The second model better matches the experimental curve.

Temperature relationship of μ_{\max} was determined with the Arrhenius curve. From the function $\mu_{\max} = f(1/T)$ activation energy can be found.

Summary:

Based on the experimental results, the quantitative mathematical model of the biochemical reaction kinetics in a pipe reactor was formulated. This model is based on a mass balance and it comprises a set of differential equations (four); the equations have taken advantage of the relationships between microorganism growth and temperature, pH, substrate concentration, product concentration, biomass concentration [$\mu = f(T, \text{pH}, c_S, c_P, c_X)$].

The pipe reactor process design and modelling can be based on the microorganism growth vs. biomass concentration relationship [$\mu = f(c_X)$], in isothermal conditions.

LITERATURE

- Birjukow W.W., Kanterie W.M. (1986) *Оптимизация периодических процессов микробиологических синте*, Moskwa, Nauka.
- Schügerl K.S Bellgardt K-H. (2000) *Bioreaction Engineering* Springer-Verlag Berlin Heidelberg
- Doran P.M. (1995) *Bioprocess Engineering Principles* Academic Press London
- Blanch H.W, Clark D.S. *Biochemical Engineering* Marcel Dekker New York (1996)
- Reuss M., Bajpai R.K (1991) *Stirred tank model* In Schügerl K. (ed) "Biotechnology" 2nd edition vol. 4. VCH Weinheim
- Kryłów M., Tal-Figiel (2000) *Badania doświadczalne kinetyki beztlenowej biodegradacji ścieków* Zeszyty Naukowych Politechniki Warszawskiej, Seria Inżynieria Chemiczna i Procesowa

