The Right Chemistry

OLI Tips #64

How to enter temperature dependent bio-reaction data

Overview

Biological reactions such as growth and decay can be affected by temperature. Most reaction rates will follow Arrhenius reaction kinetics and this functionality currently exists in the OLI ESP program. Occasionally the reaction rate will follow non-Arrhenius kinetics. OLI has now implemented a method to enter actual reaction rate data which is then fit to a spline. We will be using phenol (C_6H_5OH) as our example substrate. The addition of non-Arrhenius temperature dependent data can only be entered via the Process Build step.

Assumptions

This procedure will only work in OLI ESP version 7.0.31 and higher. We also assume that you can start and operate OLI ESP and are familiar with OLI Bioreaction.

Equations

The two bioreactions that can use the new temperature dependence are the maximum specific growth rate and the decay rate. To explain this we first need to review how OLI models bioreactions.

Substrate

Each substrate that can be used is either a specific molecule (such as phenol: C_6H_5OH) or a lumped molecule with the general formula of $C_aH_bO_cN_dCl_eS_fP_g$. Estimation methods based on theoretical oxygen demand are described elsewhere. The reaction pathway is automatically defined based on the stoichiometry.
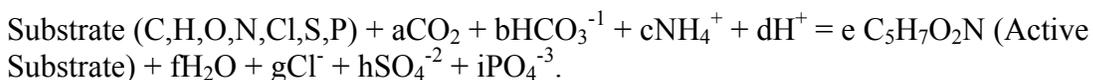
Biomass

The biomass (bugs) are assumed to have the following stoichiometry: $C_5H_7O_2N$. Phosphorous is assumed to be 0.2N. Other constituents may be present but they are not rigorously modeled.

Heterotrophic Synthesis

Synthesis is the most important reaction in terms of temperature dependence. In general the more heat that is added the faster the synthesis takes place until too much heat is added after which the biomass begins to die.

The general synthesis reaction is:

Substrate (C,H,O,N,Cl,S,P) + aCO_2 + $bHCO_3^{-1}$ + cNH_4^+ + dH^+ = e $C_5H_7O_2N$ (Active Substrate) + fH_2O + gCl^- + hSO_4^{-2} + iPO_4^{-3}.

For our example substrate of phenol, this equation is:

$C_6H_5OH_{AQ}$ + 1.4 HCO_3^{-1} + 1.4 $NH4^{+1}$ = 1.4 BUGHACTIVSUS + 1.6 H_2O + 0.4 CO_{2AQ}

Heterotrophic Decay – Aerobic, Anoxic

Temperature also affects the decay of the biomass

Aerobic: BUGHACTIVSUS + 4 O_{2AQ} = 0.2 BUGHINERTSUS + 1.6H_2O + 4CO_{2AQ} + 0.8NH_{3AQ}

Anoxic-NO3: BUGHACTIVSUS + 3.2H^+ + 3.2NO_3^{-1} = 0.2BUGHINERTSUS + 3.2H_2O + 4CO_{2AQ} + 1.6N_{2AQ} + 0.8NH_{3AQ}
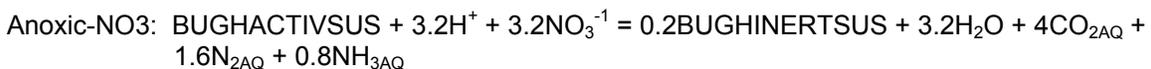
Heterotrophic Synthesis reaction rate

The rate of heterotrophic growth is a function of the specific growth rate, substrate concentration and the presence (or lack thereof) of oxygen, nitrates and carbonates.

The rather complicated formula is:

$$r_{HG} = \mu_H \left[\frac{S}{K_S + S + \frac{S^2}{K_I}} \right] (A_1 + A_2 + A_3)(XA_H)$$

Equation 1

The definition of the constants are:

r_{HG}	Rate of heterotrophic growth, g cell/m³hr
μ_H	Maximum specific growth rate constant, 1/hr
S	Substrate concentration, g substrate/m³
K_s	Half-saturation constant, g substrate/m³
K_I	Self inhibition constant, g substrate/m³
XA_H	Active, heterotrophic microorganism concentration, g cells/m³.

*When there is a lot of oxygen present, this ratio approaches 1: **Aerobic Factor***

$$A_1 = \frac{DO}{K_{O,H} + DO}$$

Equation 2

*When the concentration of oxygen is low the first part approaches 1. If there is a large amount of nitrate present, the second term dominates: **Anoxic Factor***

$$A_2 = \left(\frac{K_{O,H}}{K_{O,H} + DO} \right)\left(\frac{S_{NO3}}{K_{NO3} + S_{NO3}} \right) n_g$$

Equation 3

*When there is insufficient oxygen or nitrate, the first and second term approach 1. If sufficient carbonates are present: **Anaerobic Factor***

$$A_3 = \left(\frac{K_{O,H}}{K_{O,H} + DO} \right)\left(\frac{K_{NO3}}{K_{NO3} + S_{NO3}} \right)\left(\frac{S_{CO3}}{K_{CO3} + S_{CO3}} \right) n_{ferm}$$

Equation 4

Where the constants are:

DO	Dissolved oxygen concentration, g O_2/m³
$K_{O,H}$	Heterotrophic half-saturation constant for oxygen, g O_2/m³.
S_{NO3}	dissolved nitrate concentration for nitrogen, g N/m³
K_{NO3}	Half-saturation constant, g N/m³
S_{CO3}	dissolved carbonate concentration for carbonates g C/m³

K_{CO3}	Half-saturation constant, g C/m^3
n_g	anoxic growth factor.
N_{ferm}	anaerobic growth factor

Heterotrophic Substrate Utilization Rate

The growth of the microorganisms is the determined parameter in the utilization of the substrate. The yield of the reaction also affects the rate of substrate consumption.

$$r_s = r_{HG} \frac{(MW_s)}{Y_g * COD_s}$$

Equation 5

Where
r_s		is the rate of substrate utilization (g substrate/hr-m^3)
MW_s		is the substrate molecular weight (g substrate/mole substrate)
Y_g		True heterotrophic growth yield

Heterotrophic decay reaction rate

$$r_{HD} = b_H (A_1 + A_2) XA_H$$

Where r_{HD} = rate of heterotrophic decay, g cells/hr-m^3, b_H = heterotrophic decay rate constant, 1/hr. A_1, A_2, and XA_H are described above.

Temperature Affects on Maximum Specific Growth Rate – Arrhenius

The following formula governs the Arrhenius form of the maximum specific growth rate:

$$\mu_H = A_\mu e^{\left(\frac{-u_\mu}{RT}\right)}$$

Equation 6

Where
μ	=	maximum growth rate constant (heterotrophic or autotrophic)
u_μ	=	Arrhenius temperature characteristic for growth (cal/mole-K)
T	=	Temperature in K
R	=	Gas constant, 1.9872 cal/mole-K

$$A_\mu \quad = \quad \text{Arrhenius constant for growth}$$

$$A_\mu = \mu_{REF} e^{\left(\frac{-u_\mu}{RT_{REF}}\right)}$$

Equation 7

μ_{REF} = reference growth rate constants, 1/hr at T_{REF}
T_{REF} = reference temperature.

All these values are available via the chemistry model generator or via the Process Build Block entry.

Temperature Affects on the decay Rate – Arrhenius

The following formula governs the Arrhenius form of the decay rate:

$$\mu_b = A_b e^{\left(\frac{-u_b}{RT}\right)}$$

Equation 8

Where
b = decay rate constant (heterotrophic or autotrophic)
u_b = Arrhenius temperature characteristic for decay (cal/mole-K)
T = Temperature in K
R = Gas constant, 1.9872 cal/mole-K
A_b = Arrhenius constant for decay

$$A_b = b_{REF} e^{\left(\frac{-u_b}{RT_{REF}}\right)}$$

Equation 9

μ_{REF} = reference growth rate constants, 1/hr at T_{REF}
T_{REF} = reference temperature.

All these values are available via the chemistry model generator or via the Process Build Block entry.

What do you do if your reactions do not follow simple Arrhenius reaction kinetics? You have the ability to enter your data. This will be explained in the following example:

Example

In this example we have a biological system that is not responding with respect to temperature according to Arrhenius kinetics. Therefore will have to enter some data that has been measured.

We have the following reaction data for maximum specific growth and decay.

Table 1

Temperature, C	Maximum Specific Growth rate, 1/hr	Decay rate, 1/hr
20	1.0	0.002
25	1.25	0.003
30	1.50	0.006
40	1.75	0.007
45	1.60	0.006

Start ESP

Create the Chemistry Model

Let's begin by starting ESP and entering bio-reaction data for phenol (C5H6OH).

1. Start ESP
2. Select ESP/Process
3. Create a New Process: BIOTEMP1
4. Create a New Chemistry Model: BIOTEMP1
    a. Select the **Aqueous Framework**
    b. Do not select any private databanks
    c. Enter the substrate using the AltEntry/BioEntry action.
    d. Select only the first set of Biomass entries for Active and Inert biomass
    e. Use the default biomass stoichiometry
    f. Create a new substrate and enter the ESP name C6H5OH
    g. Accept the default energy reactions.
    h. Select denitrofication only
    i. Do not select Autotrophic reactions.
    j. Generate the model completely as you would a normal bio-model. Select only heterotrophic reactions.

Process Build

1. Select Process/Build
2. Select Biotreatment blocks
3. Select "Act Sl Bioreactor"
4. Enter a name for the bioreactor
5. Select Parameters

6. Select BioReaction constants
7. Select Heterotrophic
8. Select the substrate C6H5OH
9. This will display a slightly altered form:

```
C6H5OH Subst
Constants
RATE   Arrhenius Fun
DECAY Arrhenius Fun
RATE   Exp Data
DECAY Exp Data
Inhibition Function
Exit
```

Figure 1

10. Select Rate EXP Data

```
Units   Help

  Activated Sludge                              BIOTEMP1 Process
  BioReactor:                                   Process Build
                                                Reaction Constants
  Heterotrophic Reaction
  Substrate: C6H5OH
        Temp          Growth Rate      Temp          Growth Rate
        C             1/hr             C             1/hr




Enter at least two data points.
<Esc> Quit   <F1> Help   <F3> End (Save)   <F10> Actions   <Enter> Continue
```

Figure 2

Enter the data from Table 1 for maximum specific growth rate;

```
Temp          Growth Rate    Temp          Growth Rate
C             1/hr           C             1/hr
20            1
25            1.25
30            1.5
40            1.75
45            1.6
```

Figure 3

> 11. Press the <F3> or <End> key to continue.
> 12. Repeat the data entry procedure for the DECAY Exp Data (see Figure 1)

```
Temp          Decay Rate     Temp          Decay Rate
C             1/hr           C             1/hr
20            .002
25            .003
30            .006
40            .007
45            .006
```

Figure 4

> 13. Press the <F3> or <End> key to continue
> 14. Create a feed stream with the following composition
>   a. Temperature   20   C
>   b. Pressure   1   atmosphere
>   c. Total   5.55E+06   mole/hr
>   d. H2O   55.508
>   e. C6H5OH   0.003
>   f. NH3   0.003
> 15. Create a second feed stream with following composition:
>   a. Temperature   20   C
>   b. Pressure   1   atmosphere
>   c. Total   100000   mole/hr
>   d. H2O   0.023
>   e. O2   0.21
>   f. N2   0.79
> 16. Set the following block parameters
>   a. Computation Option Isothermal = 30 C

b. Reactor Volume = 1E+06 L
c. Oxygen Use = Default
17. Leave all other parameters unchanged.
18. Add a vapor and effluent streams
19. Remove any clarifier or recycle stream if added.
20. Save and leave the block

Process Analysis

1. Calculate the process
2. Review the block results
3. Select the bioreactor
   a. Select BioReaction Constants
   b. The reactor is at 30 C
      i. Maximum Specific Growth rate should be 1.5
      ii. Decay rate should be 0.006
4. Change the block parameters in process build such that the isothermal option is now 35 C
5. Rerun the calculation
6. The 35 C data point is missing in Table 1 (done on purpose).
   a. Maximum specific growth rate should be 1.70031 1/hr – this is interpolated between the 30 and 40 C data points
   b. The decay rate is 0.00737 which is also interpolated.
7. Rerun the bioreactor at 15 C
   a. Maximum Specific Growth Rate = 0.75 1/hr
   b. Decay Rate = 0.001 1/hr

The last run at 15 C is outside the data range. The program extrapolated the value by using the lowest two temperatures and fit a straight line to them. The same extrapolation is applied when the operating temperature is above the data set.