A-2 Study on Emission Suppression Systems of Ozone Layer Destructive Substances and Alternatives (Abstract of the Final Report)

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This research aims proposing the best technical and social systems to appropriately recover, recycle, and decompose the ozone layer destructive substances and their alternatives. We are conducting the studies on the following sub-themes.

A-2 (1)① Study on Social System to Recover, Recycle and Decompose Ozone-depleting Substances Contained in Car Air-conditioners

In order to design the optimum recovery, transportation, and disposal system for CFCs emitted from car air-conditioners, we calculated the annual amount of CFCs discarded nationwide over a long period using time series analysis and estimated the distribution of regional CFCs discarded by each prefecture.

It was shown that the quantity will increase from 19,280 t/y in 2001 to 24,475 t/y in 2010. CFCs discarded from car air-conditioners account for 16% of the total quantity of CFCs discarded nationwide. It is therefore necessary to construct an efficient and practical system for recovering and decomposing CFCs from car air-conditioners based on the law as soon as possible. It is particularly important to optimize the regional distribution of decomposition disposal facilities and ensure that the nationwide distribution of specified recycling facilities matches the regional capacity for decomposing CFCs.

Sufficient capacity could be attained by using existing industrial and municipal waste incineration facilities.

The LCA approach was used to estimate the environmental loads associated with ozone depletion and global warming as impact categories for the several scenarios for collecting and decomposing of CFCs. As a result, it was found that the impact on ozone depletion is remarkably large, and that to ensure the impact on global warming is not ignored in terms of LCA, an efficient recovery and decomposition system must be urgently constructed. Improving the efficiency of recovering CFCs could help reduce the environmental load because release to the atmosphere in the recovery process is the main contributor to total emissions in the life-cycle of CFCs.

A-2 (1)②Research on Social System of Collection, Recycling, and Decomposition of Fluorocarbon from Business Refrigerators and Air Conditioners

Costs of the system; collection transportation decomposition of the fluorocarbon from abandoned business refrigerators and air conditioners were estimated and clarified. And, the improvement points of the system were examined from the results.

First, a current collection system for the business refrigerator and air conditioner were investigated. A estimation method of the collection cost was developed, and it was found that most of cost depend on the personal expenses and depreciation. Next, a estimation method of distribution of the stock amount in air conditioner from the floor space of the building was developed. The stock amount in the refrigerators were estimated for each equipment and type of business. The cost and the environmental load for the system in considering of the amount and the transport distance in each region were estimated from the obtained stock distribution.

A-2 (1)③Study on Suitable Technical System for Decomposition of Halons

This research aims to clarify the best decompose system of halons. The decomposition reaction kinetics of three kinds of halons and methyl bromide were investigated in laboratory under various conditions such as their concentrations, coexisting concentrations of oxygen and hydrocarbon and temperature. It was found that the objective compounds decomposed in the following order: methyl bromide>halon2402>halon1211>halon1301.

The decomposition reaction rates of halon1301 and 2402 were expressed by the first order equation of the concentration of them. The decomposition of halons was extremely promoted with coexisting hydrocarbon, and excessive hydrocarbon restrained producing CO. The decomposition of halon 1301 with

hydrocarbon could be expressed with an equation introduced by assumption of the radical reactions. By these reaction rate analyses, the best conditions of actual decomposition could be determined.

Decomposition efficiency of the halons and methyl bromide and concentration of volatile organohalogen compounds were confirmed in the actual industrial waste incineration facilities having rotary kilns. Halon 1211, halon2402 and methyl bromide were decomposed sufficiently. On the other hands, the decomposition efficiencies of halon1301 were not stable and the concentration of CO was increased.

Therefore, we clarified the best conditions the halon should be introduce below 100ppm into the kiln by premixing with air.

A-2 (1)④Behavior of Byproducts Formed During Halon Destruction System

Combustion experiment of personal computer (PC) mixed with halon 1301 was performed at a lab-scale incinerator equipped with scrubber and activated carbon adsorption tower. The mixed material sample contained fire retardants, and the halon additional percentage was high, 8.9%, at the input sample weight rate. However, the destruction rate of the halon was also high, 99.996%. Some dioxins, in particular polybrominated DDs/DFs, were contained in PC materials at ppm level. Total emission amount was 0.0016 mg/kg-material. This emission amount was all from the incineration residue, and the destruction percentage was 99.995% in the system. Brominated dioxin level was 0.11 ng-TEQ/Nm^3 at the outlet of activated carbon adsorption tower. Influence of the halon addition was not observed.

A-2 (2) Studies on Collection, Transportation and Disposal System for CFCs Emitted from Electric Appliance Wastes

In order to design the optimum collection, transportation and disposal system for CFCs emitted from electric refrigerators and small air-conditioners, we calculated the annual amounts of CFCs discarded nationwide over a long period using time series analysis and estimated the distribution of regional CFCs discarded by each prefecture.

The amount of CFCs from refrigerators and air-conditioners was estimated to account for 30% of the total quantity of CFCs discarded nationwide. It is therefore necessary to construct an efficient and practical system for recovering and decomposing CFCs from refrigerators and air-conditioners based on the law as soon as possible. It is particularly important to optimize the regional distribution of decomposition disposal facilities and ensure that the nationwide distribution of specified recycling facilities matches the regional capacity for decomposing CFCs.

The LCA approach was used to estimate the environmental loads associated with ozone depletion and global warming as impact categories for the several scenarios for collecting and decomposing of CFCs. As a result, it was found that the impact on ozone depletion is remarkably large, and that to ensure the impact on global warming is not ignored in terms of LCA, an efficient recovery and decomposition system must be urgently constructed. Improving the efficiency of recovering CFCs could help reduce the environmental load because release to the atmosphere in the recovery process is the main contributor to total emissions in the life-cycle of CFCs.

A-2 (3) Development of A System for Non-thermal Plasma Chemical Decomposition of Polyfluorocarbons

Applicability of nonthermal plasma to the removal of fluorocarbons (FCs) such as CFCs, HCFCs, HFCs, and PFCs was investigated with reactors such as ferroelectric packed-bed (FPR), silent discharge (SDR), pulsed corona (PCR), and surface discharge (SPR) at various concentrations of FCs and additives in background gases.

First the initial concentrations of FCs were varied from 200 ppm to 1000 ppm. Compared to FPR, SDR, and PCR reactors showed a lower performance in the decomposition of PFC-14 in dry N_2. Humidity (H_2O) suppressed the conversions of PFC-14 and the HFCs (HFC-32 and -23) with any of the above reactors. Gaseous oxygen also decreased their conversions with FPR and PCR, but increased those with SDR. These findings suggest that the distribution of active oxygen species generated from O_2 depends on the plasma-generating method.

Next the removal of various FCs in high concentrations was investigated using a surface-discharge type plasma reactor (SPR). In order to enhance the effectiveness of plasma chemical processing, we investigated the effects of catalyst packing in the reactor and adding second gases to the reactant. Removal efficiency increased in the plasma reactor packed with TiO_2 pellets, whereas no positive effect was observed with Al_2O_3 pellets. When the gases such as H_2O, O_2, and H_2 were added to the carrier gas (Ar), removal efficiency was also enhanced.

A-2 (4) Study on Emissions Reductions of Methyl Bromide and Alternative Chemicals

Methyl Bromide (CH_3Br) is a major fumigant used in Japan to control soil-borne diseases in many crops. The use of CH_3Br as a soil fumigant is to be phased out till 2005. Techniques including the use of gas-tight films such as VIFs (Very Impermeable Films) can reduce the amount of

CH_3Br application and its emission, and increase the retention time in the soil. Our experiments showed that CH_3Br emission was reduced to less than 1% of the applied amount by using the sheet containing a TiO_2 photocatalyst.

Restrictions on CH_3Br use in Japan due to air quality concerns prompted air monitoring and improved application methods of soil fumigants in horticultural areas. The monitoring method was optimized. Air concentrations were measured near the occupied structures in horticultural areas, Ibaraki Prefecture. In case of the Ami area, growers used 1,3-dichloropropene popularly, so 1,3-dichloropropene in the atmosphere was detected frequently. Air concentrations measured off-site during several months ranged from none detected to 616 $\mu g/m^3$, and most samples contained several $\mu g/m^3$ of 1,3-dichloropropene. The highest measured concentration of CH_3Br was 190 $\mu g/m^3$, but these high concentrations were temporary. Most measured concentrations of CH_3Br, chloropicrin, and MITC(Methyl Isothiocyanate) were less than quantitation limits. The sampling site of the Ina area had a seedling grower near, so CH_3Br was detected frequently. Air concentrations measured off-site during several months ranged from none detected to 937 $\mu g/m^3$, and most samples contained more than some $\mu g/m^3$ level of CH_3Br and 1,3-dichloropropene. High concentrations of CH_3Br were detected every soil fumigation.

Restrictions on CH_3Br usage required an intensive search for improved technologies to reduce both dosage and emission from fumigated plots into the atmosphere, while maintaining its effectiveness for disease and weed control. Further, such monitoring are required as part of an ongoing effort to evaluate seasonal exposures to soil fumigants and determine if current restrictions provide adequate safety for people who lived and working in areas where soil fumigations occur to multiple fields.

A-2 (5) Substitute Method for Methyl Bromide on Quarantine Treatment

The effects of the high pressurized CO_2 , phosohin, sulfuryl fluoride and methyl iodide gases as a substitute method for methyl bromide in quarantine treatment were examined. *Sitophilus zeamais* and *Rhyzopertha dominica* in wheat grains and corn grains were treated with high pressurized CO_2 gas. The larvae of *R. dominca* in wheat were perfectly killed with 30kg(1kg × 980.6hPa) × 5 minutes. In the case of corn, the larvae of *R. dominica* was killed at 15kg × 10 minutes. The eggs of *S. zeamais* in wheat were perfectly killed with 30kg × 5 minutes. The larvae of *S. zeamais* in wheat were perfectly killed with 20kg × 10 minutes, 25kg × 5 minutes, 30kg × 5minutes. There was no effect of the high pressurized CO_2 treatment on the characters of wheat

grains.

The eggs of *S. zeamais* and *S. granarius* were treated with PH_3 and SO_2F_2 and were kept at 15℃ for 24 and 48h. The eggs of *S. zeamais* and *S. granarius* were completely unable to produce adult at 2+30mg/l (PH_3+SO_2F_2) dosage in both the durations. The larvae of *S. zeamais* in brown rice were completely killed at both the duration (24 and 48hours) and at all the doses of PH_3(2mg/l), SO_2F_2(30mg/l) and their combination (2+30mg/l). Different immature stages viz., egges, larvae and pupae of *S. zeamais* were fumigated at 15℃ with various concentration of methyl iodide at 24 and 48hours. The eggs and larvae of *S. zeamais* were completely killed at 3mg/l and the pupae were completely killed at 5mg/l in both the durations. Adult emergence in *S. granarius* completely suppressed at all the dose and durations when pupae were treated with PH_3 (0.1 and 1mg/l) and SO_2F_2 (5and 30 mg/l) at 10 and 30 minutes with 15kg/cm^2.