Analysis of High Rate Composting of Organic Waste (1)

Akie TSURUIZUMI, Hiroshi OHTA

有機廃棄物の高速 Composting の解析

鶴泉彰恵，太田 洋

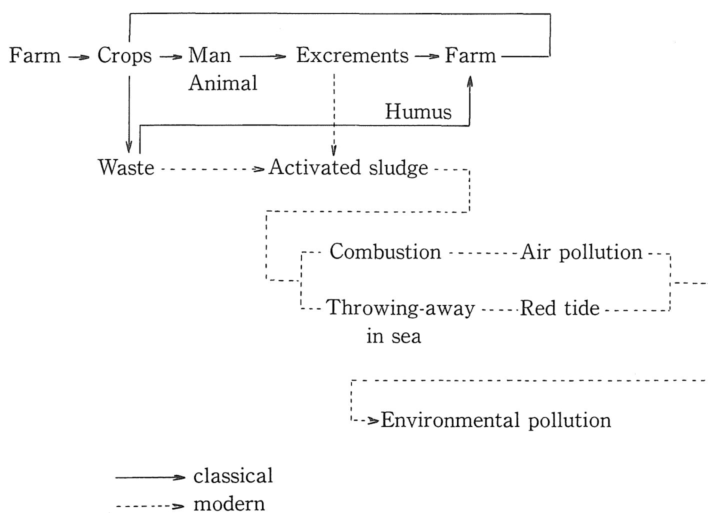
Composting has not been treated quantitatively as well as stoichiometrically. Polycondensation of organic waste on composting and maturation of the compost are, therefore, judged by human senses such as color or odor, and thus the effectiveness of cluster on composting is estimated qualitatively.

In the present report the reaction system of enzyme of microorganism not yet treated scientifically has been treated in the following order although macroscopically.

With fowl droppings as a representative of organic waste containing relatively a large amount of nitrogen, microorganisms suitable for composting have deen searched for in soil,cultured,classified into groups according to their physiological characteristics, and the decomposition reaction at a definite temperature has been analyzed through caluculations of the enthalpy change between the original and the product systems, the reaction rate constant, and the theoretical oxygen demand to express the degree of decomposition of the composted matter effectiveness of the microorganism numerically and adequately.

1. Introduction

The compositng may be defined as a process of transformation of chemically unstable organic waste (having a large chemical potential) into a stable organic matter with enthalpy decrease, and in other words, a process of artificial production of humus. Municipal waste, human and animal excrements, and activated sludge are the end-products of valuable matters obtained from valuable resources with enormous energy consumption. If these are converted into a valuable matter through redox reaction of the metabolic products of microorganism, the resources would be cycled and environmental pollution be avoided so that energy and resources are saved to be significant both nationally and globally. The classical and the modern processes may be compared in the following scheme.



Environmental Research Center
環境工学研究所

Classically the waste and the excrements were returned to the farm to convert into humus in 0.5 — 1.5 years by the so-called fertility and to be effective for soil reforming and as fertilizer. Recently, according to the industrial waste treatment law, they must be combusted or thrown away in sea to cause air pollution in the land with consumption of valuable petroleum or red tide in the sea. Humus makes soil colloidal aggregate to improve the fertility, i. e. oxygen diffusion,activity and stability of microorganism, water and fertilizer reservations, and readyness of cultivation. But humus is slowly decomposed by soil bacteria finally to carbon dioxide, water and nitrogen gas (the soil respiration). It is said that soil should contain 5 ～ 7 % humus but nowadays the content is estimated to be only 2 ～ 3 %. As the decrease in fertility is supplied with chemical fertilizer, its demand is increasing year by year. The decomposition rate of humus is estimated to be 5 ～ 7 % a year and the necessary amount to be about 700 kg per 10 are. The whole amount necessary for all farms in Japan could be supplied by the humus produced from the excrements as raw material to save about 30 % of the chemical fertilizer produced with large energy consumption. Animal excrement is estimated to be about twice as much as the human and the effectiveness of the fodder about 20 % so that it is the best raw material for artificial humus production. Additionally it is an origin of bad odor and water pollution and cannot be used as animal protein. In the present study, microorganisms were searched for of high rate composting of fowl droppings in 2 ～ 6 days without environmental pollution, classified according to the physiological characterictics, and the enzymatic reaction was discussed from the standpoints of enthalpy change, the reaction rate, and the theoretical oxygen demand from the material balance.

In the present study, the organisms, i. e. aerobic actinomycetes, were classified into three groups and the reaction was vigorous. In order to obtain the elementary reaction rate of the enzyme, therefore, a mild condition was desirable, the system being kept at 55 °C, taken out of the thermostat six times a day, and stirred to avoid the heat acumulation and to enhance the contact with oxgen.

2 . Experimentals and Results

2.1 Isolation of effective microorganism in soil and its enrichment culture

2.1.1 Culture in a natural soil medium

The soil is full of microorganisms, natural humus is produced by the action of soil bacteria in it, and the primary fermentation in the early stage is, as is well known, due to the action of aerobic actinomycetes and mold. It takes 0.5 ～ 1.5 years to from maturated humus as decomposition of cellulose and lignin (the secondary fermentation) is slow.

Accordingly a farm was divided into 1 m^2 each, the soil was mixed with small amounts of saccharide to supply the necessary free energy for growth of microorganisms, of yeast and beef extracts to supply the necessary matters to form the body, and a known amount of organic waste as shown in Table 1, and the microorganisms were cultured at 50 ～ 60 % moisture and 20 ～ 30 °C for 1 month to find effective ones.

Table 1 Surface soil culture of microorganisms in the field

1	Blank
2	Starch
3	Rice straw (cutting 1 cm)
4	Beef extract
5	Insulation oil
6	Human feces
7	Dung ＋ Rice straw
8	Starch ＋ Rice straw ＋ Beef extract ＋ Insulating oil
9	Saw dust ＋ Dung

2.1.2 Culture of soil bacteria in a liquid medium

The suitable composition of a liquid medium is shown in Table 2 for aerobic actinomycetes, mold, or cellulose decomposition bacteria, and the apparatus in Fig. 1 for aeration culture.

The liquid medium was added with about 1 g of the cultured soil and aerated at 300 ml／min and 50 °C. Microorganism groups CRA_1 and CRA_2 were obtained from the cultured soil No 7 and 3, and CRA_3 from a mixed soil of No 1 ～ 9. Each group was transfered onto a plate culture, then into the liquid culture, and the process was repeated twice more to enrich and acclimate in a sugar-sodium nitrate medium. Thus, the thermophilic bacteria could be obtained.

Table 2 Sugar-sodium nitrate-agar medium and fungus

Medium	
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
Distilled water	1000 ml
(pH 7.2)	
Bacteria	
CRA 1	
CRA 2	
CRA 3	

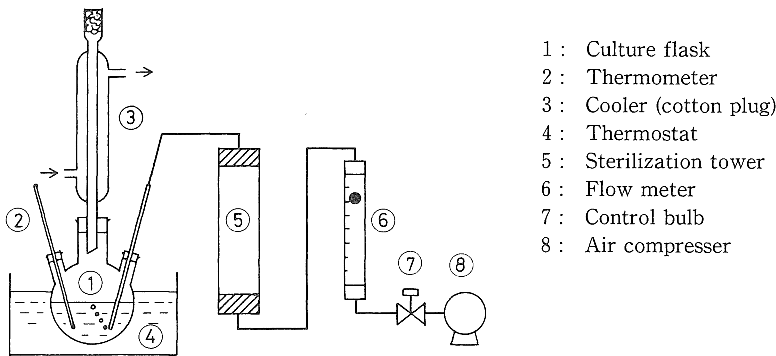


Fig 1 Apparatus of aeration culture

2.2 Carbon ratio and cation exchange capacity of the enriched bacteria

The carbon ratio (C/N) and cation exchange capacity (CEC) are the important factors to estimate the composting. In order to estimate the most difficult one (the decomposition of cellulose), Tōyō filter paper pulp as it is and hydrolyzed in 0.05 N NaOH (at pH 7.2 ~ 7.5) were moistened each with the enriched CRA_3 culture medium and kept at 50 % moisture and 30 °C or 50 °C. The changes in C/N and CEC values are shown in Fig. 2 ~ 3.

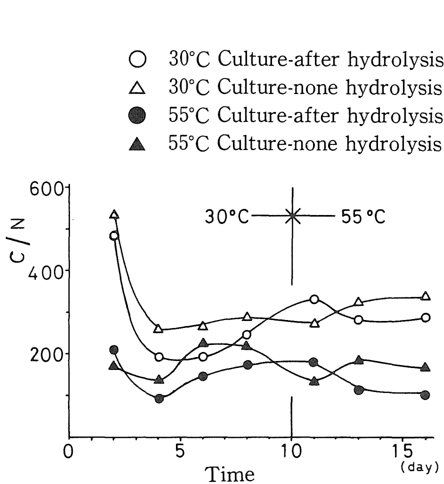


Fig 2 Variation of carbon ratio by CRA 3

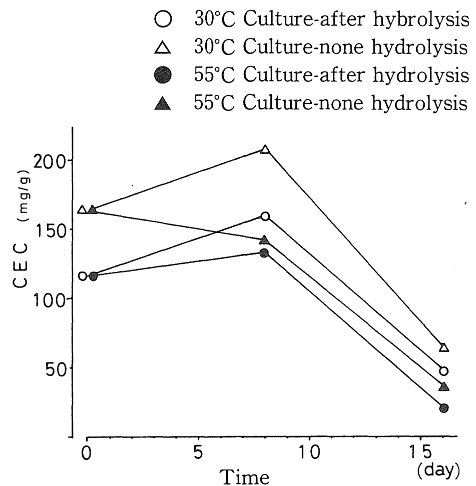


Fig 3 Variation of cation exchange capacity by CRA 3

Decrease in the C/N values is greater at 55 °C than at 30 °C as it represents the decomposition by the microorganism. The effect of hydrolysis of cellulose as the pretreatment is not clear as the period is too short.

Increase in the CEC value indicates that the decomposition is at the maximum about on the seventh day, and faster at 30 °C, as has been known that the secondary fermentation (decomposition of cellulose and lignin) is faster below 30 °C.

As the results, the microorganisms in the CRA_1 and CRA_2 are found to be effective for composting.

2.3 Classification and identification of microorganisms in CRA_1 and CRA_2

The aerofobic bacteria in CRA_1 and CRA_2 were classified and identified as usual and found to consist in,

Streptomyces thermoviolaceus subsp. pingens (CAA_1)
Streptomyces thermoviolaceus subsp. thermoviolaceus (CAA_2)
Streptomyces thermovulgaris (CAA_3)
Streptomyces thermophilus (CAA_7)
Thermoactinomyces glaucus (CAA_8)
Thermoactinomyces vulgaris (CAA_9)
Thermopolyspola rectivirgula (CAA_{13})
Bacillus subtilis (DPA_1)
Bacillus cereus var. mycoides (DPA_3)
Cellulomonas gelida (FCA_1)
Streptomyces griseus (DSA_1)

and overall 90 % actinomycetes and the remainder bacillus and mold.

For the characteristics of these bacteria, Bergey's Manual of Determinating Bacteriology (8th ed.) was consulted with and the following similar bacteria were selected additionally.

CAA_4,CAA_5,CAA_6,CAA_{10},CAA_{11},CAA_{12},CAA_{14}; DPA_2,DPA_4; DSA_2,DSA_3; CRA_1,CRA_2,CRA_3.

The scientific nomenclature of all the bacteria is shown in Table 3 classified according to their nature, and the optimum culture media for their strains in Table 4.

Table 3 List of fungus

Fungus	Exp. sym.
General Compost Bacteria (Actinomycetes) Aerobic Bacteria	
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
Decompostion 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 gelida	FCA 1
Deodor Bacteria (Actinomycetes) Aerobic Bacteria	
Streptomyces griseus	DSA 1

Streptomyces antibioticus	DSA	2
Streptomyces antibioticus	DSA	3
Crude Bacteria (Actinomycetes)		
Streptomyces AD 1	CRA	1
Streptomyces AD 2	CRA	2
Streptomyces AD 3	CRA	3

Table 4 List of medium and fugus

Medium		Fungus	
Yeast extract-malt extract-agar			
Bacto yeast extract	4.0g	CAA	1
Bacto malt extract	10.0	CAA	2
Bacto dextrose (Anhydrous)	4.0	CAA	6
Bacto-agar	20.0	CAA	7
Distilled water	1000 ml		
	(pH 7.3)		
Bennett's agar			
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		
	(pH 7.3)		
Bennett's agar			
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	DSA	3
	(pH 7.3)		
5g medium			
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		
	(pH 7.3)		
Bacteria medium			
Bacto-peptone	10.0g	FCA	1
Beef extract	10.0		
Sodium chloride	3.0		
Bacto-agar	15.0		
Distilled water	1000 ml		
	(pH 7.2)		
T G C medium			
Potato	200.0g	DPAN	1
Glucose	5.0	DPAN	2
TGC	10.0		
Calcium carbonate	15.0		
Bacto-agar	15.0		
Distilled water	1000 ml		
	(pH 7.0)		

Yeast extract-malt extract-agar		
Yeast extract	4.0g	DSA 1
Malt extract	10.0	
Dextrose (Anhydrous)	4.0	
Bacto-agar	20.0	
Distilled water	1000 ml	
	(pH 7.3)	
Nutrient agar		
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	
	(pH 7.0)	
Sugar-sodium nitrate-agar		
Sugar	30.0g	CRA 1
Sodium nitrate	2.0	CRA 2
Potassium dihydrogen phosphate	1.0	CRA 3
Magnesium sulfate ($7H_2O$)	0.5	
Potassium chloride	0.5	
Ferrous sulfate ($7H_2O$)	0.01	
Distilled water	1000 ml	
	(pH 7.2)	

2.4 The growth velocity on pure culuture of the selected strain

The period for the growth velocity to reach the exponential phase was measured on pure culture of the strains in Table 3 in the optimum culture medium in order to inoculate the strain at the phase and to obtain the generation time of each strain. The conditions were at 50 ～ 55 °C and aeration 100 ～ 300 ml／min in the apparatus shown in Fig. 1. The growth curves of pure culture are shown in Fig. 4-1 to 4-4, and the proportional growth curves of acclimation culture (the differential of the growth curves) in Fig. 5. The maximum of the latter corresponding to the generation time 72 hours(3 days) in Table 5 agrees well with that in the literature. The number of bacteria was measured by a Thoma's hemacytometer.

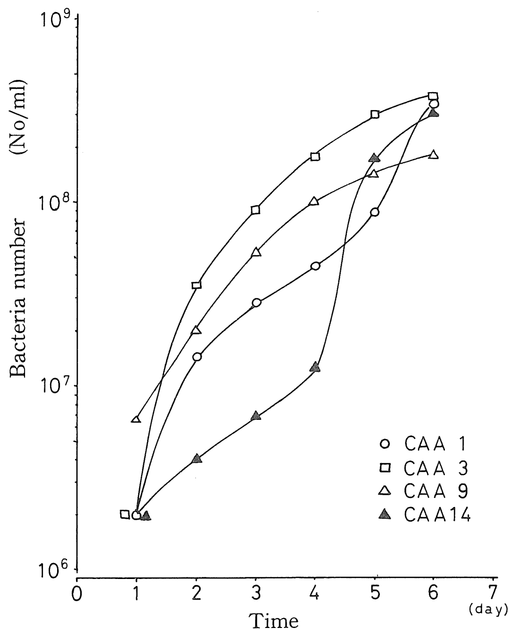


Fig 4-1 Growth curve of pure culture (1)

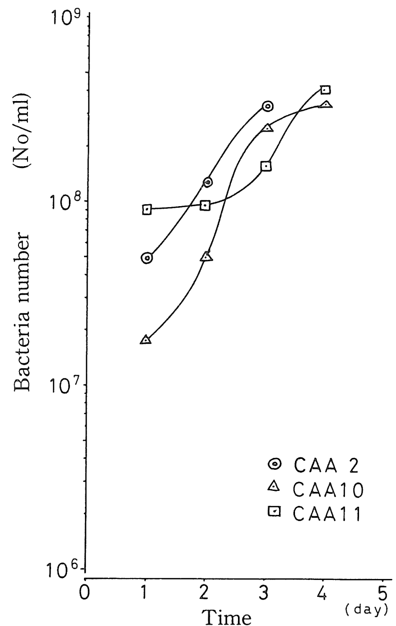


Fig 4-2 Growth curve of pure culture (2)

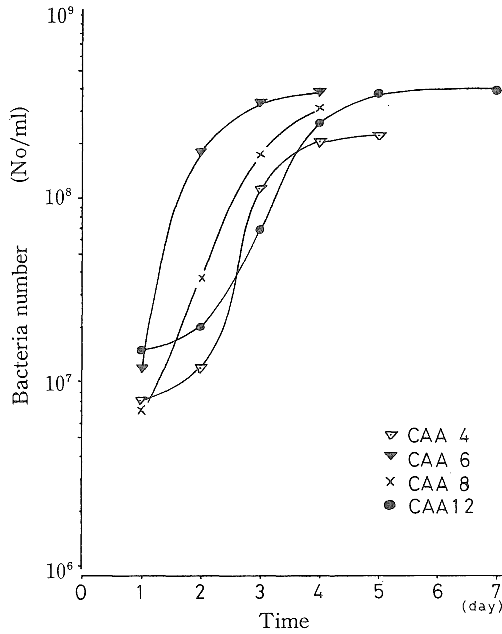


Fig 4-3 Growth curve of pure culture (3)

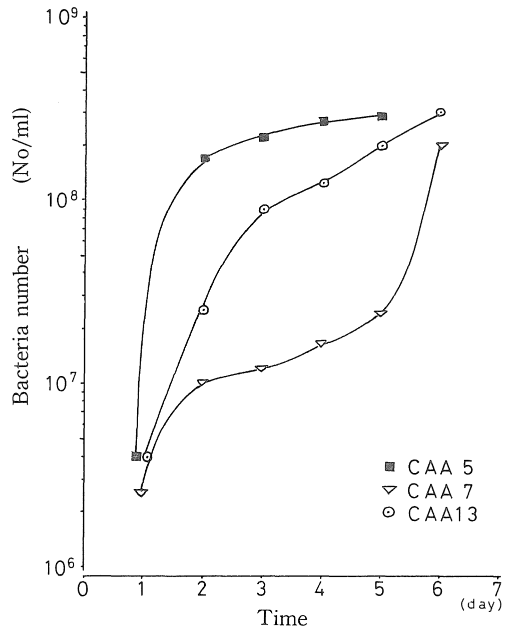


Fig 4-4 Growth curve of pure culture (4)

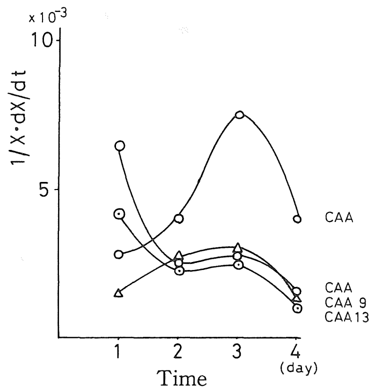


Fig 5 Proportional growth curve of pure culture

Table 5 Generation time of fungus

Fungus		Generation time
CAA	1	1100 min
CAA	2	1060
CAA	3	1040
CAA	4	1060
CAA	5	1024
CAA	6	1580
CAA	7	1860
CAA	8	648
CAA	9	1457
CAA	10	930
CAA	11	1800
CAA	12	1418
CAA	13	1395
CAA	14	1060

2.5 Growth velocity of the selected strain on acclimation culture

In order to apply to fowl droppings, the selected strain was acclimated in a medium containing it. Thus, NZ-amine 0.6 g and fowl droppings 12 g were dissolved in distilled water 1000 ml, and a 300 ml aliquot was sterilized and inoculated with each strain of pure culture ($4 \sim 6$) $\times 10^8$ bacteria in number.

The growth curves of acclimation culture are shown in Fig. 6-1 to 6-4, and the proportional growth curves of acclimation culture in Fig. 7, the period of logarithmic phase being 48 hours (2 days).

2.6 Classification of selected strains

The strains in Table 3 are classified into the following 3 groups according to their thermostability and acclimation growth velocity;

(1) containing all the strains,
(2) containing mainly thermostable actinomycetes,
CAA_1,CAA_8,CAA_9,CAA_{11},CAA_{12},
DPA_1,DPA_2,FCA_1,DSA_1,DSA_2,DSA_3,CRA_3.

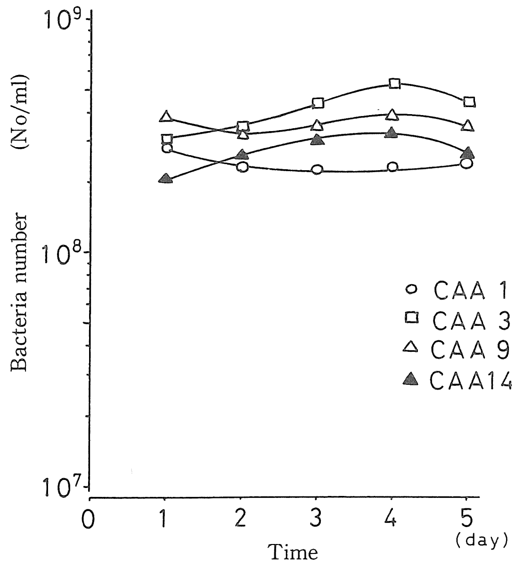


Fig 6-1 Growth curve of acclimation culture (1)

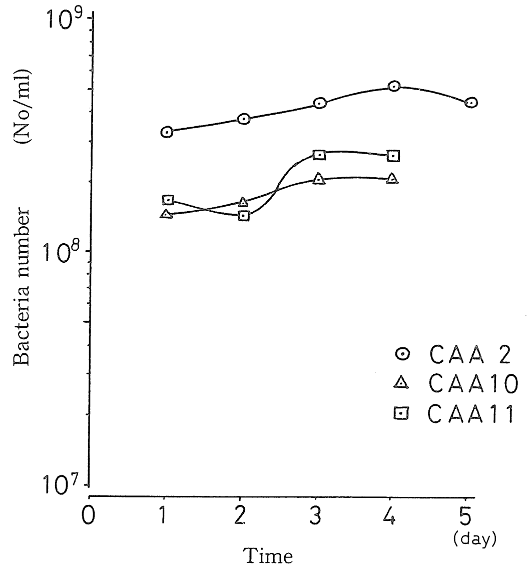


Fig 6-2 Growth curve of acclimation culture (2)

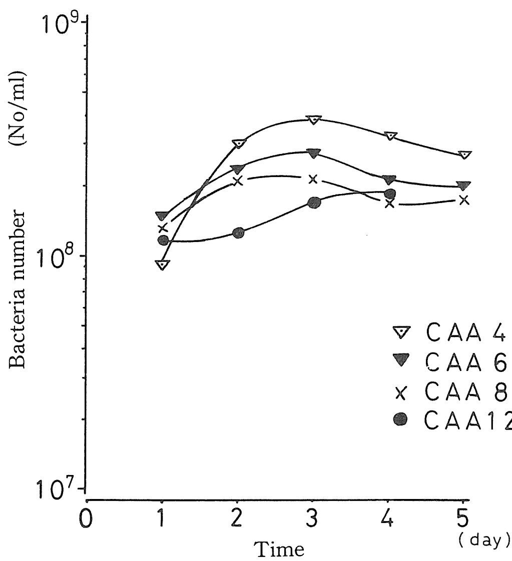


Fig 6-3 Growth curve of acclimation culture (3)

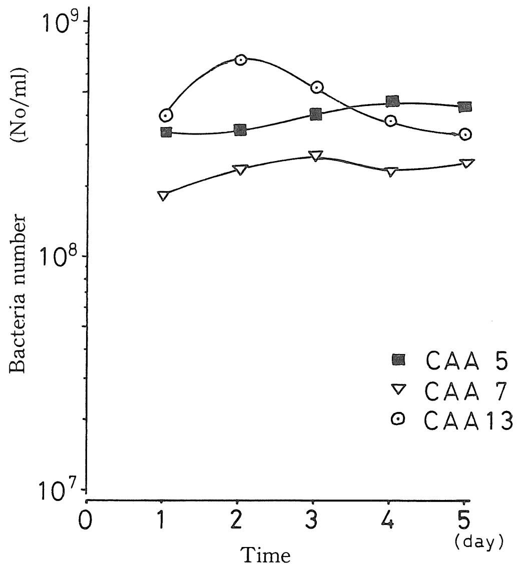


Fig 6-4 Growth curve of acclimation culture (4)

(3) effective in fowl dropping acclimation culture,
CAA_1,CAA_6,CAA_9,CAA_{10},CAA_{14},
DPA_3,DPA_4,FCA_1,DSA_1,DSA_2,DSA_3,
CRA_1,CRA_2,CRA_3.

The strains in each group were mixed with each other along with peptone-decomposition and deodoring bacteria for groups 2 and 3 to obtain three mixed strains 1 to 3.

2.6.1 Inoculation of the mixed strains on substrate

Each of the mixed strains was cultured in the optimum culture medium in Table 4 as usual at 50 ～ 55 °C until the exponential phase was attained, a 20 ml aliquot containing (3 ～ 4) × 10^8 bacteria／ml was mixed with fresh and sterilized rice bran 50 g to contain moisture 30 %, and preserved in an incubator at 5 °C.

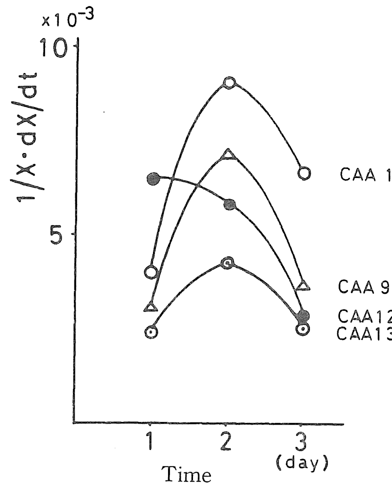


Fig 7 Proportional growth curve of acclimation culture

2.7 Fermentation test of organic waste

2.7.1 Pretreatment of organic waste

Fowl dropping was mixed with saw dust and used as an organic waste. Saw dust was separated from dust and sand, ball-milled to 60 ~ 100 mesh, and 30 ~ 40 g was mixed with fowl droppings 190 ~ 260 g to contain moisture 50 ~ 60 %.

2.7.2 Mixing of the organic waste with the mixed strains

Preserved strains in an incubator (2.6.1) were took out each 2 g then were mixed with each other strains in the same group to obtain mixed strains (1), (2), (3).

The organic waste was mixed with 5 % of the mixed strains to obtain the following samples;

(a) The mixed organic waste as blank,
(b) The mixed organic waste mixed with the mixed strains 1,
(c) The mixture with 2,
(d) The mixture with 3.

2.7.3 Fermentation process

Each sample was stirred in a 1000 ml beaker, and kept at 28 ~ 30 °C for 2 days and further at 55 °C for 5 days, being stirred six times a day to avoid heat accumulation and to contact with air as stated before.

2.7.4 Elementary analysis and carbon ratio of the fermentation product

The product was powdered to ~ 100 mesh and a 100 ~ 150 mg aliquot was analyzed by Yanagimoto MTA-500 for carbon and nitrogen, and another aliquot by Yanagimoto MTT-2 for hydrogen. The results (on the base excluding moisture and ash; being defined as volatile matter and expressed in g-VM) and the carbon ratio are shown in Table 6 ~ 7, RM_{a-d} and $6D_{a-d}$ corresponding to the samples before and after the fermentation, respectively. A large aliquot was analyzed as the sample is complex, but the error for hydrogen may be large as the apparatus has been designed for a 2 mg sample.

Table 6 Elementary analysis and carbon ratio of original system

	RM_a	RM_b	RM_c	RM_d
H	4.60	4.49	4.46	4.84
C	44.36	45.57	45.62	45.55
N	3.97	4.00	3.90	4.02
O	47.07	45.94	46.02	45.59
C/N	11.17	11.39	11.69	11.33

Table 7 Elementary analysis and carbon ratio of reaction system (reaction residual substance-compost)

	$6D_a$	$6D_b$	$6D_c$	$6D_d$
H	4.86	4.98	5.07	4.98
C	45.48	45.96	45.73	45.74
N	4.24	7.85	5.07	6.94
O	45.42	41.21	44.13	42.34
C/N	10.72	5.90	9.00	6.50

2.7.5 Yield of the organic waste after fermentation

The ratio 6D/RM is shown in Table 8 and corresponds to the rate of composting, which will be discussed in the following section.

Table 8 Yield by fermentation (6 days)

Original system	RM_a 115.36	RM_b 150.89	RM_c 136.04	RM_d 150.29
Reaction system	$6D_a$ 103.48	$6D_b$ 81.46	$6D_c$ 107.50	$6D_d$ 87.88

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 concentration of dissolved oxygen in the culture medium is difficult to determine. The approximate value was determined as follows:
when sterilized water containing 5 ～ 19mg/l glucose, sucrose, or levulose was aerated at 26 ～ 29°C and 100 ～ 300 ml/min, the oxygen saturation concentration was 6.3 ～ 7.4mg/l in any case.

The mean radius of actinomycetes is about 2.5μ, and the oxygen comsumption rate of a bacterium is expressed by the equation,

$$\frac{dw}{dt} = K_L S (C - C^*),$$

w : amount of oxygen transfer (mol)
t : time (min)
K_L: oxygen transfer coefficient on the liquid-film (cm/min)
S : surface area of a bacterium (cm^2)
C : oxygen concentration in the bulk culture medium (mol/cm^3)
C^*: oxygen concentration on the bacterium surface (mol/cm^3)

and as the moisture content of the bacteria is 75%

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

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

$$\frac{K_L \cdot r}{D} = 2,$$

r : 2.5μ
D : diffusion coefficient of oxygen in the liquid $\fallingdotseq 1.8 \times 10^{-5} cm^2/sec$

K_L: $(2)(1.8)(10^{-5})(1/2.5)(10^4) = 0.144$cm/sec

S : $4\pi r^2 = 7.86 \times 10^{-7} cm^2$

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

$$C - C^* = \frac{dw}{dt} \cdot \frac{1}{K_L S}$$

$$= (1.14)(10^{-14})(1/0.144)(1/7.80)(10^7)$$

$$= 1.27 \times 10^{-7} \text{mmol } O_2/cm^3$$

$$= 0.004 \text{mg/l}$$

The difference is so small that 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 100ml/min aeration.

3.2 Relation of composting and enthalpy

3.2.1 Chemical change in composting

Organic compounds in soil decomposed by metabolism of microorganisms to give low molecular weight compounds such as phenols, quinones, and amino compounds from protein at the first stage, and the low molecular weight compounds condensate to dark-colored polymer enzymologically or chemically by the action of oxygen in air, oxidase, and inorganic ions, with evolution of considerable amounts of carbon dioxide, ammonia, nitrogen, and water.

Thus, primary humus is formed by the primary fermentation (high rate composting defined by us), and followed by decomposition of cellulose and lignin to be converted into the stable humus.

The constitution of humus is much complicated but can be interpreted as follows. The nucleus compounds with substituent (s) are added with a crosslinking unit to form a micro unit as shown in Fig. 8, and several of the micro units condensate to a macro units (a monomer) as shown in Fig. 9, where (1) is di- and triyhdroxy phenols and quinones, (2) cyclic nitrogen, (3) nitrogen in the chain, and (4) hydrocarbon radical; the nucleus compound (usually aromatic as shown above), substituents, and crosslinking units being shown in Table 9.

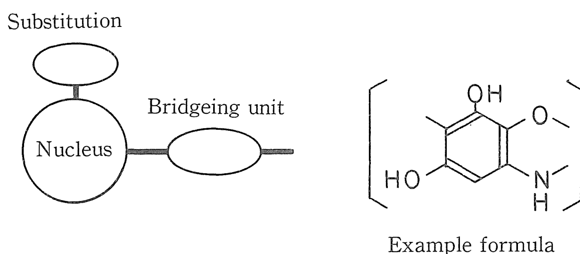


Fig 8 Micro-structural unit of humus (Thiele and Kettner)[4]

Table 9 Chemical structure of humus

Nucleus	
Substitution radical	-OH (Alcoholic), -OH (Phenolic), -COOH, >CO, -CHO, $-CH_3$ $-OCH_3$, $-NH_2$, $-SO_3H$, $-PO_3H_2$
Bridgeing unit	-O-, -NH-, -S-, =N-, $-CH_2-$, $-CH_2-O-$

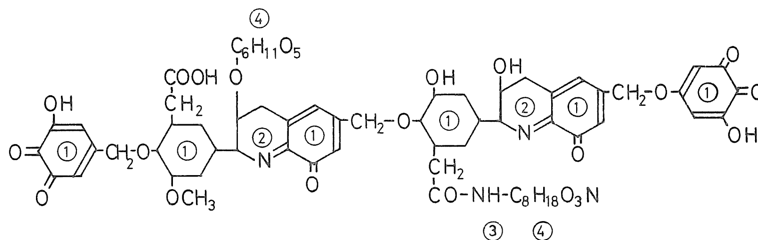
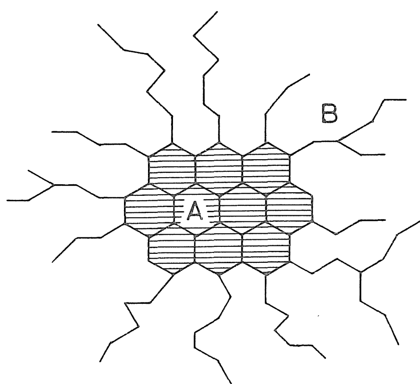


Fig 9 Mono-structure of humus (Dragunov. S S.)[4]

The monomers in Fig. 9 polycondensate further, when the side chains of a large potential energy should decrease to form a stable six-membered net-work. The side chains are decomposed by the catalytic action of enzyme to carbon dioxide, ammonia, nitrogen, and water. As the chemical reaction proceeds to decrease the potential energy, the enthalpy of the product system is smaller than that of the original. Thus, the composting process may be treated with enthalpy as a parameter.

The stable six-membered net-work may be illustrated as Fig. 10, whose constitution has increased in σ and π-bonds to be darker in color. Truely the composting degree has been judged by the color as stated before.

On the other hand, some of the elements in the side chain are lost in the course of composting as the gases as stated above so that the decrease in the organic compound equivalent may also be used as the parameter.



A : Cyclic polymer carbon (nucleus of aromatic comp.)
B : Linear polymer carbon (side chain)

Fig 10 Fundamental structural model (unit of polymer structure)[4]
(Kasatochkin V. I)

Table 10 Experimental molecular formula of original system and reaction system*

RM_a	$C_{13}H_{16}O_{10}N$	346**	$6D_a$	$C_{13}H_{16}O_9N$	330
RM_b	$C_{13}H_{16}O_{10}N$	346	$6D_b$	$C_7H_9O_5N$	187
RM_c	$C_{14}H_{16}O_{10}N$	358	$6D_c$	$C_{11}H_{14}O_8N$	288
RM_d	$C_{12}H_{17}O_{10}N$	335	$6D_d$	$C_8H_{10}O_5N$	200

* reaction residual substance
**molecular weight

Table 11 Carbon, hydrogen, oxygen % in experimental molecular formula

	Molecular formula	Molecular Weight	C %	H %	O %
RM_a	$C_{13}H_{16}O_{10}N$	346	45.1*	4.6**	46.2***
$6D_a$	$C_{13}H_{16}O_9N$	330	47.3	4.8	43.6
RM_b	$C_{13}H_{16}O_{10}N$	346	45.1	4.6	46.2
$6D_b$	$C_7H_9O_5N$	187	44.9	4.8	42.8
RM_c	$C_{14}H_{16}O_{10}N$	358	46.9	4.4	44.7
$6D_c$	$C_{11}H_{14}O_8N$	288	45.8	4.9	44.4
RM_d	$C_{12}H_{17}O_{10}N$	335	43.0	5.1	47.8
$6D_d$	$C_8H_{10}O_5N$	200	48.0	4.0	40.0

* $13 \times \frac{12}{346} \times 100$

** $16 \times \frac{1}{346} \times 100$

*** $10 \times \frac{16}{346} \times 100$

3.2.2 Enthalpy difference between the original and the product system

From the data in Table 6 ～ 7 and Table 8, the molecular formulas may be assigned for each system as shown in Table 10.

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

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

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

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 percentages of carbon, hydrogen, and oxygen of the compound of molecular formula in Table 10 being given in Table 11, and R, h, and ΔH being calculated as folloows:

Calculation of R,

RM_a : $R = 0.251\,(2.66 \times 45.1) + (7.94 \times 4.6) - 46.2 = 27.6$
$6D_a$: $R = 0.251\,(2.66 \times 47.3) + (7.94 \times 4.8) - 43.6 = 30.2$
RM_b : $R = 0.251\,(2.66 \times 45.1) + (7.94 \times 4.6) - 46.2 = 27.6$
$6D_b$: $R = 0.251\,(2.66 \times 44.3) + (7.94 \times 4.8) - 42.8 = 28.8$
RM_c : $R = 0.251\,(2.66 \times 46.9) + (7.94 \times 4.4) - 44.7 = 28.8$
$6D_c$: $R = 0.251\,(2.66 \times 45.8) + (7.94 \times 4.9) - 44.4 = 29.2$
RM_d : $R = 0.251\,(2.66 \times 43.0) + (7.94 \times 5.1) - 47.8 = 26.8$
$6D_d$: $R = 0.251\,(2.66 \times 48.0) + (7.94 \times 5.0) - 40.0 = 31.9$

Calculation of h,

RM_a : $h = 127 \times 27.6 + 400 = 3905.2$
$6D_a$: $h = 127 \times 30.2 + 400 = 4235.4$
RM_b : $h = 127 \times 27.6 + 400 = 3905.2$
$6D_b$: $h = 127 \times 28.8 + 400 = 4057.6$
RM_c : $h = 127 \times 28.8 + 400 = 4057.6$
$6D_c$: $h = 127 \times 29.2 + 400 = 4108.4$
RM_d : $h = 127 \times 26.8 + 400 = 3803.6$
$6D_d$: $h = 127 \times 31.9 + 400 = 4451.3$

Caluculation of ΔH,

$$\Delta H_a = \frac{3905.2 \times 115.36 - 4235.4 \times 103.48}{115.36 - 103.48} = 1029.0 = 1.0290\,\mathrm{kcal/kg\text{-}VM}$$

$$\Delta H_b = \frac{3905.2 \times 150.89 - 4057.6 \times 81.46}{150.89 - 81.46} = 3726.4 = 3.7264\,\mathrm{kcal/kg\text{-}VM}$$

$$\Delta H_c = \frac{4057.6 \times 136.04 - 4108.4 \times 107.50}{136.04 - 107.50} = 3866.3 = 3.8663\,\mathrm{kcal/kg\text{-}VM}$$

$$\Delta H_d = \frac{3803.6 \times 150.29 - 4451.3 \times 87.88}{150.29 - 87.88} = 2891.6 = 2.8916\,\mathrm{kcal/kg\text{-}VM}$$

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;

$$\Delta H_c \geqq \Delta H_b > \Delta H_d > \Delta H_a.$$

And the activity of the cluster would be in the order of

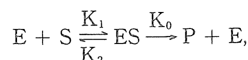
$$c \geqq b > d.$$

It has been reported[1] that ΔH is 4 ～ 6kcal/kg-VM with a maturated compost. The ΔH's of the above cases are about a half, so do the degrees of composting.

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 with time. On the other hand, the compounds in Table 10 would be decomposed so that decrease in the molecular weight may be taken 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 inhibiting 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,



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

K_1, K_2, K_0 : reaction rate constants
P : the reaction product

$$[E_0] = [E] + [ES]$$

E_0 : total cocentration of enzyme.

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

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

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

and when [S] is large, the V*

$$V^* = K_0[E_0]$$

$$= \frac{V[S]}{[S] + K_m}$$

For [S], the N concentration was adjusted to 3.97 ～ 4.02% in RM_a ～ RM_d as shown in Table 6, and for [E], bacteria of almost an equal number was inoculated, and the reaction was carried out at 55°C with intermittent stirring stated before.

The molecular weight of each of the series after 24 and 72 hours were obtained by elementary analysis as follows:

$1D_a$ 338, $1D_b$ 313, $1D_c$ 345, $1D_d$ 303;
$3D_a$ 333, $3D_b$ 248 $3D_c$ 330 $3D_d$ 266.

From these data and those in Table 10, the rates of molecular weight change against the time and hence the reaction rate constants were calculated as shown in Table 12, and Fig. 11. The change in the RM_a system was too small, the reactions were of the first order in the RM_b, RM_c, and RM_d, systems, and the reaction rate constants calculated are as follows:

$$K_b = \frac{0.185}{100 \times 60 \times 60} \times 2.303 = 1.18 \times 10^{-6} sec^{-1}$$

$$K_c = \frac{0.06}{100 \times 60 \times 60} \times 2.303 = 0.38 \times 10^{-6} sec^{-1}$$

$$K_d = \frac{0.15}{100 \times 60 \times 60} \times 2.303 = 0.95 \times 10^{-6} sec^{-1}$$

Thus, the result $K_b > K_d > K_c$ shows that the activity of the bacteria is in the order of b, d, c.

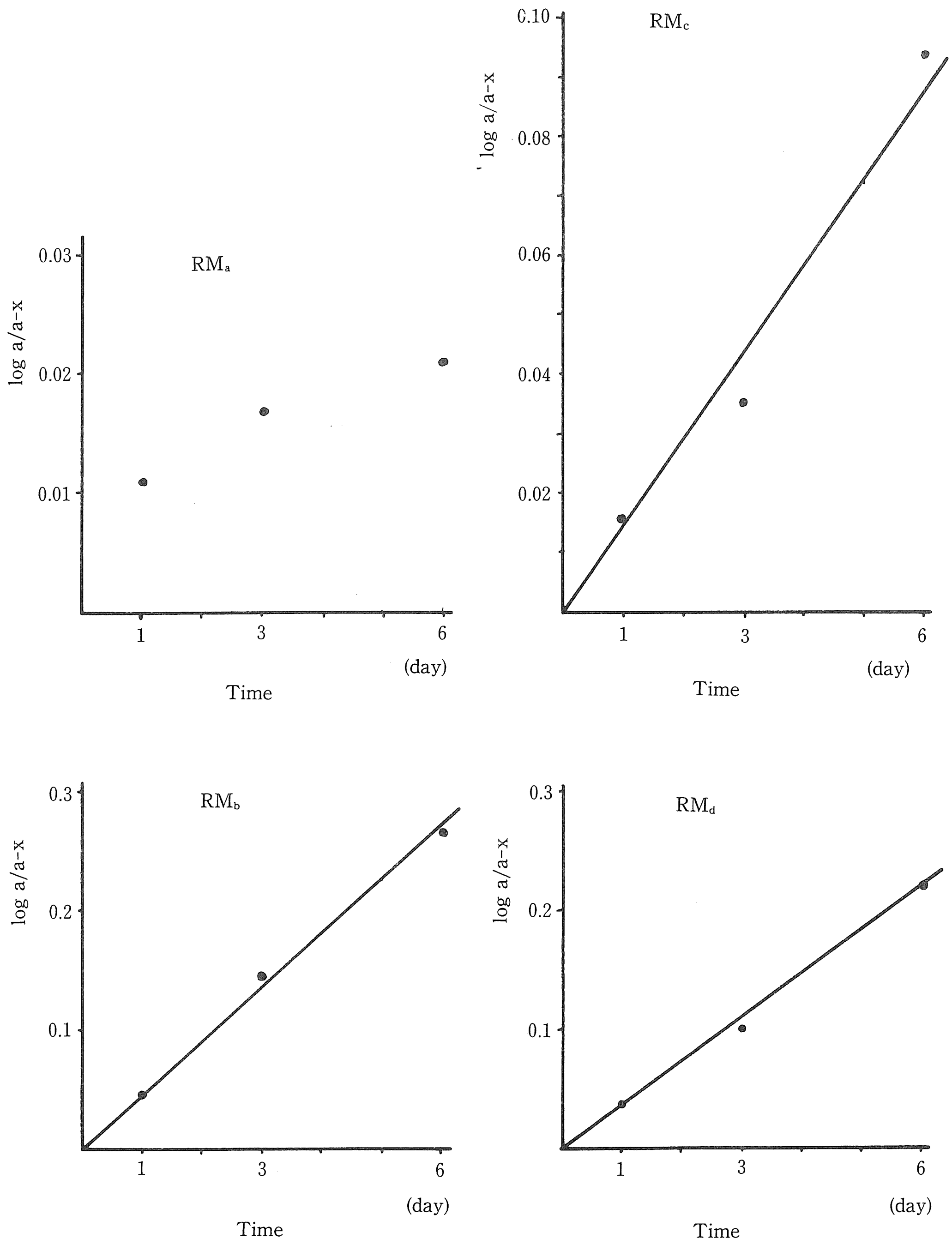


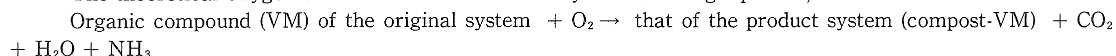
Fig 11 Reaction velocity (RM_a, RM_b, RM_c, RM_d System)

Table 12 Reaction velocity of each systems

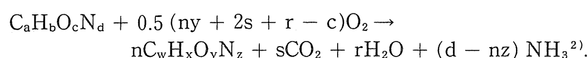
RM_a system				
Time (hr)	O(RM_a)	24($1D_a$)	72($3D_a$)	144($6D_a$)
Decrease (x)	0	8	13	16
Remain (a-x)	346	346- 8	346-13	346-16
Log a/a-x		0.011	0.017	0.021
RM_b system				
Time (hr)	O(RM_b)	24($1D_b$)	72($3D_b$)	144($6D_b$)
Decrease (x)	0	33	98	159
Remaim (a-x)	346	346-33	346-98	346-159
Log a/a-x		0.044	0.145	0.268
RM_c system				
Time (hr)	O(RM_c)	24($1D_c$)	72($3D_c$)	144($6D_c$)
Decrease (x)	0	13	28	70
Remain (a-x)	358	358-13	358-28	358-70
Log a/a-x		0.016	0.035	0.094
RM_d system				
Time (hr)	O(RM_d)	24($1D_d$)	72($3D_d$)	144($6D_d$)
Decrease (x)	0	28	69	135
Remain (a-x)	335	335-28	335-69	335-135
Log a/a-x		0.038	0.101	0.224

3.4 Theoretical oxygen demand for the reaction

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



Organic compound (VM) of the original system $+ O_2 \rightarrow$ that of the product system (compost-VM) $+ CO_2 + H_2O + NH_3$



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

$C_aH_bO_cN_d$: 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 system is calculated;

For the RM_a-$6D_a$ system,

	molecular formula	molecular weight	organic compound (g-VM)
RM_a	$C_{13}H_{16}O_{10}N$	346	115.36
$6D_a$	$C_{13}H_{16}O_9N$	330	103.48

$a = 13,\ b = 16,\ c = 10,$ and $d = 1,$

$w = 13,\ x = 16,\ y = 9,$ and $z = 1.$

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

$M = 115.36/346 = 0.33$

$n = 103.48/(0.33 \times 330) = 0.95$

$r = 0.5\,[16 - (0.95 \times 16) - 3(1 - 0.95 \times 1)\,] = 0.33,$

$S = 13 - 0.95 \times 13 = 0.65.$

The oxygen demand (O_a),

$O_a = 0.5\,[\,(0.95 \times 9) + (2 \times 0.65) + 0.33 - 10]\,(0.33)\,(33)$

$= 0.95.$

The material balance,

The original (VM)	115.36 g	The product (VM)	103.48 g
Oxygen	0.95	Carbon dioxide	9.44
		Water	1.96
Total	116.31	Ammonia	0.28
		Total	115.16

For the RM_b-$6D_b$ system,

	molecular formula	molecular weight	organic compound (g-VM)
RM_b	$C_{13}H_{16}O_{10}N$	346	150.89
$6D_b$	$C_7H_9O_5N$	187	81.46

a = 13, b = 16, c = 10, and d = 1,
w = 7, x = 9, y = 5, and z = 1.

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

$M = 150.89/346 = 0.44$
$n = 81.46/(0.44 \times 187) = 0.99$
$r = 0.5\,[16 - (0.99 \times 9) - 3(1 - 0.99 \times 1)\,] = 3.53$
$s = 13 - 0.99 \times 7 = 6.07.$

The oxygen demand (O_b),

$O_b = 0.5\,[\,(0.99 \times 5) + (2 \times 6.07) + 3.53 - 10]\,(0.44)\,(32)$
$= 74.76$

The material balance,

The original (VM)	150.89 g	The product (VM)	81.46 g
Oxygen	74.76	Carbon dioxide	117.52
		Ammonia	0.07
Total	225.65	Water	27.96
		Total	227.01

For the RM_c-$6D_c$ system,

	molecular formura	molecular weight	organic compound (g-VM)
RM_c	$C_{14}H_{16}O_{10}N$	358	136.04
$6D_c$	$C_{11}H_{14}O_8N$	288	107.50

a = 14, b = 16, c = 10, and d = 1,
w = 11, x = 14, y = 8, and z = 1.

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

$M = 136.04/358 = 0.38$
$n = 107.50/(0.38 \times 288) = 0.98$
$r = 0.5\,[16 - (0.98 \times 14) - 3(1 - 0.98 \times 1)\,] = 1.11$
$s = 14 - 0.98 \times 11 = 3.22.$

The oxygen demand (O_c),

$O_c = 0.5\,[\,(0.98 \times 8) + (2 \times 3.22) + 1.11 - 10]\,(0.38)\,(32)$
$= 32.77.$

The material balance,

The original (VM)	136.04 g	The product (VM)	107.50 g
Oxygen	32.77	Carbon dixide	53.84
		Ammonia	0.13
Total	168.81	Water	7.59
		Total	169.06

For the RM_d-$6D_d$ system,

	molecular formula	molecular weight	organic compound (g-VM)
RM_d	$C_{12}H_{17}O_{10}N$	335	150.29
$6D_d$	$C_8H_{10}O_5N$	200	87.88

$a = 12$, $b = 17$, $c = 10$, and $d = 1$,
$w = 8$, $x = 10$, $y = 5$, and $z = 1$.

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

$$M = 150.29/335 = 0.45$$
$$n = 87.88/(0.45 \times 200) = 0.98$$
$$r = 0.5\,[17 - (0.98 \times 10) - 3(1 - 0.98 \times 1)] = 3.57$$
$$s = 12 - 0.98 \times 8 = 4.16$$

The oxygen demand (O_d),

$$O_d = 0.5\,[(0.98 \times 5) + (2 \times 4.16) + 3.57 - 10]\,(0.45)\,(32) = 48.89$$

the material balance,

The original (VM)	150.29 g	The product (VM)	87.88 g
Oxygen	48.89	Carbon dioxide	82.37
		Ammonia	0.15
Total	199.18	Water	28.27
		Total	198.67

Thus, the theoretical oxygen demand calculated as above are,

a series (no cluster)	4.0 ml/hr-100g-VM
b series cluster	240.8 〃
c series cluster	117.1 〃
d series cluster	158.2 〃

Then, the order is in

$$O_b > O_d > O_c > O_a.$$

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

$$b > d > c.$$

According to Jeris experiment[3] with a practical apparatus in the presence of an excess oxygen, the oxygen demand was 400 ～ 1400ml/hr-100g-VM, the lowest limit being twice as much as the present one. Therefere, the degree of the present composting is about a half of the maturation, and agrees well with the result from the enthalpy change.

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 larger 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	$\Delta H_c \geqq \Delta H_b > \Delta H_d > \Delta H_a$,
the reaction rate constant	$K_b > K_d > K_c > K_a$, and
the oxygen demand	$O_b > O_d > O_c > O_a$,

the order of activity of cluster should be

$$b > d > c,$$

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.

References

1) H. Kubota Report : Tokyo Institute of Technology (1977).
2) Linvil G. Rich : Unit process of Sanitary engineering, Toppan Print Co., Japan (1961).
3) Jeris, J. S., Regan, R. W. : Compost Science, Jan-Feb., 10 (1973).
4) M. M. Kononov : Organicheskoe Veshestvo Tschvy (1963).