Research on Gasification and Power Generation from Waste Paint Dregs^{*}

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Abstract

In this study, the pyrolysis characteristic of waste paint dregs has been investigated by comparing with wood chips at 500°C, 700°C and 900°C with a laboratory-scale reactor. The results showed that the gaseous yield significantly increased for waste paint dregs than that for wood chips with increase of pyrolysis temperature. Therefore, it is possible to gasify waste paint dregs like wood chips at high temperature to obtain efficient combustible gas for a dual-fueled engine. And the behaviors of heavy metals in the waste paint dregs were also investigated. It showed that Pb was volatile, Ti and Zn were non-volatile in the temperature range of 500 °C ~900 °C. Then, demonstration gasification and power generation experiments were carried out by a plant of commercial scale, using waste paint dregs and wood chips as fuel. The results agreed with the laboratory experiments, namely the heating value of pyrolysis gas produced from waste paint dregs increased with increase of gasification temperature, while that produced from wood chips didn't increase significantly with increase of gasification temperature. Pb was also volatile as in the laboratory experiment. The power generator efficiency of the diesel engine was 34% when the energy input ratio of fuel gas produced from waste paint dregs was 60%.

Key words: Waste Paint Dregs, Wood Chips, Gasification, Heavy Metal, Power Generation

1. Introduction

It is required that the industrial structure should be changed from mass consumption and mass disposal to resources recycling, and for the properly disposal and effective use of solid wastes, many companies in Japan are conducting independent efforts. In paint manufacturing industries, development of recycle system for properly disposing waste paint is also conducting. The waste paint consists of liquid ingredient and solid ingredient. The liquid ingredient (solvent) can be separated and recovered virtually by means of high temperature and high vacuum distillation, and can be reused to wash the equipments for paint production⁽¹⁾. However, there is no method of reusing and recycling the solid ingredient (waste paint dregs). At present, almost all the waste paint dregs are disposed by landfill, but the residual capacity of landfilling areas in Japan is decreasing, so it is urgent to establish method of recycling the solid waste paint dregs.

The waste paint dregs consist of the resins and the pigments. The resins can be recycled by means of thermal recycle due to their combustible characteristics. But it is not suitable to recycle the waste paint dregs by means of co-combustion and heat recovery by using large-scale incinerators, because there are many heavy metal components in the pigments which are needed to be managed properly. As rare heavy metals are included in the

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pigments, it is desired that they will be recycled at the site they are produced together with recycling of the heavy metals. Installing small-scale incineration apparatus inside the factory to recover and utilize the heat is one of methods of the thermal recycling, but the development of gasification and power generation is more attractive because higher power generation efficiency is expected comparing with the combustion process.

However, there are several problems remained for the commercial application of gasification and power generation for waste paint dregs. For example, no previous studies about the gasification behavior of waste paint dregs are found; there are no guidelines about gasification behavior and optimal operation conditions; there is no power generation report by using the gasification gas of waste paint dregs. Further, there are many studies about behavior of heavy metals in sludge⁽²⁾⁻⁽⁵⁾, coal⁽⁵⁾⁻⁽⁸⁾, and biomass⁽⁹⁾⁻⁽¹²⁾, but no reports about behavior of heavy metals in waste paint dregs are found.

In this study, the pyrolysis characteristics of waste paint dregs and the volatility characteristics of the heavy metals contained in waste paint dregs have been investigated using a laboratory-scale reactor. Furthermore, gasification and power generation experiments of waste paint dregs and heavy metal volatility were investigated using a two-staged gasification plant of 50 kg/hr scale, STAR-MEET system (STeam/Air Refroming type Multi-staged Enthalpy Extraction Technology).

2. Experimental

2.1 Waste Paint Dregs Sample

In this study, waste paint dregs discharged from an actual paint production factory was used for the experimental sample. The resins and pigments in the waste paint dregs mainly consist of alkyd resin and melamine resin (Fig.1) and heavy metals, respectively⁽¹⁾. The property of the waste paint dregs is shown in Table 1. In this study, experiments of a wood chips (Table 1) were also performed to compare with the gasification characteristic of waste paint dregs.

Table 1. Properties of waste paint dregs and wood chips

		Paint dregs	Wood chips
	Unit	Value	
Proximate analysis			
Volatile	wt%*	59.8	83.8
Fixed carbon		5.0	14.1
Ash		35.2	2.1
HHV	MJ/kg*	26.2	17.8
Ultimate analysis			
C	wt%**	61.1	48.1
H		7.4	6.7
N		2.8	0.2
O		28.5	44.7
S		<0.1	<0.2
Cl		0.2	<0.1

(* : d.b , ** : d.a.f)

Fig.1 Typical molecular structures of resins in waste paint dregs

(a) Alkyd resin (b) Melamine resin

The composition of ash (pigments) in waste paint dregs is shown in Table 2. Table 2 indicates that the main component of heavy metals in waste paint dregs is TiO_2 , and 4.5% of Pb is also included.

2.2 Lab Scale Experimental Setup

Experimental Apparatus and Procedure

To investigate the basic gasification characteristic of waste paint dregs, an externally heated small fixed bed reactor was used (Fig.2) by simulating the gasification/pyrolysis atmosphere of the actual fixed bed gasifier. Effects of temperature on the distributions of pyrolysis products (gas, char and tar) of waste paint dregs and on gas production were investigated.

Table 2. Heavy metal contents of waste paint dregs

Heavy metal contents (wt %)			
TiO ₂	12.7	CuO	0.4
CaO	6.7	Cr ₂ O ₃	0.3
PbO	4.5	Al ₂ O ₃	<0.2
Fe ₂ O ₃	3.9	MgO	<0.1
ZnO	3.0	P ₂ O ₅	<0.1
BaO	1.8	NiO	<0.1
SiO ₂	0.5	CoO	<0.1

Fig.2 Lab scale experimental setup

The sample was supplied into the reactor firstly, and then the air in the reactor was displaced by argon gas. Temperature of the reactor was raised by an electric furnace to a target value, after which the experiments were conducted by keeping the reactor temperature constant until the end of the pyrolysis reaction. The analysis methods of gas composition, tar and char were the same as in the previous study⁽¹³⁾. Experimental conditions are shown in Table 3.

Table 3. Laboratory-scale experimental conditions

		Paint dregs	Wood chips
	Unit	Value	
Placed in advance	g	200	150
Flow rate of Ar	L/min	0.4	0.4
Temperature	°C	500	500
		700	700
		900	900

Analysis of Heavy Metals

To clarify the volatile characteristic of heavy metals after experiments, the distributions of heavy metals in the reactor residues, tar collected by tar impingers, and water in tar impingers were measured. The heavy metals in tar and water were measured by a plasma emission spectrophotometer (SPECTRO/ Rigaku CIROS-120EOP), and those in the reactor residues were measured by a X-ray fluorescence spectrometer (Shimadzu XRF-1800).

2.3 Demonstration Apparatus of Gasification and Power Generation STAR-MEET System

To investigate the gasification and power generation characteristics of waste paint dregs, a demonstration apparatus (STAR-MEET) was used whose system flow is shown in Fig.3. Waste paint dregs were continuously supplied from the top of the gasifier and were gasified. In the reformer, tar in the gasification gas from the gasifier reacted with the mixture of high temperature air and steam, and was converted to H₂ and CO. Then the reformed gas was purified by a ceramic filter, a scrubber and an activated carbon absorber. Finally, power generation was performed with a dual-fueled diesel engine by supplying the syngas and light oil as an auxiliary fuel. In this study, the high temperature air supplied into the gasifier was preheated by an electric heater. The mixture of high temperature air and steam supplied into the reformer was heated by heat exchange of combustion gas produced by combusting a part of syngas and small amount of LPG gas. The details about the

apparatus operation, measurement and analysis of samples were described in a previous paper⁽¹⁴⁾. The operational conditions of RUN1 and RUN2 are shown in Table 4.

Fig.3 The flow of the STAR-MEET system

Table4. Operational conditions of the demonstration plant

		RUN1	RUN2
Air(Nm ³ /hr)	Supplied into gasifier	65.7	45
Temperature(°C)		600	300
Air(Nm ³ /hr)	Supplied into reformer	82.6	101
Steam(kg/hr)		10	15
Temperature(°C)		500	150
Reformer Temperature(°C)		800	
Amount of feed material placed in advance(kg)		100	100
Feed rate(kg/hr)		48	50

Dual-Fueled Diesel Engine

The flow rate and heating value of the syngas produced in the STAR-MEET system were fluctuated with operational time. A dual-fueled diesel engine can generate power stably by controlling the supply amount of light oil even if the input energy of the syngas fluctuates, and it is applicable to small-scale gasifier. Figure 4 and Table 5 show the diagrams and specifications of the dual-fueled diesel engine used.

Fig. 4 Dual-fueled diesel engine

Table5. Specifications of dual-fueled diesel engine

Item	Unit	Specification
Cylinders		4
Displacement volume	cc(cc/cylinder)	3331(833)
Combustion system		Direct injection
Rated power	kW(PS)	36.8(50)
Engine speed	rpm	1500

The engine was started by using light oil only and engine speed was kept at constant after the warm-up operation. Then the engine load was set at 26 kW, and the mixture of syngas and air was supplied into the combustion chamber through the turbocharger. The supply amount of light oil can be controlled to match with the load of engine. The details

about the dual-fueled diesel engine were described in a previous paper⁽¹⁵⁾.

3. Experimental Results and Discussion

3.1 Results and Discussion of Lab Scale Experiments

Pyrolysis Characteristic

To clarify the pyrolysis characteristic of waste paint dregs, effects of temperature on the distributions of pyrolysis products (gas, solid residues and tar) and gas production were investigated. Experiments were also performed with wood chips for comparison.

The mass balance of the pyrolysis products (ash free base) and gas production (ash free base) are shown in Figs.5 and 6, respectively.

Fig.5 Pyrolysis product distributions of waste paint dregs and wood chips

Fig.6 Main gas productions of waste paint dregs and wood chips

It can be seen that the main differences of pyrolysis characteristic between waste paint dregs and wood chips were the relationship of the gas production with pyrolysis temperature and steam generation from wood chips.

Pyrolysis gas production of waste paint dregs increased with temperature, tar and char production decreased with temperature, which is similar to pyrolysis characteristic of wood chips. However, magnitude of the increase rate of gas production by increasing the pyrolysis temperature was greater for waste paint dregs than that of wood chips. For example, when temperature increased from 500°C to 900°C, the production of H₂ increased 5 times for waste paint dregs, whereas twice for wood chips. The heating value of waste paint dregs is higher than that of wood chips, so it is considered that the bond energy of waste paint dregs in unit weight is also higher than that of wood chips. Therefore, higher

energy was required to break the bond of waste paint dregs than that of wood chips. Consequently, the effect of temperature on the pyrolysis of waste paint dregs was more significant than that of wood chips. This means that an appropriate management of the temperature in the gasifier is important for the gasification of waste paint dregs.

Steam generation was observed in experiments of wood chips, whereas no steam generation was observed in experiments of waste paint dregs. Although oxygen exists in molecules of wood chips (main components are cellulose and lignin) and waste paint dregs (main component are alkyd resins), oxygen exists in cellulose and lignin in the form of the hydroxyl, whereas oxygen exists in alkyd resins in the form of the ester structure. The hydroxyl was easily broken than the ester structure, and causing steam generation during wood chips pyrolysis.

Volatile Characteristic of Heavy Metals

To clarify the behavior of heavy metals under the pyrolysis atmosphere, the concentrations of heavy metals in the bottom ash, tar and water in impingers were measured and the distributions of four representative heavy metals (Pb, Cr, Ti and Zn) in the three products are shown in Table 6.

Table 6. The distributions of Pb, Ti, Cr and Zn in products

		Unit	Raw material	Bottom ash	Tar	Water
500°C	Pb	%	100	51.35	5.61	0.01
	Cr		100	70.35	74.28	N.D
	Ti		100	78.73	0.11	N.D
	Zn		100	60.71	N.D	N.D
700°C	Pb		100	51.91	5.70	0.01
	Cr		100	65.97	15.21	N.D
	Ti		100	78.96	0.16	N.D
	Zn		100	58.85	N.D	N.D
900°C	Pb		100	44.49	9.58	0.01
	Cr		100	56.95	N.D	N.D
	Ti		100	64.57	0.06	N.D
	Zn		100	40.45	N.D	N.D

N.D: Not detected

Quantitative discussion is difficult due to the large measurement errors and loss of mass, but it is possible to confirm the difference of volatile characteristic of each heavy metal species.

It is observed that Pd and Cr were transferred into tar. Pb is reported to have high volatility in the temperature range from 800°C to 1000°C in previous studies^{(5), (9)}. And Pb is also estimated to exist in the form of gas phase in the temperature range of 700°C~800°C by the phase equilibrium calculation⁽¹⁾. This can explain the behavior of Pb under the present experimental condition.

On the other hand, Cr is reported to be nonvolatile in the temperature range from 300°C to 1400°C⁽²⁾. However, over 10% of Cr was transferred to tar at 500°C and 700°C. While there were some measurement errors, but part of Cr was indeed transferred into tar in the present experiment. In the future, it is necessary to investigate the effect of reaction atmosphere on Cr volatile characteristic in details.

Very small amount of Ti and Zn were transferred into tar and water in impingers, which means that almost all of Ti and Zn were condensed into the bottom ash. This result was consistent with the results of previous studies^{(4) - (6), (11), (12)}, in which Ti and Zn were reported to be nonvolatile.

Because the nonvolatile heavy metals, such as Ti and Zn, are condensed into the bottom ash, it is possible to recover them from bottom ash by means of the extraction method. On the other hand, it is difficult to deal with the volatile heavy metals such as Pb.

To recycle waste paint dregs, it is important to develop the technology for collecting volatile heavy metals downstream of the gasifier, as well as trying to replace the volatile heavy metals in pigment by nonvolatile heavy metals.

3.2 Results and Discussion of Demonstration Experiments

Effect of Temperature on Gasification Characteristic

It was confirmed that temperature strongly affected the pyrolysis characteristic of waste paint dregs in lab-scale experiments. Hence, the effect of temperature in the gasifier on the gasification characteristic of waste paint dregs was investigated. In the demonstration experiments, temperature in the gasifier and the gas production reached to a stable state after about one hour from the start of the experiments. Therefore, the representative data at the stable state were obtained after 1.5 hours from the start of the experiment. RUN1 represented the optimal operational condition with high gasification temperature, and RUN2 represented the condition with lower gasification temperature to compare with RUN1 (Fig.7). The locations of temperature measurement in the gasifier correspond to those of thermocouples T1~T6 shown in Fig.2. It was observed that there was about 500°C temperature difference at the location of 400 mm height from the bottom of the gasifier (marked as T3 afterward) between RUN1 and RUN2.

Fig.7 Comparison of the temperature distributions in the gasifier in RUN1 and RUN2

Table 7 Gas compositions and HHVs in RUN1 and RUN2

	Unit	RUN1		RUN2	
		Pyrolysis gas	Reformed gas	Pyrolysis gas	Reformed gas
H ₂	vol%	5.58	4.96	2.57	1.7
CO		8.94	9.01	2.99	2.18
CO ₂		4.91	9.28	3.94	3.94
THC		1.50	2.41	1.27	0.73
HHV	MJ/m ³ _N	2.52	2.91	1.17	0.86

Gas compositions and the heating values of gases in RUN1 and RUN2 are shown in Table 7. THC represents the total value of CH₄, C₂H₄, C₂H₆ and C₃H₈. It can be seen that the combustible gas concentrations and the heating value of the pyrolysis gas obtained in RUN1 were higher than those obtained in RUN2. For this fixed bed gasifier, our experience shows that the temperature of T3 represents the temperature of the gasification zone, and it was confirmed in the demonstration experiments that the temperature of T3 strongly affected the gas concentration and the heating value of the pyrolysis gas.

Effect of Fuel Species on Gasification Characteristic

The experiment with wood chips was performed by using the same gasifier for comparison. The relationship between the gasification temperature (T3) and the heating

value of the pyrolysis gas produced is shown in Fig.8. For wood chips, the heating value of the pyrolysis gas was almost constant in the temperature range from 600°C to 1000°C. Whereas for waste paint dregs, the heating value of the pyrolysis gas was strongly dependent on the temperature T3. This fact was consistent with the result obtained from lab-scale experiments and suggested that it is important to manage the temperature in gasifier appropriately for gasification of waste paint dregs.

Fig.8 Relationships between HHVs of pyrolysis gas and T3 for wood chips and waste paint dregs

Reforming Characteristic

In this process, the quantities of air and steam supplied into the reformer were automatically controlled to keep the temperature in the reformer at 800°C. In RUN1, the heating value of the reformed gas was over 15% higher than that of the pyrolysis gas. It can be explained that tar in the pyrolysis gas was reformed by steam and was converted into CO and H₂.

Power Generation

The power generation was only performed in RUN1. The experimental condition and the reformed gas compositions of RUN1 are shown in Table 4 and Table 7, respectively. The average heating value of the reformed gas obtained in RUN1 was about 2.91 MJ/m³_N, and the gas flow rate and the heating value fluctuated with operation time. Stable operation of the engine can be realized by supplying 60% of the thermal input by the reformed gas and 40% by light oil, even if the heating value of the reformed gas fluctuated. The power generation efficiency of the engine was 34%, which was slightly lower than that of using light oil only as a fuel.

Energy Balance

An energy balance of the demonstration experiment is shown in Fig.9.

Fig.9 Diagram of the energy balance

100% of energy supplied into this process was defined as the sum of the energy supplied by waste paint dregs and light oil. The gross thermal efficiency of 12% was obtainable when 81% of supplied energy came from waste paint dregs and 19% of supplied energy came from light oil. As stated above, in the demonstration experiment, the high temperature air supplied into the gasifier was produced by an electric heater and the steam supplied into the reformer was heated by combusting some LPG gas. It can be seen that the energy supplied by an electric heater and LPG gas can be replaced by combusting a part of fuel gas and a part of power output. In addition, the gross thermal efficiency can be upgraded several percents by means of the optimal design, because the air supplied into the gasifier can be preheated by using the sensible heat of the fuel gas instead of using a part of electrical power output.

Volatile Characteristic of Heavy Metals

The concentrations of Pb and Cr (hexavalent) in the bottom ash in the gasifier, in the flyash collected in the ceramic filter and in the water in the scrubber were measured, and the distributions of Pb and Cr in these three products are shown in Table 8. It shows that the yield of Pb was very low and Cr (hexavalent) was not detected. The mass balances of these heavy metals are poor, because the heavy metals in slag left in the gasifier, in sediments in the scrubber bottom, in the activated carbon in the filter and in the gas at the outlet of the activated carbon filter could not be measured. In addition, it will be necessary to measure the heavy metals contained in the material that adhered to the inner walls of pipes and equipments located between the gasifier and the outlet of the activated carbon filter in the future.

Even though a quantitative discussion is difficult, it was clear that the volatile behavior of Pb agreed with that obtained in the lab-scale experiments, and it is necessary to consider Pb treatment at the commercial design stage. In the future, the volatile characteristic correlation of other heavy metals between the lab-scale and the demonstration experiments is planned to be clarified by obtaining more accurate data.

Table 8. The distributions of Pb and Cr in gasification products

	Unit	Raw material	Bottom ash	Fly ash	Scrubber water
Pb	%	100	11.4	7.5	0.2
Cr		100	N.D*	N.D	N.D

*N.D : Not detected

4. Conclusions

To investigate the gasification characteristic of waste paint dregs, the optimal operation condition, power generation efficiency and the volatile characteristic of heavy metals, the experiments were performed by using the lab-scale setup and the demonstration apparatus, and the following results were obtained.

Results obtained by using the lab-scale setup:

Effect of the temperature on the pyrolysis of waste paint dregs was more important than that of wood chips.

It was confirmed that Pb was volatile and Ti and Zn were nonvolatile.

Results obtained by using the demonstration apparatus:

The heating value of the reformed gas was about $2.91 \text{ MJ/m}^3_{\text{N}}$.

Stable power generation was possible when 60% of the thermal input to the engine came from the gasification gas of waste paint dregs and 40% came from light oil.

In the 1 t/day small-scale gasification apparatus, the gross thermal efficiency of 12% was obtainable when 81% of supplied energy came from waste paint dregs and 19% of supplied energy came from light oil .

It was also confirmed that Pb was highly volatilized.

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