A STUDY FOR THE DEVELOPMENT OF NEW COMPOUND GASIFICATION PROCESS OF WASTE PLASTICS AND SLUDGE

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ABSTRACT

A conventional gasification process of waste polyvinyl chloride (PVC) has a serious problem of producing a poisonous hydrogen chloride (HCl) which causes corrosion of a reactor wall or a heat exchanger. On the other hand, a gasification of a drainage sludge is sometimes meaningless since a calorific value of the produced gas is too low to be used as a gas fuel. In order to solve these problems, a new compound gasification process in which PVC and dry sludge are mixed and gasified together in the fluidized bed was proposed and tested by using a small scale fluidized bed. The important results were as follows:

1) Hydrogen chloride gas (HCl) from PVC was significantly removed by slaked lime in the sludge when mole ratio of slaked lime to HCl was 5:1 in the bed. A slaked lime is often added to the sludge as a flocculant in the desiccation process.

2) A calorific value of produced gas from PVC was 6000 to 7000 Kcal/Nm^3 whilst that from sludge was around 2000 Kcal/Nm^3 without slaked lime and 4000 to 5000 Kcal/Nm^3 with slaked lime in the gasification temperature between 600°C to 800°C.

Introduction

In Japan, 300,000 tons of waste polyvinyl chloride (PVC) is generated every year. This waste PVC is partly converted to gas fuel by gasification process. However, a conventional gasification process of waste polyvinyl chloride (PVC) has a serious problem of producing a poisonous hydrogen chloride (HCl) which causes corrosion of a reactor wall or a heat exchanger. HCl gas also causes air pollution if it is purged to atmosphere. Therefore, removal technology of HCl by wet or dry method is urgently required.

On the other hand, 150 million m^3 of waste drainage sludge is generated every year from the drainage disposal station. Disposal of these great amount of waste sludge is another serious problem. At the present stage, this waste sludge is partly burnt by an incinerator. However, burning of sludge usually needs an aid fuel since sludge itself is a low calorific value. Additionally, it sometimes causes emissions of NO_X, SO_X, particles and heavy metals such as Pb, Hg and Cd.

In order to solve these problems, we propose a new process called "Compound Gasification Process of Waste PVC and Sludge." Waste drainage usually includes slaked lime which is added as the cohesion agent in the dehydration process and also it includes nitrogen compound which would be mostly converted to NH_3 in the gasification process. So that, it can be expected that HCl from PVC would be

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catched by slaked lime as the form of $CaCl_2$ and residual HCl might be catched by NH_3 as the form of NH_4Cl. Furthermore, medium calorific value gas of 3000 to 4000 Kcal/Nm^3 can be expected to be produced from this compound gasification process as high calorific value gas from PVC is mixed with low calorific value gas from sludge. Besides, oxides of sulphur (SOx) can be absorbed as the form of $CaSO_3$ by quick lime (CaO).

The purpose of this study is to investigate the possibilities of this new process which is expected to have many advantages as described above. The fundamental experimental work of PVC carbonization, sludge gasification and PVC-sludge compound gasification were carried out by using a small scale high temperature fluidized bed. Amounts of produced gas, char, tar and emissions of HCl, NH_3 were measured. The dechlorination effect by compound gasification was investigated experimentally. Finally, an enthalpy analysis of the compound gasification process was carried out.

1. EXPERIMENTAL APPARATUS AND METHOD

In these experiments PVC tips and dry sludge particles were gasified in a bed of microspherical alumina particles fluidized by nitrogen gas with a constant flow rate.

The flow sheet of experimental system is shown in Fig. 1. The fluidized bed used for gasification has the scale of 37 mm inner diameter and 160 mm bed height. The bed temperature can be controlled by an electrical furnace in the temperature range from 400°C to 1000°C. Nitrogen from a nitrogen cylinder was supplied via the steam generator and controller into the bottom of the reactor to act as the fluidizing gas. Air used for combustion of char was supplied from the compressor. Water content in the fluidizing gas can be varied from 0% to 12% by the steam controller where saturated water vapour in nitrogen gas could be changed by temperature. The gaseous product, including tars, flowed into a gas bag though a cold trap followed by a gas cleaner. The tar and NH_3 were removed in a cold trap. The residual NH_3 and HCl were removed in a gas cleaner.

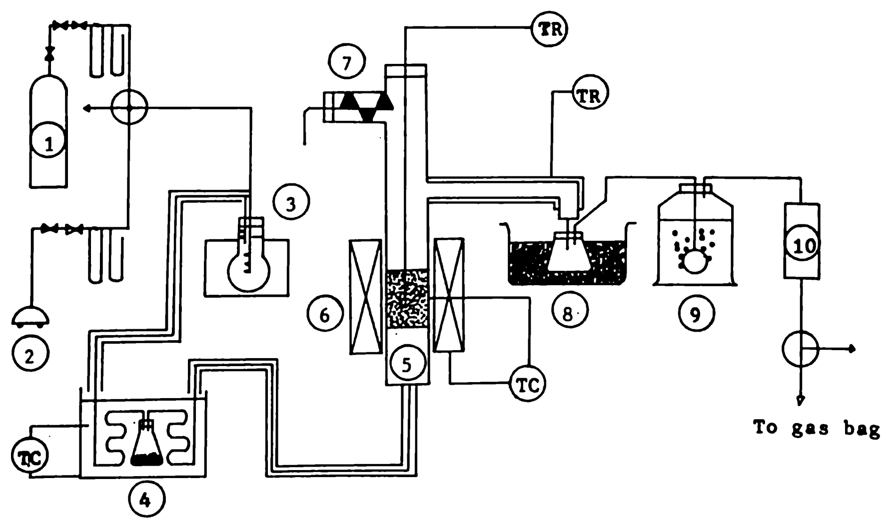
The size, proximate analysis and ultimate analysis of PVC and sludge employed for experiments were shown in Table 1. In addition to sample shown on Table 1, 30 wt% of slaked lime was added to the sample sludge in some experimental runs as slaked lime is often used as the cohesion precipitation agent in the dehydration process of sludge[1] and it was expected to contribute to the reduction of HCl from PVC. The amount of slaked lime added to a sludge in the actual drainage treatment station is 5 to 50 wt% and averagely 20 wt% based on dry sludge.

The experimental conditions such as gasification temperature, feed rate, etc. are given in Table 2. All of the PVC tips or the dry sludge particles were fed into the fluidized bed within the first two minutes. So the gasification of the tips or the particles was batchwise as far as the solid materials were concerned whereas the operation of the fluidized bed was at a steady state.

The concentration of each produced gas in the gas bag was measured by a gas chromatography of the thermal conductance detector type. The volumetric amount of each gas produced from the unit biomass material can be calculated as follows,

$$V_A = \frac{V_{N_2} C_A}{100 - C_A}$$

where V_{N_2} is the volumetric amount of nitrogen which is used as the fluidizing gas and flows into the gas bag during the sampling. V_{N_2} can be measured by gas meter prior to entering the fluidized bed. C_A is the concentration of A species in the gas bag. To measure the char left behind, combustion of the char particles in the fluidized bed was carried out by introducing air into the fluidized bed instead of N_2. Then the amount of char was estimated by measuring the total amount of CO_2 in the flue gas. The amount of tar formed was found as the difference between the weight of the cold trap at the beginning and end of each trial. As the lime to the cold trap was heated at 250°C by ribbon heater, the amount of tar which was liquefied under 250°C could be measured. An amount of HCl gas emitted from the gasification of PVC was measured by analyzing Cl^- in the gas cleaner, assuming that HCl was completely dissociated to H^+ and Cl^-. The quantitative analysis of Cl^- was carried out by titration method using silver nitrate. An amount of NH_3 formed from the gasification process of sludge was measured by analyzing NH_3 in the gas cleaner with ion electrode. Prior to experiments, it was confirmed that HCl and NH_3 was completely absorbed into the cleaner liquid as any trace of HCl and NH_3 was not detected from the 2nd cleaner of the two series cleaners. The glass electrode with pH meter was used for the measurement of pH of the cleaner liquid.



1. Nitrogen cylinder
2. Air compressor
3. Steam generator
4. Steam controller
5. Fluidized bed
6. Electric furnace
7. Feeder
8. Cold trap
9. Gas cleaner
10. Glass wool packed bed

Fig. 1 FLOW SHEET

Table 1

Size, proximate analysis and ultimate analysis of PVC and sludge

	PVC	Sludge
Particle diameter	ϕ3 X 5 mm	ϕ5 mm
Moisture	0 wt%	5.6 wt%
Element analysis		
Ash	0 wt%	70.4 wt%
C	40.1 wt%	17.7 wt.%
H	5.5 wt%	3.1 wt.%
Cl	52.0 wt.%	
N		2.6 wt.%

Table 2

Experimental condition

PVC & Sludge feed rate	1.5g/min
N_2 Gas feed rate	1.01/min
Gasification temperature	400, 600, 800, 1000°C
Fluidized bed size	
inner diameter	ϕ37 mm
bed height	160 mm
mean particle diameter	300μm

2. EXPERIMENTAL RESULTS AND DISCUSSIONS

2-1 Characteristics of PVC Carbonization

Prior to the compound gasification, carbonization of pure PVC was carried out. The yield of gas, tar and char, composition of produced gas and emission of HCl were measured.

First, the formation yields of gas, tar and char at each carbonization temperature from 400°C to 1000°C were shown in Fig. 2. The gas yield was increased as the temperature was increased. The tar yield was slightly decreased as the temperature was increased. Here, Tar 1 which is liquefied under 250°C was measured from the weight change of cold trap. Tar 2 which was liquefied over 250°C was calculated from mass balance. Total tar yield was still high even in the high temperature range of 800°C to 1000°C. High yield of tar which is not favourable for the purpose of gasification can be explained as follows. The destruction energy of c-c bond in the constitution polymer of PVC is high. As the result, hydrocarbon higher than C_6 which is the main constituent of tar might be left behind after gasification. Accordingly, the gasification efficiency of this carbonization process becomes low compared with a partial oxidation process or steam cracking process where oxygen and hydrogen source are obtained from the fluidized gas. However, the gasification efficiency would be improved by the compound gasification with sludge as hydrogen and water can be given from the gasification of sludge. Furthermore, the gasification efficiency can be improved by increasing the residence time of produced gas in the high temperature region as the higher hydrocarbons in the produced gas would be cracked and changed to lower hydrocarbons in the high temperature region.

The composition and calorific value of produced gas is shown on Table 3. The calorific value was relatively high compared to sludge since the proportion of hydrocarbon, for example CH_4 was high.

Next, an emission of HCl in the carbonization temperature between 400°C to 1000°C was shown in Fig. 3. Although, an emission of HCl was slightly increased as the carbonization temperature became high, the level was kept in the zone between 1.0×10^{-2} and 1.1×10^{-2} even if the temperature was increased up to 1000°C. The conversion from chlorine originally included in the PVC to HCl which was calculated from HCl absorbed in the gas cleaner was 70 to 80%. However, the previous study[2] shows that dechlorination of PVC takes place at two stages – first at around 300°C and second at 450°C and final conversion rate reaches 100% in the temperature above 600°C. So that, another 20 to 30% chlorine might be left in the tar.

2-2 Dechlorination Effect by Slaked Lime

Slaked lime was introduced into the fluidized bed of PVC carbonization to investigate the dechlorination effect by slaked lime. The result was shown in Fig. 4. The horizontal axis indicates mixing mole ratio of introduced slaked lime to HCl converted from PVC which was estimated from the previous experimental data of Fig. 3. The vertical axis shows the residual HCl in the product gas after introduction of slaked lime. The result shows that the level of residual HCl became lower as mole ratio of slaked lime to HCl was increased. When mole ratio of slaked lime to HCl

Table 3

Volume and calorific value of gas produced from PVC

Bed Temp. (°C)	Volume of gaseous products (ml/g-net)								Gross Calorific Value (Kcal/Nm³)
	H_2	CO	CH_4	C_2H_4	C_2H_6	C_3H_6	CO_2	Total	
600	21	14	13	5	4	3	13	73	7000
800	66	49	35	15	2	2	26	195	5800
1000	179	92	41	6	0	0	33	351	4200

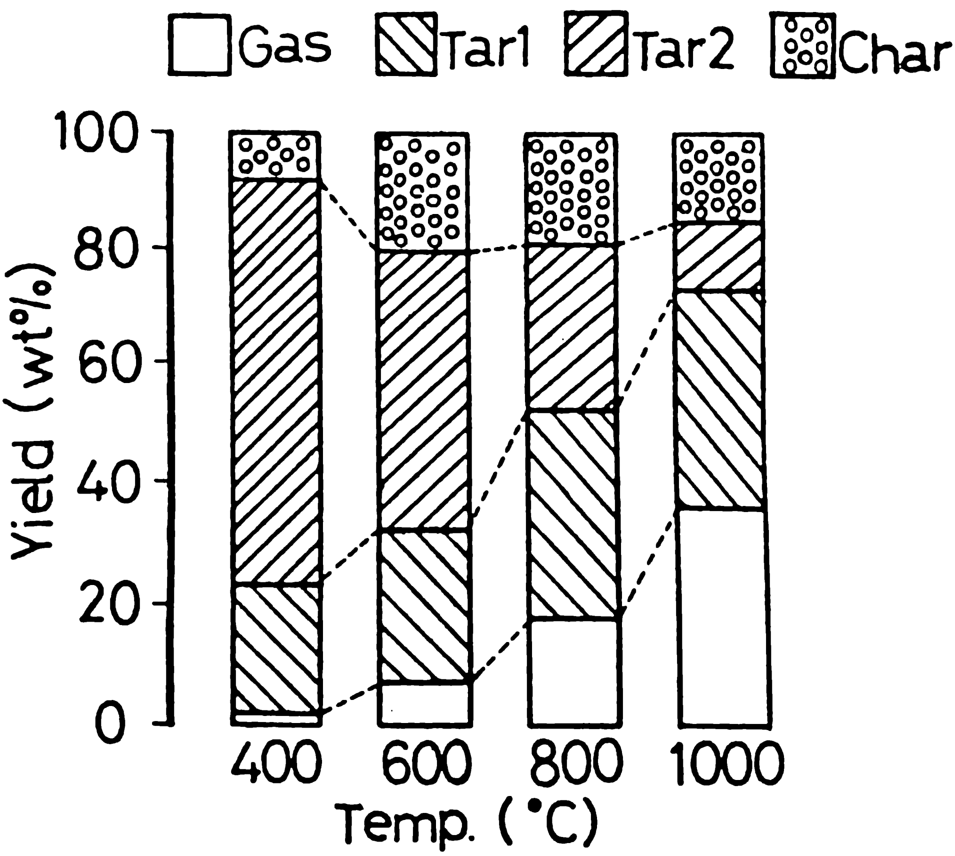


Fig. 2 Ratio of yields of gas, char and tar at each carbonization temperature for PVC

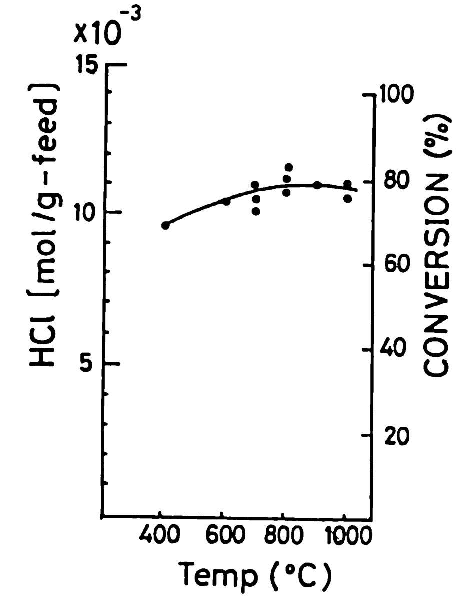


Fig. 3 Emission of HCl from PVC carbonization

went up to 5, no HCl was detected in the product gas (The limit of detection was 5 X 10^{-4} mol).

From above results, it could be shown that dechlorination effect by slaked lime was quite significant.

It was indicated by Kubota[3] that reduction rate of HCl has the limit from the reaction equilibrium when CO_2 and H_2O coexist in the product gas. However, the reduction rate of HCl in the carbonization process is expected to become high since the concentration of CO_2 and H_2O in the product gas are relatively low compared with combustion process.

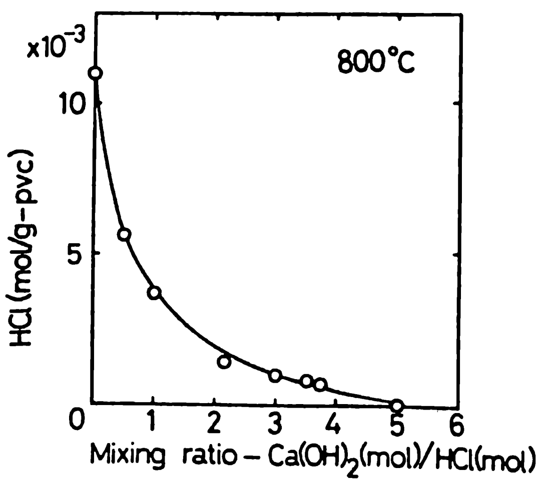


Fig. 4 Dechlorination effect by slaked lime

2-3 Gasification of Sludge

The yields of gas and char were measured when the gasification of sludge took place in the temperature range from 600°C to 1000°C. Water vapour in the fluidized gas was varied from 0 to 12%. This figure was based on the previous result[4] obtained from the continuous fluidized gasification of dry sludge (10% H_2O) when the maximum concentration of water vapour was 20%.

The result was shown in Fig. 5. The gas yield was increased as the gasification temperature was increased. The effect of water vapour was significant at 600°C. Both gas and char yield was decreased as the concentration of water vapour was increased. According to an analysis of produced gas composition, the decrease of gas yield corresponds to the decrease of CO and CO_2. These results suggest that yield of tar was increased by an addition of water vapour.

When slaked lime was introduced into the sludge, the gas yield at 600°C and 800°C was significantly reduced. This was because CO_2 was absorbed by CaO through the reaction $CO_2 + CaO \rightarrow CaCO_3$. However, since the direction of this reaction is reversed as $CaCO_3 \rightarrow CaO + CO_2$ at around 900°C, the gas yield was not increased by adding slaked lime at 1000°C.

The volume and the calorific value of produced gas was shown on Table 4. It went up to 3000-5000 Kcal when slaked lime was added into sludge whilst sludge without slaked lime produced only 2000 Kcal/Nm^3 calorific value gas. Usually the calorific value of produced gas from partial oxidation process is under 1000 Kcal/Nm^3. This is due to the dilution effect by nitrogen in air.

An emission of NH_3 from the sludge gasification was shown in Fig. 6 at each temperature. The vertical line shows an emission of NH_3 and also the conversion from nitrogen in the sludge to NH_3. The emission of NH_3 was significantly increased by adding slaked lime. This result suggest that slaked lime accelerates alkaline hydrolysis of protein in the sludge. The effect of water vapour on the formation of NH_3 was not significant until the concentration of water vapour becomes 10%. However, according to the previous experiment[4] where 100% steam was used in the gasification of sludge, the conversion rate from nitrogen compound in the sludge to NH_3 was over 50%, so that, some increase might be expected when the concentration of water vapour becomes high.

Next, pH of the gas cleaner liquid of produced gas was shown in Fig. 7. The effect of water vapour in the fluidized gas and that of slaked lime were shown in the same figure. Both water vapour in the fluidized gas and slaked lime increased pH level. This result correspond to that in Fig. 6 where the formation of NH_3 was increased by H_2O and slaked lime. If NH_3 formed in the gasification process of sludge was absorbed into the neutrality water, the level of pH should become 10.1 – 10.3. However, the highest pH actually observed was under 9.5. The pH level might be decreased as the result that organic compound of the sludge changed to an organic acid in the cleaner liquid. This result indicates the difficulty of neutralyzing HCl from PVC only by NH_3 from sludge without slaked lime.

Table 4

Volume and calorific value of gas produced from sludge*

Bed Temp. (°C)	Volume of gaseous products (ml/g-net)								Gross Calorific Value (Kcal/Nm³)
	H_2	CO	CH_4	C_2H_4	C_2H_6	C_3H_6	CO_2	Total	
600	2 (9)	11 (3)	1 (2)	1 (0)	0 (0)	0 (0)	37 (1)	52 (15)	1650 (5180)
800	10 (38)	24 (8)	5 (4)	4 (2)	1 (1)	1 (1)	67 (15)	112 (69)	2620 (3980)
1000	21 (59)	40 (45)	9 (13)	7 (8)	0 (1)	1 (1)	72 (83)	150 (210)	2000 (3280)

*The figures in bracket show the result in the case of 12% steam in N_2 and 30% slaked lime in the sludge while the figures without brackets show the result of pure sludge gasification.

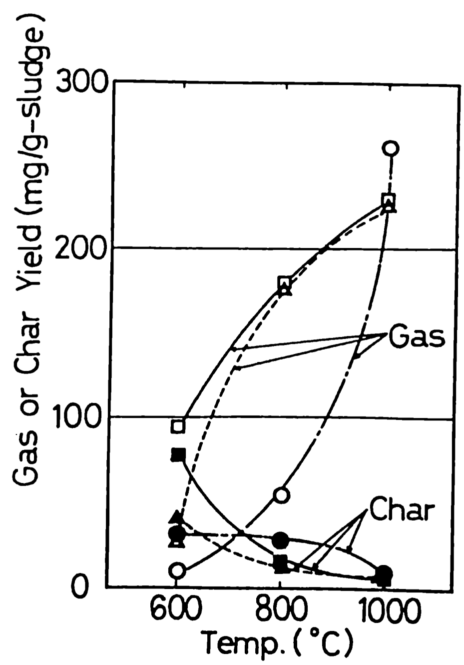


Fig. 5 Yield of gas, tar and char at each gasification temperature for sludge

□■ N_2 △▲ N_2 + 12% Steam
○● N_2 + 12% Steam and Sludge + 30 wt% $Ca(OH)_2$

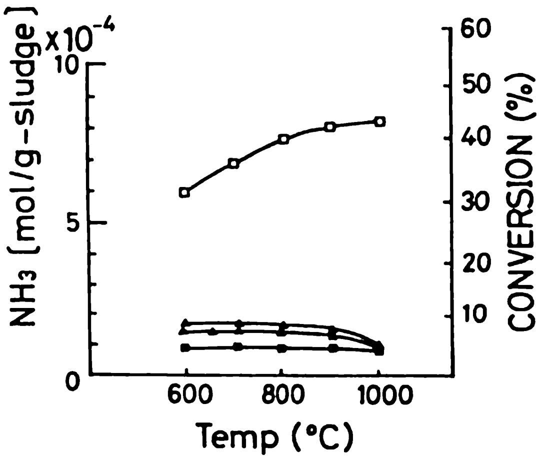


Fig. 6 Emission of NH_3 from sludge gasification

■ N_2 ▲ N_2 + 7% Steam
△ N_2 + 12% Steam
□ N_2 + 12% Steam and Sludge + 50 wt% $Ca(OH)_2$

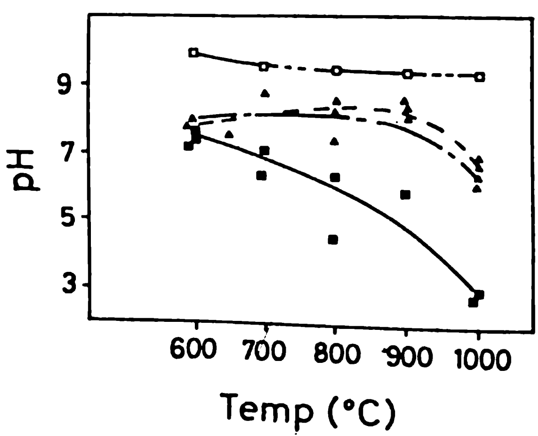


Fig. 7 pH of gas cleaner liquid for sludge gasification

2-4 Compound Gasification of PVC with Sludge

The characteristics of sludge-PVC gasification in particular dechlorination effect was investigated experimentally. The dechlorination effect by NH_3 from sludge can be expected in addition to that by slaked lime in the compound gasification process. The mixing ratio of sludge to PVC being changed, two stage dechlorination effect by NH_3 and slaked lime was investigated by measuring pH level and $NH_4^+ Cl^-$ concentration of the cleaner liquid which was put after the fluidized bed. The result was shown in Fig. 8. In this experiment, the mole ratio of Ca to HCl was kept constant even if mixing ratio of sludge to PVC was changed as the main purpose of this experiment was to know the dechlorination effect by NH_3. As the mixing ratio of sludge to PVC was increased, pH level of the cleaner liquid approached neutral point and the quantity of chlorine catched by NH_3 was increased. This result shows that by controlling PVC-sludge mixing ratio, the level of HCl in the produced gas can be reduced and the cleaner liquid can be purged without pH adjustment.

As far as the calorific value of produced gas are concerned, the produced gas from the compound gasification process has higher calorific value compared with that from sludge. This is because a high calorific value gas from PVC is mixed with that from sludge. In the actual process, it is hard to select only PVC from other plastics so that higher calorific value plastics such as polyethylene and polystylene co-exist with PVC. As the result, it can be expected that the calorific value of produced gas would be improved furthermore in the actual process.

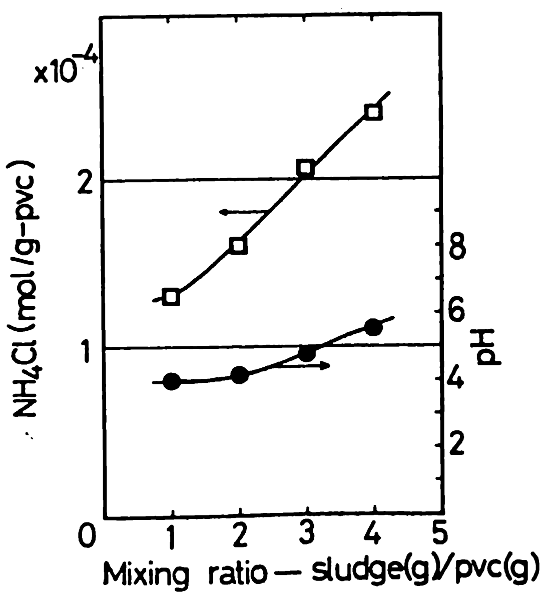


Fig. 8 pH of gas cleaner liquid for sludge -PVC compound gasification

3. ENTHALPY ANALYSIS OF COMPOUND GASIFICATION PROCESS

Finally, enthalpy analysis of the compound gasification process of waste plastics and sludge was carried out to check whether heat required for carbonization can be satisfied by the combustion heat of char. The basic equation for analysis which one of the authors[5] developed on the basis of oxygen, hydrogen, carbon and enthalpy balances is as follows.

$$V_{H_2} + V_{CO} + \Sigma V_{C_iH_j}(Q_{C_iH_j}/Q_w)$$

$$= 0.3279(Q_g^*/1000)[(\alpha + \beta + \omega) - (\gamma + \delta)] \quad (1)$$

where,

$V_{C_iH_j}$: cubic meters of hydrocarbon produced at standard state based on unit Kg of feed stock [Nm^3/Kg]

V_{CO}, V_{H_2} : cubic meters of carbon mono-oxide and hydrogen produced at standard state respectively based on unit Kg of feed stock [Nm^3/Kg]

$Q_{C_iH_j}, Q_w, Q_c$: heat of combustion for hydrocarbon, hydrogen, carbon [Kcal/Kg·mol]

Q_g^* : gross calorific value of feed stock [Kcal/Kg]

α : $1 - 7838C(1-\eta_c)/Q_g^*$

C : weight fraction of carbon in feed stock

η_c : carbon efficiency

β : ratio of amount of preheat referring to gross calorific value of
δ feed stock

γ : ratio of heat amount in exist gas including latent heat of vaporiza-
ω tion referring to gross calorific value of feed stock

δ : ratio of heat-loss referring to gross calorific value of feed stock

ω : ratio of heat input referring to gross calorific value of feed stock

In the above equations, $V_{C_iH_j}$, V_{CO}, V_{H_2}, α and γ can be obtained from the experimental result. $Q_{C_iH_j}$ and Q_w can be obtained from the thermodynamic data and Q_g of PVC and sludge were obtained from literature.[6-7] Furthermore, one can put $\beta = 0$ when air and material are not preheated and $\delta = 0$ for the case of no heat loss through the reactor wall. By substituting these values into Eq. (1) one can calculate ω which corresponds to heat input based on the unit amount of feed stock.

The results were shown on Table 5. The columns from No. 1 to No. 3 on Table 5 shows the result for the case of compound gasification where PVC to sludge ratio is 1:2. The columns from No. 4 to No. 6 shows the result for the case of pure sludge gasification. For the former case, the heat required for the gasification H_a can be satisfied by heat of char combustion H_b when gasification temperature was under 800°C whilst it could not be satisfied when the gasification temperature comes up to 1000°C. On the other hand, heat of char combustion was not sufficient in all temperature zone for the gasification of the pure sludge.

These results show an additional advantages of the compound gasification compared with the pure sludge gasification.

Table 5

Enthalphy analysis of compound gasification process

No.	1	2	3	4	5	6
Temp. (°C)	600	800	1000	600	800	1000
L.H.S.	0.0894	0.325	0.620	0.0793	0.258	0.654
Qg*	5100	5100	5100	5300	5300	5300
C	0.52	0.52	0.52	0.52	0.58	0.58
η	0.76	0.89	0.96	0.90	0.90	0.99
a	0.81	0.91	0.97	0.91	0.91	0.99
ϵ	0.65	0.59	0.52	0.95	0.88	0.65
γ	0.15	0.19	0.30	0.12	0.14	0.14
δ	0	0	0	0	0	0
ω	0.045	0.074	0.230	0.21	0.26	0.19
H_a	230	380	1200	1100	1400	1000
H_b	1800	860	280	820	780	90
	$H_a < H_b$	$H_a < H_b$	$H_a > H_b$	$H_a > H_b$	$H_a > H_b$	$H_a > H_b$

L.H.S.: Left hand side of Eq. (1)
Ha: Heat required for the gasification [K cal/kg]
Hb: Heat obtained by combustion of residual char based on unit amount of feed stock [K cal/kg]

Conclusion

A new compound gasification process in which PVC and dry sludge are mixed and gasified together in the fluidized bed was proposed and tested by using a small scale fluidized bed. The important results were as follows.

1) Hydrogen chloride gas (HCl) from PVC was significantly removed by slaked lime in the sludge when mole ratio of slaked lime to HCl was 5:1 in the bed. A slaked lime is often added to the sludge as a flocculant in the desiccation process.

2) A calorific value of produced gas from PVC was 4000 to 7000 Kcal/Nm^3 whilst that from sludge was around 2000 Kcla/Nm^4 without slaked lime and 4000 to 5000 Kcal/Nm^3 with slaked lime in the gasification temperature between 600°C to 800°C.

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