

A MODIFIED THERMO-MODEL FOR VOC TREATING BIOFILTER

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Abstract : A thermodynamic model which incorporated Gibbs energy dissipation values for growth of various microorganisms on various organic substrates was developed. The thermodynamic model is specific for ethylbenzene but may be adapted to other compounds of concern by changing the physical properties associated with the selected compound. An equation to estimate the heat release from the biodegradation process was developed and was an integral part of this model. This thermodynamic model improves upon the currently available biofilter models making it possible to correlate water distribution, microbial activity, and consequent removal efficiency with spatial location in the biofilter.

Key Words : Ethylbenzene, biofilter, thermodynamic model, VOCs, biodegradation

INTRODUCTION

Heat generation from the biodegradation of substrate is one of the main reasons for the temperature variation of a biofilter, which, in turn, is the main cause of the fluctuation of water content over the depth of the biofilter.¹⁾ Therefore, an understanding of the thermodynamics of microbial degradation, related with the prediction of biomass yield in the biofilter, is very important and valuable.

The conventional thermodynamic model defines well the production of biomass during the decomposition of an organic waste. The following is a summary of the thermodynamics of biological waste treatment to estimate microbial

yields from free energy calculations for heterotrophic metabolism.²⁾

The following terms are defined herein:

ΔF_r = Free energy released per gram of pollutant COD converted to end products

ΔF_s = Free energy required to synthesize one gram of biocell COD

ΔF_p = Free energy change of substrate conversion to intermediate.

ΔF_c = Free energy in converting intermediate to one gram of biocell COD

k_1 = efficiency of transferring energy from ADP (adenosine diphosphate) to form ATP (adenosine triphosphate)

f_s = Fraction of substrate COD that goes to biosynthesis reactions.

= [(COD of cells formed)/(COD of waste converted)]

f_c = $1 - f_s$ = Fraction of substrate COD that

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goes to energy reactions.

$A = f_e/f_s$ = the mass of COD converted to energy (i.e. to end products) per unit mass of biological solids COD formed.

Y_o = gram of biomass synthesized per gram of ethylbenzene consumed.

With these definitions, an energy balance for production of new biocells can be estimated. For each gram of substrate COD utilized, the energy released by the reaction can be expressed as $-f_e C \Delta F_r$ and that captured for synthesis as $-k_1 C f_e \Delta F_r$. The energy captured for synthesis and that used for synthesis are the same, therefore:

$$-k_1 C f_e \Delta F_r = f_s C \Delta F_s \quad (1)$$

By the definition of $A (= f_e/f_s)$, the equation (1) can then be written

$$-k_1 A \Delta F_r = \Delta F_s \quad (2)$$

From the definition, ΔF_r is the free energy of the reaction through which the substrate is converted to end-products. This is equivalent to the difference between the free energy of formation of the substrate and the sum of the free energies of formation of the end products. Free energies of formation are readily available in handbooks. A list of the free energy of formation of some selected compounds is given in Table 1.

The energy transfer steps in cell synthesis from the carbon source can be expressed as follows:

$$\Delta F_s = \Delta F_c + k_1 \Delta F_p \quad (3)$$

Equation (3) can be substituted into equation (2) to yield the following expression:

$$-k_1 A \Delta F_r = \Delta F_c + k_1 \Delta F_p \quad (4)$$

Using the equation 4, the weight fraction A can be determined, since for a given organic material ΔF_r , ΔF_c , ΔF_p can be found in the

Table 1. Free energies of formation for various compounds

Compound	ΔF_r° (kcal/mol)
Ethylbenzene ¹⁰⁾	31.208
Acetaldehyde ¹⁰⁾	-31.9
Pyruvic acid ²⁾	-114.1
Propionic acid ²⁾	-92.1
Acetate ²⁾	-88.99
Propionate ²⁾	-87.47
Acetone ²⁾	-33.96
Pyruvate ²⁾	-113.32
Succinate ²⁾	-164.97
Ethanol ²⁾	-43.39
Ethane ²⁾	-7.86
Glucose ²⁾	-217.02
Lactate ²⁾	-123.64
Glutamate ²⁾	-166.11
Butyrate ²⁾	-84.6
Palmitate ²⁾	-74.0
Alanine ²⁾	-88.75
Formate ²⁾	-80.0
CO ₂ ¹⁰⁾	-94.26
H ₂ O ¹⁰⁾	-56.69
H ²⁾	-9.67

literature or determined easily.

Since

$$A = f_e/f_s = (1 - f_s)/f_s \quad (5)$$

then

$$f_s = 1/(1 + A) \text{ gm cell COD/ gm substrate COD utilized} \quad (6)$$

As the oxygen equivalent of volatile cell solids is 1.42 mg O₂/mg biomass,²⁾ the above equation can be rewritten;

$$Y_o = f_s/1.42 \text{ gm biomass/gm substrate COD utilized} \quad (7)$$

RESULTS AND DISCUSSION

Modified Thermodynamic Model for Ethylbenzene Biodegradation

Bauchop and Elsdon³⁾ proposed the concept of expressing the yield of biomass in terms of consumed ATP (Y_{ATP} in grams of biomass dry weight/mol ATP). Their conclusion was that Y_{ATP} was 10.5g/mol and constant. However, the results from more recent papers suggest Y_{ATP} may not be constant.^{4,5)} Heijnen and van Dijken⁴⁾ reported that biomass yield (Y_{ATP}) can vary

Table 2. Average Gibbs energy dissipation for growth of various microorganisms on different substrates^{4,5)}

Substrate	Gibbs Energy Dissipation (=1/ Y_{ATP}) kJ/C-mol biomass
Oxalate ²⁻	1224
Formate ⁻	1107
Glyoxylate ⁻	709
Tartrate ²⁻	584
Malonate ²⁻	757
Malate ²⁻	380
Citrate ³⁻	381
Pyruvate ⁻	316
Succinate ²⁻	422
Gluconate ⁻	311
Formaldehyde	587
Acetate ⁻	529
Lactate ⁻	296
Dihydroxyacetone	257
Glucose	284
Glycerol	345
Mannitol	338
Propionate ⁻	556
Ethleneglycol	617
Acetoin	457
Butanediol	469
Aceton	813
Methanol	729
Ethanol	712
Propanol	725
n-Alkanes	662
Butane	1061
Methane	1011

widely, with the range of 2 to 30 g/mol ATP. They said biomass yield (Y_{ATP}) depends strongly on the microorganism and its growth substrates. Heijnen *et al.*⁵⁾ reported the average Gibbs energy dissipation values for growth of various microorganisms on various organic substrates (Table 2). Gibbs energy dissipation can be expressed as $1/Y_{ATP}$ and the energy available from a mole of ATP is 12.5 kcal.

Prediction of microbial yield and heat generation from substrate degradation is demonstrated by the following example in which ethylbenzene is utilized as the substrate. Figure 1 shows the proposed pathway for the degradation of ethylbenzene based upon the literature.⁶⁻⁸⁾ According to the proposed degradation pathway (Figure 1), the biodegradation of ethylbenzene may proceed through one of two pathway, meta or ortho. Through the meta pathway, propionate, acetate, and pyruvate are generated as intermediates. Through the ortho pathway, succinate, acetate, and ethane are generated as intermediates.

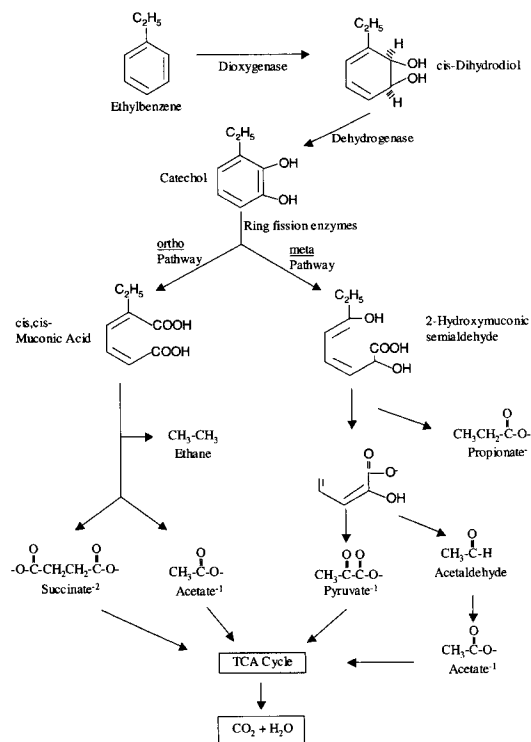
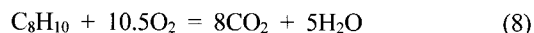
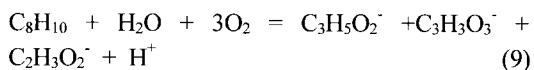


Figure 1. Proposed pathway for the degradation of ethylbenzene.⁶⁻⁸⁾

The molecular weight of ethylbenzene (C₈H₁₀) is 106.17 and one gram of ethylbenzene is equivalent to 3.16 gram of chemical oxygen demand (COD). Theoretical bio-oxidation equation of ethylbenzene is:



From equation (8), free energy released per mole of ethylbenzene to end products (ΔF_r) is calculated as -1069 kcal/mol and is equivalent to -3.18 kcal/g COD. Through meta and ortho biodegradation pathways, one mole of ethylbenzene produces three moles of propionate, acetate, and pyruvate or three moles of succinate, acetate, and ethane. If we consider the meta pathway first, the intermediates are propionate (C₃H₅O₂⁻), acetate (C₂H₃O₂⁻), and pyruvate (C₃H₃O₃⁻) and the following equation can be used;



The free energy released from ethylbenzene to intermediates (ΔF_p) of propionate, acetate, and pyruvate is -274 kcal/mol and is equivalent to -0.82 kcal/g COD. The molecular weight of one mole of carbon (C-mole) of biomass is estimated to be 24.6 grams. The energy required for the synthesis of 1 gram of biomass can be determined from the value in Table 2. It is estimated that the oxygen equivalent of biocell is 1.42 mg O₂/mg biomass, the free energy required to convert each intermediate to one gram of cell COD (ΔF_c) can then be determined. The calculated ΔF_c of some selected intermediates appears in Table 3. In the case of ethane, the average values of butane and methane were used from Table 2.

One mole of ethylbenzene produces three mole of propionate, acetate, and pyruvate, the free energy required for the synthesis of 3 grams of produced biomass COD ($\Delta F_c'$) is equal to the sum of ΔF_c (pyruvate), ΔF_c (propionate), ΔF_c (acetate) and is calculated as 9.58 kcal/gram cell COD. Equation (3) can be ad-

Table 3. ΔF_c values from some of the selected intermediates to one gram of cell COD

Intermediates	Average Gibbs Energy Dissipation Values per gram of produced biomass (kcal/g biomass)	ΔF_c (kcal/gm cell COD)
Pyruvate	3.07	2.16
Propionate	5.40	3.80
Acetate	5.13	3.62
Succinate	4.10	2.88
Ethane	10.06	7.08
Acetone	7.89	5.56

justed for the case of ethylbenzene as follows;

$$\Delta F_s = \Delta F_c'/3 + k_1 \Delta F_p'/3 \quad (10)$$

Equation (1) can also be adjusted as follows in the case of ethylbenzene;

$$-k_1 C_f \Delta F_r'/3 = f_s C \Delta F_s \quad (11)$$

Combining the equation (10) and (11),

$$-k_1 C_f \Delta F_r'/3 = f_s C (\Delta F_c'/3 + k_1 \Delta F_p'/3) \quad (12)$$

As $\Delta F_c' = [\Delta F_c(\text{pyruvate}) + \Delta F_c(\text{propionate}) + \Delta F_c(\text{acetate})]$, equation (12) can be;

$$-k_1 C_f \Delta F_r'/3 = f_s C \{k_1 \Delta F_p'/3 + [\Delta F_c(\text{pyruvate}) + \Delta F_c(\text{propionate}) + \Delta F_c(\text{acetate})]/3\} \quad (13)$$

Equation (2) can be converted to determine the mass of COD converted to energy per unit mass of biological COD formed, A;

$$A = -\Delta F_s / (k_1 * \Delta F_r) \quad (14)$$

In the case of the meta pathway, the mass ratio A was equal to 4.76 and f_s is 0.17 gram cell COD/gram ethylbenzene COD utilized. From the equation (7), Y_o is determined to be 0.39 gram biomass per gram of ethylbenzene utilized. Through the same procedure, the mass ratio and the growth of cell mass through the

ortho pathway can be estimated. The appendix shows the details for this procedure. Thermodynamic values for selected intermediates appear in Table 3. If ethylbenzene is assumed to be degraded equally through the meta and ortho pathways, average values from Table 4 can be used to estimate the energy balance over a biofilter.

According to the second law of thermodynamics, there is always some waste heat; that is, it is impossible to transfer energy with 100 percent efficiency. Efficiency of ATP energy transfer (k_i) was assumed to be 0.6 based upon the literature.²⁾ Therefore, an estimated forty percent of total energy converted is emitted as heat. As mentioned previously, the net portion of the substrate converted to biocell is f_s and the remainder of the substrate is f_e which used for the energy to sustain biosynthesis. If the total amount of consumed substrate is C , then the heat released from the portion of substrate conversion for the energy is $(1-k_i)Cf_e \Delta F_r$.

The degradation process from substrate to intermediates is exothermic (Figure 2). Heat is released from the portion of substrate conversion to biosynthesis and that amount of heat may be predicted by the expression, $(1-k_i)f_s C \Delta F_p$. Therefore, the total amount of heat released from the biodegradation process (H) can be expressed by the following equation;

$$H = (1 - k_i) C f_e \Delta F_r + (1 - k_i) f_s C \Delta F_p \tag{15}$$

Figure 2 also illustrates the amount of heat generated from the biodegradation process. With

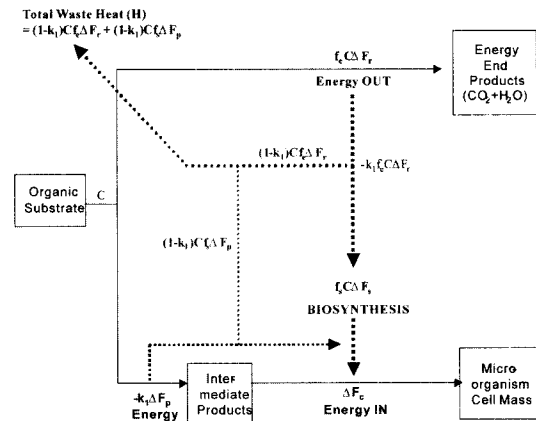


Figure 2. Schematic of energy transferred during the biodegradation (Heterotrophic Growth).

equation (15), heat released from the biodegradation of ethylbenzene can be estimated. Through the meta pathway, heat released is calculated as 372 kcal/mol and through ortho pathway, it is 384 kcal/mol. Therefore, the average heat release from the biodegradation of ethylbenzene was estimated to be 378 kcal/mol.

Significance of the Thermodynamic Model

When the substrate is degraded, some portions of the removed substrate are used for the biosynthesis of microorganisms in the biofilter and the remaining portions of the degraded substrate are mineralized to end products (such as carbon dioxide and water). Through the mineralization of substrate, energy is created and transferred to support the biosynthesis of microorganisms. According to the second law of thermodynamics, when energy is transferred, a certain amount of energy is wasted. This wasted energy is the released as heat. This heat from the biodegra-

Table 4. Thermodynamic values for the meta and ortho pathway of ethylbenzene biodegradation

Selected thermodynamic values	Meta Pathway	Ortho Pathway	Average	Morales <i>et.al.</i> ⁹⁾
f_s (Fraction of substrate COD that goes to biosynthesis reactions)	0.174	0.126	0.150	0.135
f_e (Fraction of substrate COD that goes to energy reactions)	0.826	0.874	0.850	0.865
$A (=f_e/f_s)$	4.761	6.921	5.841	6.407
Y_o (gram biomass synthesized/gram ethylbenzene consumed)	0.387	0.281	0.334	---

dation of the substrate reduces the water content of the media through evaporation. The water content of the media at the upper stage increases through subsequent condensation caused by the temperature difference. This water content change in the media in turn affects the microorganism growth rate. As the water content increases, the microorganism growth rate increases. As the water content decreases, the microorganism growth rate also decreases. Finally, the increased microorganism growth rate again increases the removal efficiency in the next stage of the biofilter and decreased microorganism growth rate decreases the removal efficiency in the previous stage. Figure 3 illustrates the organic removal mechanism in a biofilter.

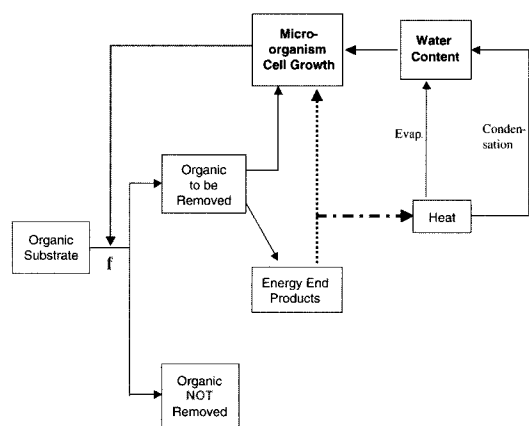


Figure 3. Organic Removal Mechanism in a Biofilter.

The qualitative results from the thermodynamic model agree with observations of the ethylbenzene biofilter.¹⁾ At the experiment performed by Son and Striebig,¹⁾ more microbial activity was observed at the inlet where more ethylbenzene was readily available during the initial experimental period. Vigorous ethylbenzene degradation at the inlet generated heat in the lower stage of the biofilter. This heat increased the temperature of that stage of the biofilter media, resulting in evaporation of water from that stage. Through evaporation of water, the water content of that stage gradually decreases. Finally, the decreased water content caused the degradation activity of that stage to

be reduced. On the other hand, the evaporated water from the previous stage condensed at the upper stage. The condensed water at the upper stage increased the water content of that stage gradually. More microbial growth followed as conditions became too dry in lower stages to allow adequate microbial growth and more ethylbenzene degradation occurred at the higher stage. Through the heat release and evaporation procedure, the water content of that stage also decreased, resulting in a reduction in the degradation rate of that stage. Through the repetition of this cyclic mechanism and its movement through all the stages of the biofilter, the shift of the most dominant ethylbenzene degradation stage occurs from inlet to outlet over the entire depth of the biofilter. The procedure is summarized in Figure 4.

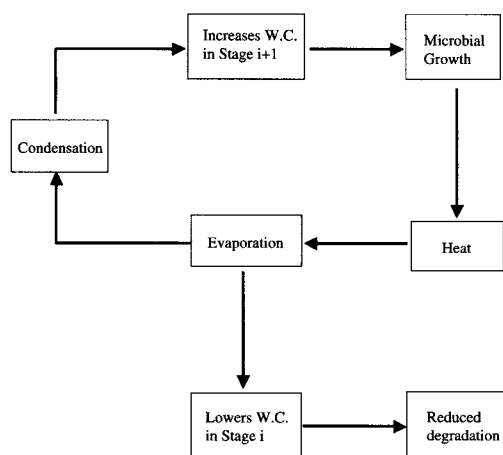


Figure 4. Growth, Heat, and Evaporation Cycle in a Biofilter.

Estimation of the heat generation from the microbial degradation is essential to improve the currently available biofilter models. From the early 1980s, numerous biofilter models have been developed which employ rate limiting factors for different types of biofilter models. It becomes necessary to employ the heat generation factors from microbial degradation, which significantly impacts the water content fluctuations, and the estimation of the growth of microorganisms in the biofilter. Therefore, this

thermodynamic model significantly improves the available biofilter models compared to the conventional thermodynamic model.

CONCLUSION

This author improved the conventional thermodynamic model with the average Gibbs energy dissipation values for growth of various microorganisms on various organic substrates (Table 2). Gibbs energy dissipation can be expressed as $1/Y_{ATP}$ and the energy available from one mole of ATP is 12.5 kcal. The improved thermodynamic model is very specific for each selected pollutant compound, rather than a general model for all types of pollutants. Morales *et.al.*⁹⁾ conducted a carbon balance in a toluene degrading biofilter. They measured the total amount emitted CO_2 from the biofilter, and dissolved carbonate and biodegradable material (intermediates and polymers) in the biofilter. Including the further mineralization of intermediates, fate of the transformed toluene carbon to biomass in the biofilter was estimated as 13.5%. This value corresponds closely with the values predicted by the improved thermodynamic model (Table 4).

This thermodynamic model may be used to predict the heat generation from the microbial degradation of pollutants. Estimation of the heat generation from the microbial degradation is essential to improve the currently available biofilter model. Heat generation from microbial degradation significantly impacts the water content fluctuations, and Y values for the estimation of the growth of microorganism in the biofilter. The water content and growth have been directly correlated with the degradation rate and consequently removal efficiency. Therefore, this thermodynamic model makes a significant contribution to improve the accuracy and reliability of currently available biofilter models.

NOMENCLATURE

ΔF_r = Free energy released per gram of

pollutant COD converted to end products

ΔF_s = Free energy required to synthesize one gram of biocell COD

ΔF_p = Free energy change of substrate conversion to intermediate.

ΔF_c = Free energy in converting intermediate to one gram of biocell COD

k_1 = efficiency of transferring energy from ADP (adenosine diphosphate) to form ATP (adenosine triphosphate)

f_s = Fraction of substrate COD that goes to biosynthesis reactions.
= [(COD of cells formed)/(COD of waste converted)]

f_e = $1 - f_s$ = Fraction of substrate COD that goes to energy reactions.

A = f_e/f_s = the mass of COD converted to energy (i.e. to end products) per unit mass of biological solids COD formed.

Y_o = gram of biomass synthesized per gram of ethylbenzene consumed.

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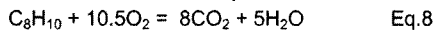
APPENDIX

Thermodynamic Calculations for Ethylbenzene.

CONVERSION FACTOR

1 calorie (cal) = 4.184 J

Theoretical Oxidation Equation



mole O₂/mole Ethylbenzene = 10.5

Molecular Weight of Ethylbenzene (g) = 106.17

Molecular Weight of O₂ (g) = 32

ethylbenzene g = 3.16 g COD (=10.5*32/106.17)

Typical Composition of Microorganism CH_{1.8}O_{0.5}N_{0.2}

Molecular Weight = 24.6

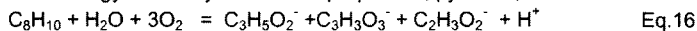
From Equation 8, (values of each compound from Table 1)

Free Energy of Reaction = -1069 kcal/mole ethylbenzene
(=8*(-94.26)+5*(-56.69)-31.208-0)

Free Energy of Reaction = -3.181 kcal/g COD
(= -1069/(106.17*3.16)) [(kcal/mol)/(g/mol)*(g COD/g)]

A. Meta Pathway

Free Energy from ethylbenzene to propionate, pyruvate, and acetate



From Equation 16, (values of each compound from Table 1)

Free Energy of Reaction = -274 kcal/mole ethylbenzene
[=(-88.99)+(-87.47)+(-113.32)+(-9.67)-31.208-(-56.69)-0]

Free Energy of Reaction = -0.815 kcal/g COD
(= -274/(106.17*3.16))

The oxygen equivalent of volatile cell solids is 1.42 mg O₂/mg VSS.

k₁ = efficiency of ATP energy transfer = 0.6

Average Gibbs energy dissipation values per C-mole produced biomass

	Propionate	
(kJ / C-mol biomass)	556	(From table 2)
(kcal/C-mol biomass)	133	(= 556/4.184) [(kJ/C-mol)/(4.184kJ/kcal)]
(kcal/gm biomass)	5.40	(=133/24.6) [(kcal/C-mol)/(g/C-mol biomass)]
	Pyruvate	
(kJ / C-mol biomass)	316	(From table 2)
(kcal/C-mol biomass)	76	(= 316/4.184) [(kJ/C-mol)/(4.184kJ/kcal)]
(kcal/gm biomass)	3.07	(=76/24.6) [(kcal/C-mol)/(g/C-mol biomass)]
	Acetate	
(kJ / C-mol biomass)	529	(From table 2)
(kcal/C-mol biomass)	126	(= 529/4.184) [(kJ/C-mol)/(4.184kJ/kcal)]
(kcal/gm biomass)	5.13	(=126/24.6) [(kcal/C-mol)/(g/C-mol biomass)]

F_c = energy equivalent per gram of cell COD.

F_c (propionate) = energy equivalent from propionate per gram of produced biomass COD.

F_c (propionate) = (5.40 kcal / gm biomass) / (1.42 gm COD/gm biomass)

F_c (propionate) = 3.800 kcal/gm cell COD

F_c (pyruvate) = energy equivalent from pyruvate per gram of produced biomass COD.

F_c (pyruvate) = (3.07 kcal / gm biomass) / (1.42 gm COD/gm biomass)

F_c (pyruvate) = 2.160 kcal/gm cell COD

F_c (acetate) = energy equivalent from acetate per gram of produced biomass COD.

F_c (acetate) = (5.13 kcal / gm biomass) / (1.42 gm COD/gm biomass)

F_c (acetate) = 3.616 kcal/gm cell COD

F_c' = energy equivalent from propionate, pyruvate, acetate per 3 grams of produced biomass COD.

F_c' = F_c (propionate) + F_c (pyruvate) + F_c (acetate)

F_c' = 9.575 kcal/gm cell COD

F_s = Substrate energy used for synthesis per gram of cell COD.

$F_s = F_c'/3 + k_1 \cdot F_p'/3$

When 1 mole ethylbenzene is degraded, 3 moles of propionate, pyruvate, acetate are generated.

Therefore, for 1 mole of biomass to be generated,

$(-k_1) \cdot f_e \cdot C \cdot Fr/3 = k_1 \cdot F_p'/3 + \{F_c$ (propionate) + F_c (pyruvate) + F_c (acetate) $\}/3$

$(-k_1) \cdot f_e \cdot C \cdot Fr = k_1 \cdot F_p' + F_c$

$F_s' = 3 \cdot F_s$ 9.086 kcal/g COD (From previous calculation)

$F_r' = 3 \cdot F_r$ -3.181 kcal/g COD (From previous calculation)

$A = -F_s / (k_1 \cdot Fr) = 4.761$ [= $(-9.086/3)/(0.6 \cdot (-3.181/3))$]

$A = f_e / f_s = (1 - f_s) / f_s$

$f_s = 1 / (1 + A) =$

$f_s = 0.174$ gm cell COD / gm substrate COD utilized

$Y_o' = f_s / 1.42 = 0.122$ gm cell VSS / gm substrate COD utilized

$Y_o = 0.387$ gm cell VSS / gm ethylbenzene utilized

$f_e = 1 - f_s$

$$f_e = 0.826 \text{ gm COD / gm substrate COD utilized}$$

(UNIT : gm substrate COD used for energy to sustain synthesis / gm substrate COD utilized)

Amount of Heat Generated from the Ethylbenzene Biodegradation (H)

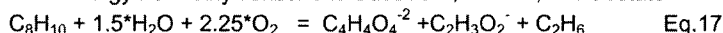
$$H = (1 - k_1) * f_e * C * Fr' + (1 - k_1) * f_s * C * Fp'$$

$$H \text{ (meta pathway)} = -372.3 \text{ kcal / mole}$$

$$[=(1-0.6)*0.826*(-1069) + (1-0.6)*0.174*(-274)]$$

B. Ortho Pathway

Free Energy from ethylbenzene to Succinate, Ethane, and acetate



From Equation 17, (values from Table 1)

$$\text{Free Energy of Reaction} = -208 \text{ kcal/mole ethylbenzene}$$

$$[=(-164.97)+(-7.68)+(-88.99)-31.208-1.5*(-56.69)-0]$$

$$\text{Free Energy of Reaction} = -0.62 \text{ kcal/g COD}$$

$$[= -208/(106.17*3.16)] [(kcal/mol)/(g/mol)*(g COD/g)]$$

Average Gibbs energy dissipation values per C-mole produced biomass

	Succinate	
(kJ / C-mol biomass)	422	(From table 2)
(kcal/C-mol biomass)	101	(= 422/4.184) [(kJ/C-mol)/(4.184kJ/kcal)]
(kcal/gm biomass)	4.10	(=101/24.6) [(kcal/C-mol)/(g/C-mol biomass)]
	Acetate	
(kJ / C-mol biomass)	529	(From table 2)
(kcal/C-mol biomass)	126	(= 529/4.184) [(kJ/C-mol)/(4.184kJ/kcal)]
(kcal/gm biomass)	5.13	(=126/24.6) [(kcal/C-mol)/(g/C-mol biomass)]
	Ethane	
(kJ / C-mol biomass)	1036	(From table 2)
(kcal/C-mol biomass)	248	(= 1036/4.184) [(kJ/C-mol)/(4.184kJ/kcal)]
(kcal/gm biomass)	10.06	(=248/24.6) [(kcal/C-mol)/(g/C-mol biomass)]

F_c = energy equivalent per gram of cell COD.

F_c (Succinate) = energy equivalent from Succinate per gram of produced biomass COD.

$$F_c \text{ (Succinate)} = (4.10 \text{ kcal / gm biomass}) / (1.42 \text{ gm COD/gm biomass})$$

$$F_c \text{ (Succinate)} = 2.884 \text{ kcal/gm cell COD}$$

F_c (Ethane) = energy equivalent from Ethane per gram of produced biomass COD.

$$F_c \text{ (Ethane)} = (10.06 \text{ kcal / gm biomass}) / (1.42 \text{ gm COD/gm biomass})$$

$$F_c \text{ (Ethane)} = 7.081 \text{ kcal/gm cell COD}$$

F_c (acetate) = energy equivalent from acetate per gram of produced biomass COD.

$$F_c \text{ (acetate)} = (5.13 \text{ kcal / gm biomass}) / (1.42 \text{ gm COD/gm biomass})$$

$$F_c \text{ (acetate)} = 3.616 \text{ kcal/gm cell COD}$$

F_c' = energy equivalent from Succinate, Ethane, acetate per 3 grams of produced biomass COD.

F_c' = F_c (Succinate) + F_c (Ethane) + F_c (acetate)

F_c' = 13.581 kcal/gm cell COD

F_s = Substrate energy used for synthesis per gram of cell COD.

F_s = $F_c'/3 + k_1 * F_p'/3$

When 1 mole ethylbenzene is degraded, 3 moles of Succinate, Ethane, acetate are generated.

Therefore, for 1 mole of biomass to be generated,

$(-k_1) * f_e * C * Fr/3 = k_1 * F_p'/3 + \{F_c$ (Succinate) + F_c (Ethane) + F_c (acetate)} / 3

$(-k_1) * f_e * C * Fr = k_1 * F_p' + F_c$

$F_s' = 3 * F_s$ 13.209 kcal/g COD (From previous calculation)

$Fr' = 3 * Fr$ -3.181 kcal/g COD (From previous calculation)

$A = -F_s / (k_1 * Fr) =$ 6.921 $[-(-13.209/3)/(0.6 * (-3.181/3))]$

$A = f_e / f_s = (1 - f_s) / f_s$

$f_s = 1 / (1 + A) =$

$f_s =$ 0.126 gm cell COD / gm substrate COD utilized

$Y_o' = f_s / 1.42 =$ 0.089 gm cell VSS / gm substrate COD utilized

$Y_o =$ 0.281 gm cell VSS / gm ethylbenzene utilized

$f_e = 1 - f_s$

$f_e =$ 0.874 gm COD / gm substrate COD utilized

(UNIT : gm substrate COD used for energy to sustain synthesis / gm substrate COD utilized)

Amount of Heat Generated from the Ethylbenzene Biodegradation (H)

$H = (1 - k_1) * f_e * C * Fr' + (1 - k_1) * f_s * C * F_p'$

H (Ortho pathway) = -384.0 kcal / mole $[-(1 - 0.6) * 0.874 * (-1069) + (1 - 0.6) * 0.126 * (-208)]$