TREATMENT OF WASTE TBP/N-DODECANE AND HALOGENATED OILS BY STEAM REFORMING

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ABSTRACT

The Japan Nuclear Cycle Development Institute (JNC) has developed the engineering-scale steam reforming (SR) system for treating TBP/n-dodecane and halogenated oils contaminated with uranium used in nuclear fuel cycle facilities. We conducted treatment experiments using simulated non-radioactive wastes to evaluate the processing performance on this equipment. The ratios of gasification of the simulated non-radioactive wastes were over 98%. The concentrations of the regulated substances such as CO, NO_x, HF and HCl in the off-gas were under the regulatory limits. Over 99.9% of hydrogen fluoride and hydrogen chloride were collected in the scrubber. All organic simulated wastes were successfully treated using the engineering-scale steam reforming system.

INTRODUCTION

Steam reforming system is an effective technology for the treatment of organic wastes. [1,2,3] The Japan Nuclear Cycle Development Institute (JNC) has developed the engineering-scale steam reforming (SR) system (the feed rate of waste is 3 kg/h) for treating TBP/n-dodecane and halogenated oils contaminated with uranium used in the nuclear fuel cycle facilities. TBP/n-dodecane and halogenated oils are considered to be troublesome wastes because phosphoric acid and hydrogen halides generated by incinerating TBP/n-dodecane and halogenated oil corrode furnace wall and off-gas treatment-system. It is too expensive to use the corrosion-resistant materials for the off-gas treatment-system of an incinerator because the incinerator needs a large off-gas treatment system to treat a great volume of off-gas containing radioactive nuclides. The SR system in JNC has a compact off-gas treatment system and the construction cost of the SR system is lower than that of the incinerator because of the two-steps treatments described in the following section. We have operated the engineering-scale SR system using simulated organic liquid wastes storaged in JNC to optimize the process conditions such as gasification temperature, oxidation temperature and air ratio (feed air to the stoichiometric air ratio).

Process of SR

A schematic diagram of the SR system is shown in Figure 1. The photo of the engineering-scale

SR system is shown in Figure 2. The SR treatment equipment in JNC consists of two main processes, which are gasification process and oxidation process. In the gasification process, TBP/n-dodecane and halogenated oils are vaporized and then decomposed into small molecule compounds by pyrolysis and hydrolysis without oxygen at about 600 °C in the gasification chamber. In the oxidation process, the small molecule compounds are oxidized into carbon dioxide (CO_2), water (H_2O) and inorganic acids by air at about 1,200 °C in the reactor. The particles with radioactive substances in the gas are removed by the filter equipped after the gasification chamber, and only the gasified organic compounds are fed to the reactor. The organic compounds in the gas are heated with air, and then oxidized to CO_2 and H_2O in the reactor. The phosphor and halogens in the decomposed gas are converted to phosphoric acid and hydrogen halides respectively. These phosphoric acid and hydrogen halides were collected in the scrubber. The main substances released to the atmosphere from the SR system are CO_2 and water vapor.

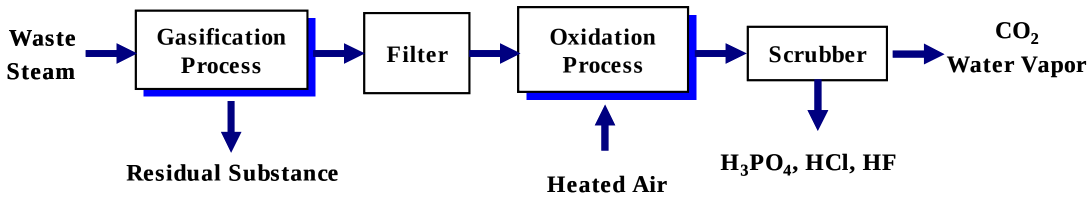

Fig. 1. Schematic diagram of SR

Experimental

Organic liquid wastes used in the present study were n-dodecane (Nikko Petrochemicals), tri-butyl phosphate (Daihachi Chemical Industry), mineral oil (Matsumura Oil, MR-200), perfluoropolyether (Ausimont, Fomblin Y-LVAC25/6) and chlorotrifluoroethylene polymer (Daikin, Daifloil#10). Sample 1 was the mixture of TBP (30 wt%) and n-dodecane (70 wt%). Sample 2 was the mixture of Mineral oil (70 wt%) and perfluoropolyether (30 wt%). Sample 3 was the mixture of Mineral oil (70 wt%), perfluoropolyether (15 wt%) and chlorotrifluoroethylene polymer (15 wt%). A gas analyzer (Testo, 350M/XL) and gas detecting tubes (Gastec) were used to analyze the off-gas. An ion chromatograph (Shimadzu, HIC-SP) was used for measuring the phosphoric acid concentration and the fluoride concentration. Total organic carbon analyzer (Shimadzu, TOC-5000A) was used for measuring total organic carbon concentration in the scrubber water. The electronic weight meter (Sefi, IBA-200) was used for measuring the weight of residual substance. The temperatures in the gasification chamber and the reactor and the regulated substance concentrations such as carbon monoxide (CO), nitrogen oxides (NO_x), hydrogen fluoride (HF) and hydrogen chloride (HCl) in the off-gas were continuously measured during the treatment.

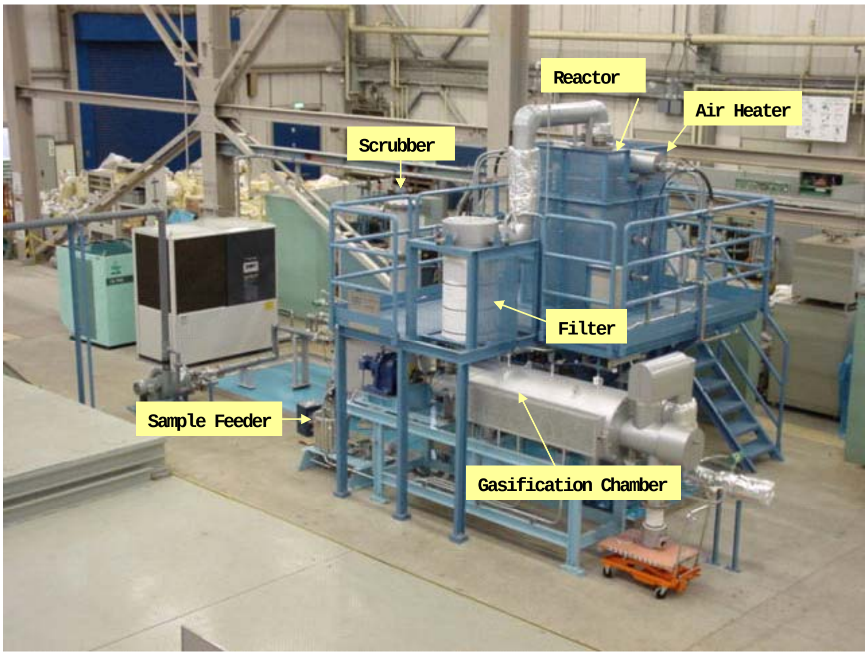

Fig. 2. Engineering – scale steam reforming system

Results and Discussion

Figure 3 shows the influence of the air ratio to CO concentration in the off-gas. When the air ratio is more than 1.6 in the case of Sample 2, CO concentration is below a detection limit. When the air ratio is lower than 1.6, CO concentration exceeded the regulatory limit (100 ppm). This is because incomplete combustion occurred. In the case of sample 1 and 3 the results are similar to those of sample 2.

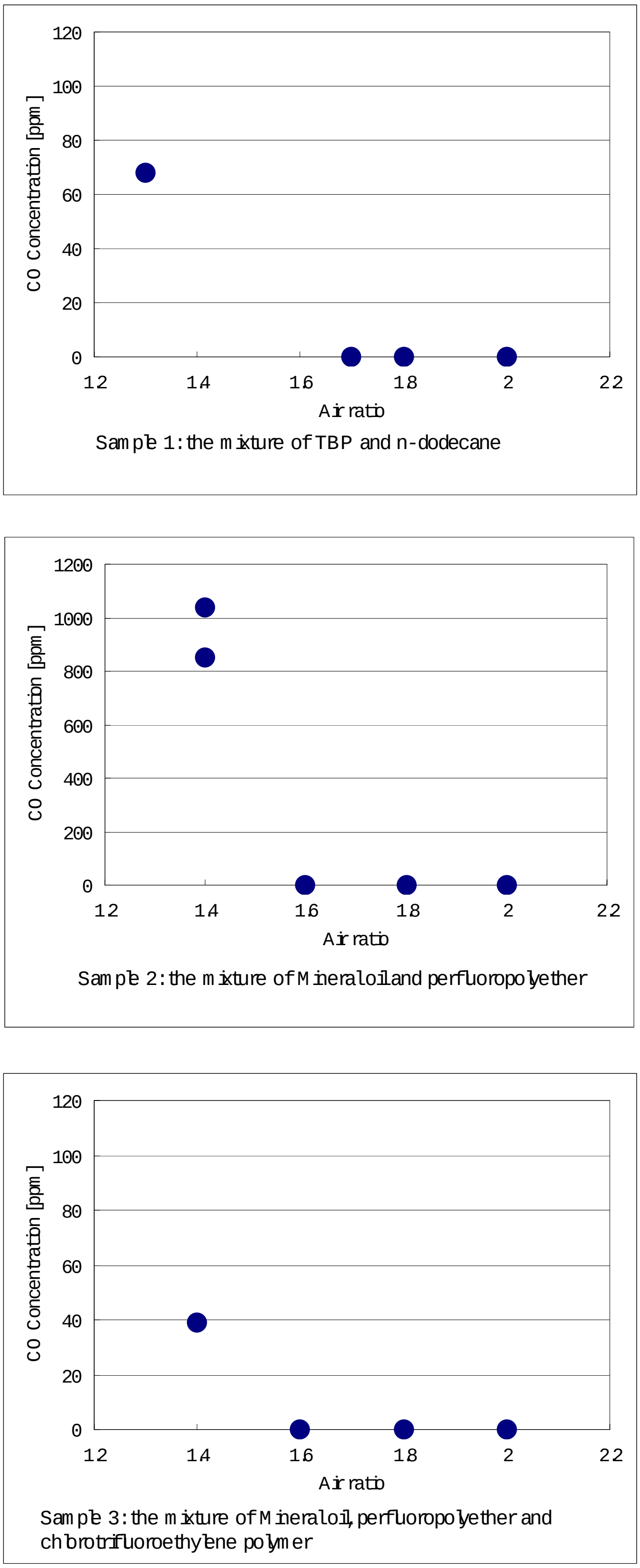

Fig. 3. Influence of air ratio to CO concentration

Table I. Results of treatment experiments using engineering - scale SR

Sample No.	Sample 1 (the mixture of TBP and n-dodecane)	Sample 2 (the mixture of Mineral oil and perfluoropolyether)	Sample 3 (the mixture of Mineral oil, perfluoropolyether and chlorotrifluoroethylene polymer
Weight of the processed sample (kg)	3.7	7.8	6.8
Weight of residual substance (kg)	0.05	0.03	0.12
Ratio of gasification (%)	98.6	99.3	98.0

The results of the treatments experiments using the engineering-scale SR system are shown in Table I. The concentrations of the regulated substances such as CO, NO_x, HF and HCl in the off-gas were under the regulatory limits (CO: 100ppm, NOx: 250ppm, HF: 3ppm, HCl: 430ppm). The ratio of gasification of Sample 2 is over 99%, and those of sample 1 and 3 are over 98%. The ratio of gasification is defined as

The ratio of gasification (%) = {1 - (Weight of residual substance) / (Weight of the processed sample)} ×100

In all samples, the ratio of the residual substance to the fed sample was 2% or less. The removal rates in scrubber on phosphoric acid, hydrogen fluoride and hydrogen chloride are shown in Table II. Over 99.9% of hydrogen fluoride and hydrogen chloride are collected in the scrubber. In the case of sample 3 the removal ratio on phosphoric acid in scrubber is about 60 %. It is likely that a part of phosphoric acid mist passed through the scrubber and released to the atmosphere because liquid particles were observed in the off-gas. A mist filter for eliminating phosphoric acid mist seems to be needed to improve the removal rate of the phosphoric acid. The performance of the mist filter is under experiment.

Table II. Removal rate on phosphoric acid, hydrogen fluoride and hydrogen chloride in scrubber

Sample No.	Sample 1 (the mixture of TBP and n-dodecane)	Sample 2 (the mixture of Mineral oil and perfluoropolyether)	Sample 3 (the mixture of Mineral oil, perfluoropolyether and chlorotrifluoroethylene polymer
H_3PO_4	58%	-	-
HF	-	>99.99%	>99.93%
HCl	-	-	>99.99%

CONCLUSION

The following results were obtained:

- All organic simulated wastes were successfully treated using the engineering-scale steam reforming system.
- The ratios of gasification of the organic compounds were over 98%.
- The concentrations of the regulation substances such as CO, NOx, HF and HCl in the off-gas were under the regulation value.
- Over 99.9% of hydrogen fluoride and hydrogen chloride were collected in the scrubber.

The experiments using the simulated wastes with uranium and the storaged real radioactive wastes are scheduled at the next step.

REFERENCES

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