Analysis of High-Rate Composting of Organic Waste (2)

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有機廃棄物の高速Compostingの解折（才2報）

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In the previous report, high rate composting of cattle excrements has been analyzed stoichiometrically, and now that of activated sludge from a municipal sewage similarly so that the biochemical process is expressed again physicochemically and chemical engineering, As reported, composting defined to be a process of transformation of an unstable organic system to a stable one by biochemical oxidation catalyzed by enzyme of a microorganism, and the enthalpy change, the redox reaction rate, and amount of the necessary oxygen are calculated to express both the complex reaction stoichiometrically and the activity of the microorganism numerically, so that it is now possible to select the most active one.

1. Introduction

Although activated sludge is now dried, combusted, or reclaimed according to the Law of Waste Treading, several problems are brought about, i, e. consumption of enormous fossil fuels, a huge constraction cost and searching of a place for the plant, air pollution, and malodor pollution. Therefore, it is necessary to survey the activated sludge treatment from the national or gloval stand point of resource or energy economy.

It is discussed in this report that activated sludge is converted into soil improving agent, i, e. artificial humus by utilizing the enzymatic action of the aerobic microorganisms.

Two groups of microorganisms were used, i.e. an activated sludge from Nagoya Municipal Sewage (HORIDOME) mixed with natural soil and cultivated (ASA-1, A series) and ASA-1 (A series) mixed with that in Table 3 in the previous report [1] (ASA-2, B series), as shown in experimentals and results in the previous report.

2. Experimentals and Kesults

2.1 Cultivation of aerobic microorganisms of activated sludge in soil

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2.1.1 Cultivation in natural soil

As in the previous report, field soil was mixed with sugar to supply free energy for growth of the microorganisms, yeast extract to supply nutrients to build the body, and a micro amount of Bennett's medium Table 1 containng meat juice, and to the culture medium was added activated sludge from Nagoya Municipal Horidome Sewage, and cured at 20-30℃ and 50-60% moisture for 1 month.

Table1. Bennett's agar medium (pH 7.3).

Yeast extract	1.0g
Beef extract	1.0
NZ Amine, type A	2.0
Dextrose (Anhydrous)	10.0
Agar	20.0
Distilled water	10000ml

2.1.2 Cultivation and breeding in a liquid medium.

A lg portions of the cultivated soil were taken various places, mixed, 1 g portion was placed on a sugar-sodium nitrate -agar medium Table 2 and kept in an incubator at 40-50℃ for 7 days.

Table 2. Sugar-sodium nitrate-agar medium (pH 7.2).

Sugar	30.0g
Potassium dihydrogen phosphate	1.0
Sodium nitrate	2.0
Magnesium sulfate ($7H_2O$)	0.5
Potassium chloride	0.5
Ferrous sulfate ($7H_2O$)	0.01
Agar	20.0
Distilled water	1000ml

The colony was cultured in a liquid medium at 300ml-air/min and 50℃ (Fig. 1 in the previous report), transferred on the agar plate and cultured in the liquid medium twice more to acclimate at 50℃, because the group breeded at 50℃ was very effective as reported in the previous report.

2.2 Identification of the breeded microorganisms

The microorganisms (ASA-1) breeded in soil consisted mainly of mold and bacillus with some actinomycetes, therefore ASA-2 group are mixture with ASA-1 and showed in previous report microorganisms Table 3 (classified according to their nature), Table 4 (The optimum culture media for their strains).

Table 3. List of fungus.

Fungus	Exp.	sym.
General Compost Bacteria (Actiniomycetes) Aerobic Bacteria	CAA	
Streptomyces thermoviolaceus subsp. pingens	CAA	1
Streptomyces thermoviolaceus subsp. thermoviolaceus	CAA	2
Streptomyces thermovulgaris	CAA	3
Streptomyces thermovulgaris	CAA	4
Streptomyces thermodiastaticus	CAA	5
Streptomyces thermonitrificans	CAA	6
Streptomyces thermophilus	CAA	7
Thermoactinomyces glaucus	CAA	8
Thermoactinomyces vulgaris	CAA	9
Thermomonospora viridis	CAA	10
Thermomonospora curvata	CAA	11
Thermopolyspora polyspora	CAA	12
Thermopolyspora rectivirgura	CAA	13
Microbispora aerata	CAA	14
Decomposition of peptone Aerobic Bacteria		
Bacillus subtilis	DPA	1
Bacillus mesentericus vulgatus	DPA	2
Bacillus cereus var. mycoides	DPA	3
Pesudomonas fluorescens	DPA	4
Fermentation of cellulose Aerobic Bacteria		
Cellulomonas gerida	FCA	1
Deodor Bacteria (Actinomycetes) Aerobic Bacteria		
Streptomyces griseus	DSA	1
Streptomyces antibioticus	DSA	2
Streptomyces antibioticus	DSA	3
Crude Bacteria		
Streptomyces A S	ASA	1

Table 4. List of medium and fungus.

Medium		Fungus	
Yeast extract, malt extract, agar (pH 7.3)			
Basco yeast extract	4.0g	CAA	1
Bacto malt extract	10.0	CAA	2
Bacto dextrose (Annydrous)	4.0	CAA	6
Bacto agar	20.0	CAA	7
Distilled water	1000 ml		
Bennett's agar (pH 7.3)			
Yeast extract	1.0g	CAA	3
Beef extract	1.0	CAA	12
NZ Amine, type A	2.0	CAA	13
Bacto dextrose (Anhydrous)	10.0		
Bacto agar	20.0		
Distilled water	1000 ml		
Bennett's agar (pH 7.3)			
Yeast extract	1.0g	CAA	4
Beef extract	1.0	CAA	5
NZ Amine, type A	2.0	CAA	11
Bacto maltose	10.0	CAA	14
Bacto agar	20.0	DSA	2
Distilled water	1000 ml		

5g medium (pH 7.3)			
Yeast extract	5.0g	CAA	8
Glycerine	50.0	CAA	9
Calcium carbonate	1.0	CAA	10
Bacto agar	20.0		
Distilled water	1000 ml		
Bacteria medium (pH 7.2)			
Bacto peptone	10.0g	FCA	1
Beef extract	10.0		
Sodium chloride	3.0		
Bacto agar	15.0		
Distilled water	1000 ml		
Yeast extract, malt extract, agar (pH 7.3)			
Yeast extract	4.0g	DSA	1
Malt extract	10.0		
Dextrose (Anhydrous)	4.0		
Bacto agar	20.0		
Distilled water	1000 ml		
Nutrient agar (pH 7.0)			
Yeast extract	3.0g	DPA	1
Bacto peptone	10.0	DPA	2
Sodium chloride	2.0	DPA	3
Bacto agar	15.0	DPA	4
Distilled water	1000 ml		
Sugar, sodium nitrate, agar (pH 7.2)			
Sugar	30.0g	ASA	1
Sodium nitrate	2.0		
Potassium dihydrogen phosphate	1.0		
Magnesium sulfate ($7H_2O$)	0.5		
Potassium chloride	0.5		
Ferrous sulfate ($7H_2O$)	0.01		
Bacto agar	20.0		
Distilled water	1000ml		

2.3 Inoculation of the identified microorganisms

The group of microorganisms in Table 3 and in ASA-1 were cultured in the optimal liquid medium Table 4 at 50-55℃, and 20ml portion containing (3-4) $\times 10^8$ bodies/ml at the proportional growth stage was inoculated on 5g of pastourized rice bran of 30% moisture, and preserved in an incubator at 5℃.

2.4 Fermentation of an organic waste

2.4.1 Pretreatment of an organnic waste

As an organic waste, a mixture of the above activated sludge and saw dust was used. Saw dust (as moisture controller and C source) was separated from dust and sand, ball-milled to 50-100 mesh, partially hydrolyzed in 0.01N sodium hydroxide at 50℃ for 24 hours, filtered, waterwashed, and mixed with the activated sludge dewatered and air-dried for several days in a 400 : 100～150 ratio to contain 50-60% moisture.

2.4.2 Mixing of the organic waste and micro-organisms

The organic waste was mixed with its 5% amount of the preserved rice bran inoculated with ASA-1 (A-series) and next series was as follow mixture with the organic waste was mixed with its

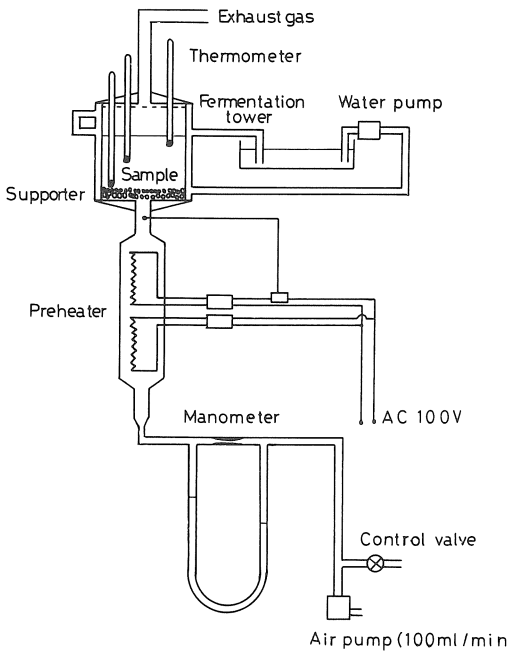

Fig. 1. Appratus of fermentation.

5% amount of the preserved rice inoculated with micoorganism in Table 3 and A-series in a 1 : 1 ratio (B series), but being activated at 30℃ for 24 hours just before mixing and pelletized to 1-3mm diameter.

2.4.3 Fermentation procedure

The mixture was filled in about 4/5 height in a 1000ml reaction vessel Fig 1 with metal nets as a bottom and cover (6-10mm diameter porcelain balls' being placed as a layer on the bottom net to allow free acces of air) and with a water jacket to circulate water at 50℃, and air preheated at 50℃ was passed 100ml/min up flowly for 6 days, the temperature being mesured at the upper, middle, and lower part of the mixture.

2.5 Analytical Results

2.5.1 Elementary analysis, carbon ratio and fermentation yield of the fermentation product.

A small amount of sample for analysis was taken out every 25 hours (RM, 1D, 2D, ·····6D being the sample at lst, after 1, 2, ···· 6 days, respectively as A series and B series), powdered to 100 mesh, dried and a 2mg portion was analyzed elementarily.

In Table 5 and 6, the results as well as the carbon ratio (C/N) and amount of volatilized matter (on the base excluding moisture and ash; being defined as volatile matter and expressed in g-VM) are given, and in Table 7, the fermentation yield. The amount of volatilized matter indicates the loss in weight in each system,i.e.the matter decomposed and lost by fermentation as CO_2, NH_3, H_2O and NO_x, so that it is an excellent parameter of degree of the composting.

It is apparent from Table 5, 6 and 7 that the loss in weight proceeds remarkably with lapse of time, being larger in the B-series than in the A-series.

Table 5. Elementary analysis and carbon ratio of original and product system (A series).

	H	C	N	O	C/N
RM	6.37	46.42	1.51	45.70	30.74
1D	6.47	47.07	1.56	44.90	30.17
2D	6.49	46.58	1.59	45.37	29.86
3D	6.49	46.22	1.59	45.70	29.07
4D	6.59	47.72	1.62	44.07	29.47
5D	6.51	47.02	1.66	44.81	28.33
6D	6.60	47.39	1.71	44.30	27.71

Table 6. Elementary analysis and carbon ratio of original and product system (B series).

	H	C	N	O	C/N
RM	6.52	47.60	1.48	44.40	32.16
1D	6.61	47.87	1.58	43.94	29.70
2D	6.59	47.11	1.62	44.68	29.08
3D	6.39	46.51	1.76	45.34	26.43
4D	6.53	46.98	1.95	44.54	24.09
5D	6.60	46.51	2.02	44.87	23.02
6D	6.52	47.17	2.10	44.21	22.46

Table 7. Yield by fermentation (6 days).

	A series	B series
Original system	230.85 g	233.45 g
Product system	192.86	145.60

3. Discussion

3.1 Effect of aeration on the aeration culture

The effect of aeration at 100ml/min (actually 100 -300ml/min) was tested on the liquid culture from the liquid film resistance.

The mean radius of actionmycetes is about 2.5μ and the oxygen cosumption rate of a bacterium is expressed by the equation.

$$dw/dt = K_L S(C - C^*)$$

w : amount of oxygen transfer (mol)
t : time (min.)
K_L : oxygen transfer coefficient on the liquid-fim (cm/min)
C : oxygen concentration in the bulk culture medium (mol/cm^3)
C* : oxygen concentration on the bacterium surface (mol/cm^3)

and as moisture content of the bacteria is 75%

$$dw/dt = 4.1 \times 10^{-11} \text{m mol } O_2/\text{hr}$$
$$= 1.14 \times 10^{-14} \text{m mol } O_2/\text{sec}$$

When a sphere (a bacterium) or radius r is present in a static liquid, then

$$K_L.r/D = 2$$

r : 2.5μ
D : diffusion coefficient of oxygen in the liquid $= 1.8 \times 10^{-5}$cm^2/sec
K_L : $(2)(1.8)(10^{-5})(1/2.5)(10^4) = 0.114$ cm/sec
S : $4\pi r_2 = 7.86 \times 10^{-7}$cm^2

The difference of dissolved oxgen in the bulk medium and on the bacterium surface is calculated,

$$C - C^* = dw/dt \cdot 1/K_L S$$
$$= (1.14)(10^{-14})(1/0.144)(1/7.80)(10^7)$$
$$= 1.27 \times 10^{-7} \text{m mol } O_2/\text{cm}^3$$
$$= 0.004 \text{ mg/l}$$

The difference is so small the saturation concentration itself should be the driving force and the diffusion of oxygen to the bacteria be independent on the liquid-film resistance at 100 ml/min aeration.

3.2 Relation of composting and enthalpy

3.2.1 Chemical change in composting

Reached a conclusion from the chemical structure model of humus by Tiele and Kettner[2],

Dragunov. S.S[2] and Kasatochkin[2].

As the composting proceeds to decrease the component of organic waste and residual molecular was built up stable six-membered structure.

Euthalpy difference between the original and product system and decrease of component between the original and product system may be used as the parameter of this analysis.

3.2.2 Enthalpy difference between the original and the product system

From the data in Table 5, 6 and Table 7, the molecular formulas may be assigned for each system as shown Table 8 and Table 9.

Table 8. Experimental molecular formula of original and product system (A series).

	Molecular formula	Molecular weight	Decreament
RM_a	$C_{36}H_{59}O_{26}N$	921	
$1D_a$	$C_{35}H_{58}O_{25}N$	892	29
$2D_a$	$C_{34}H_{58}O_{25}N$	880	41
$3D_a$	$C_{34}H_{57}O_{24}N$	863	58
$4D_a$	$C_{34}H_{56}O_{23}N$	846	75
$5D_a$	$C_{33}H_{54}O_{23}N$	832	89
$6D_a$	$C_{32}H_{54}O_{22}N$	804	117

Table 9. Experimental molecular formula of original and product system (B series).

	Molecular formula	Molecular weight	Decreament
RM_b	$C_{38}H_{61}O_{26}N$	947	
$1D_b$	$C_{35}H_{59}O_{24}N$	877	70
$2D_b$	$C_{33}H_{56}O_{24}N$	853	94
$3D_b$	$C_{31}H_{51}O_{22}N$	789	158
$4D_b$	$C_{28}H_{47}O_{20}N$	717	230
$5D_b$	$C_{27}H_{45}O_{19}N$	692	255
$6D_b$	$C_{26}H_{43}O_{18}N$	657	290

Table 10. Carbon, Hydrogen, Oxygen % in experimental molecular formula.

	Molecular formula	Molecular weight	C %	H%	O %
RM_a	$C_{36}H_{59}O_{26}N$	921	46.9*	6.4**	45.2***
$6D_a$	$C_{32}H_{54}O_{22}N$	804	47.8	6.7	43.8
RM_b	$C_{38}H_{61}O_{26}N$	947	48.2	6.4	43.9
$6D_b$	$C_{26}H_{43}O_{18}N$	657	47.5	6.5	43.8

* $36 \times \frac{12}{921} \times 100$

** $59 \times \frac{1}{921} \times 100$

*** $26 \times \frac{16}{921} \times 100$

In the present system, the unit carolific value (h) can be caluculated from the decrease in above organic compound equivalent of the assigned compound as follows:

$$h = 127R + 400 \text{ (cal/g-VM)}$$

$$R[3] = 0.251(2.66\,C\% + 7.94\,H\% - O\%)$$

the amount of oxygen necessary to oxidize all the carbon and hydrogen contained to carbon dioxide and water.

The average reaction heat ΔH can then be calculated,

$$\Delta H = \frac{(\text{h of RM})(\text{weight of RM}) - (\text{h of 6D})(\text{weight of 6D})}{(\text{weight of RM}) - (\text{weight of 6D})}$$

the percentage of carbon, hydrogen and oxygen of the compound of molecular formula in Table 8 and 9 being given in Table 10, and R, h and ΔH being caluculated as follows:

Calculation of R,

RM_a: $R = 0.251(2.66\times46.9)+(7.94\times6.4)-45.2 = 32.7$

$6D_a$: $R = 0.251(2.66\times47.8)+(7.94\times6.7)-43.8 = 34.2$

RM_b: $R = 0.251(2.66\times48.2)+(7.94\times6.4)-43.9 = 33.9$

$6D_b$: $R = 0.251(2.66\times47.5)+(7.94\times6.5)-43.8 = 33.6$

Calculation of h,

RM_a: $h = 127\times32.7+400 = 4552.9$

$6D_a$: $h = 127\times34.2+400 = 4743.4$

RM_b: $h = 127\times33.9+400 = 4705.3$

6D : $h = 127\times33.6+400 = 4667.2$

Calculation of ΔH,

$$\Delta H_a = \frac{4552.9\times230.85-4743.4\times192.86}{230.85-192.86} = 3585.8$$

$$\Delta H_b = \frac{4705.3\times233.45-4667.2\times145.60}{233.45-145.60} = 4768.4$$

The enthalpy of the product system is smaller by ΔH than that of the original, being the more stabilized or composted, the larger the ΔH. Hence the activity of cluster could be estimated in the order of ΔH;

$$\Delta H_b > \Delta H_a$$

and the activity of he cluster would be in order of

B series > A seris

3.3 The reaction (fermentation) rate of the composting

For calculation of the reaction rate, it is most disirable to know the amount of evolved gases as stated in 3.2.1 but actually the composition of the mixed gas changed irregularly time. On the other hand, the compounds in Table 8 and 9 would decomposed so that decrease in the molecular weight may be take as the parameter.

As the reaction is enzymatic, the following factors should be taken into account for the first

-order reaction:
the concentrations of enzyme [E] and substrate [S], the temperature, the pH and the presence of promoting and inhiting matters. As stated before, protein is decomposed in the primary stage so that [S] corresponds to the nitrogen concentration. And the reaction can be written,

$$E + S \underset{K_2}{\overset{K_1}{\rightleftarrows}} ES \xrightarrow{K_0} P + E$$

K_1, K_2, K_0 : reaction rate constants
p : the reaction product
$[E_0]=[E]+[ES]$
E_0 : total concentration of enzyme

When [S] is small, the reactin velocity (V) can be written,

$$V = \frac{K_0}{K_m}[E_0][S]$$

$$K_m : \frac{[E][S]}{[ES]} = \frac{K_2 + K_0}{K_1}, \text{ Michaelis constant}$$

and when [S] is large, the V*

$$V^* = K_0[E_0] = \frac{V[S]}{[S] + K_m}$$

For S, the N concentraation was adjusted to 1.48 -1.51% in RM as shown in Table 5, 6 and for E, bacteria of almost an equal number was inoculated, and the reaction was carried out at 55℃.

From these data and those in Table 8 and 9, the rate of molecular weight change against the time and hence the reaction rate constants were caluculated as shown in Table 11, and Fig 2. The change in the A series was too small, the reactions were of the first order in the each series, and the reaction rate constants caluculated are as follows:

$$K_a = \frac{0.108}{120\times60\times60}\times2.303 = 0.57\times10^{-6}\ [sec^{-1}]$$

$$K_b = \frac{0.319}{120\times60\times60}\times2.303 = 1.70\times10^{-6}\ [sec^{-1}]$$

Thus, the result $K_b > K_a$ shows that the activety of the bacteria is in the order A and B series.

Table 11. Reaction rate of each series.

A series							
Time (hr)	0	24	48	72	96	120	144
Decreament(x)	0	29	41	158	75	89	117
Remain (a-x)	921	892	880	863	846	832	804
ln a/a-x	—	0.032	0.046	0.065	0.085	0.102	0.136

B series							
Time (hr)	0	24	48	72	96	120	144
Decreament(x)	0	70	94	158	230	255	190
Remain (a-x)	947	877	853	789	717	692	657
ln a/a-x	—	0.077	0.105	0.183	0.278	01314	0.366

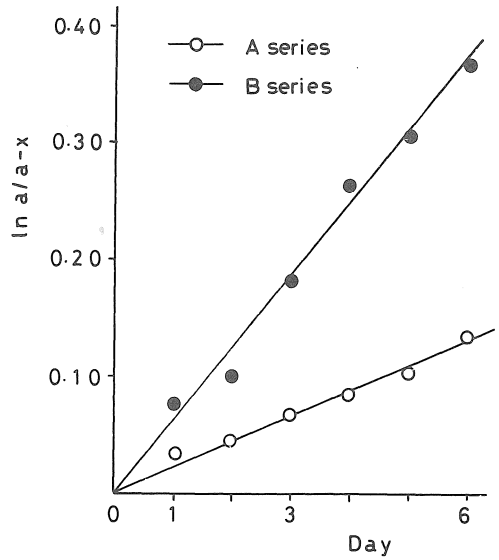

Fig. 2. Reaction rate constant.

3.4 Theoretical oxygen demand for the reaction

The theoretical oxygen demand can be caluculated by the following equation,

Organic compound (VM) of the original system + O_2 → that of the product system (Compost-VM) + $CO_2+H_2O+NH_3$

$$C_aH_bO_cN_d + 0.5(ny+2s+r-c)O_2 \rightarrow nC_wH_xO_yN_z + sCO_2 + rH_2O + (d-nz)NH_3$$ [4]

$C_aH_bO_cN_d$: molecular formula of the organic compound before the composting.
$0.5(ny+2s+r-c)O_2$: oxygen demand.
$nC_wH_xO_yN_z$: molecular formula of the organic compound after the composting.
sCO_2 : the amount of carbon dioxide evolved.
rH_2O : that of water
r : number of H atom converted into water and ammonia $=0.5[b-nx-3(d-nz)]$.
$(d-nz)NH_3$: the amount of ammonia evolved.
s : number of C atom reacted with oxygen $=a-nw$

With the above relations, the theoretical oxygen demand in each series is calculated;

For the A series,

	molecular formula	molecular weight	organic compound(g-VM)
RM_a	$C_{36}H_{59}O_{26}N$	921	230.85
$6D_a$	$C_{32}H_{54}O_{22}N$	804	192.86

a = 36, b = 59, c = 26, d = 1
w = 32, x = 54, y = 22, z = 1

The mol numbers of the compounds before and after the composting,

$M = 230.85/921 = 0.25$
$n = 192.86/(0.25 \times 804) = 0.96$
$r = 0.5\{59 - (0.96 \times 54) - 3(1 - 0.96 \times 1)\} = 3.52$
$s = 36 - (0.96 \times 32) = 5.28$

The oxygen demand (O_a),

$$O_a = 0.5\{(0.96 \times 22) + (2 \times 5.28) + 3.52 - 26\} \times 0.25 \times 32 = 36.80$$

The material balance,

The original (VM)	230.85 g
Oxygen	36.80 g
Total	267.65 g

The product (VM)	192.86 g
Carbon dioxide	58.08 g
Ammonia	0.17 g
Water	15.84 g
Total	266.95 g

For the B series,

	molecular formula	molecular weight	organic compound (g-VM)
RM_b	$C_{38}H_{61}O_{26}N$	947	233.45
$6D_b$	$C_{26}H_{43}O_{18}N$	657	145.60

a = 38, b = 61, c = 26, d = 1
w = 26, x = 43, y = 18, z = 1

The mol numbers of the compounds before and after the composting,

$M = 233.45/947 = 0.24$
$n = 145.60/(0.24 \times 657) = 0.92$
$r = 0.5\{61 - (0.92 \times 43) - 3(1 - 0.92 \times 1)\} = 10.60$
$s = 38 - (0.92 \times 26) = 14.08$

The oxygen demand (O_b),

$$O_b = 0.5\{(0.92 \times 18) + (2 \times 14.08) + 10.60 - 26\} \times 0.24 \times 32 = 112.59$$

The material balance,

The original (VM)	233.45 g
Oxygen	112.59 g
Total	346.04 g

The product (VM)	145.60 g
Carbon dioxide	148.68 g
Ammonia	0.33 g
Water	45.79 g
Total	340.40 g

Thus, the theoretical oxygen demand calculated as above are,

A series : 122.0ml/hr.100g-VM
B series : 234.4ml/hr.100g-VM

Then, the order is in

$$O_b > O_a$$

The larger the oxygen demand, the large the activity of the cluster,

B series > A series

4. Conclusion

The complex organic waste has been treated on the standpoint of physical chemistry and chemical technology and shown to be more stabilized (composted) with large enthalpy change, reaction rate constant and oxygen demand, so that the activity of cluster could be expressed numerically. It is concluded that

(1) As the order has been found to be
the enthalpy change $\Delta H_b > \Delta H_a$
the reaction rate constant $K_b > K_a$, and
the oxygen demand $O_b > O_a$
the order of activity of cluster should be
B series > A series
although some discrepancis are observed.

(2) The difinition of composting given at the beginning has been proved to be adequate.

(3) The experimental results and the extent of composting could thus be accurately estimated or compared.

(4) The composting could be treated scientifically.

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