COMBUSTION OF BRIQUET AS NEW SOURCE AND EMISSION INVENTORY OF DIOXINS (PCDD/DFs AND DLPCB) IN KOREA

Ok G[1,2], Kim D-U[1,2], Kim C.S[1,2], Jung B.G[1,2], Lee S-H[1,2], Hwang S.M[1,2]
[1.]Graduate school of Earth Environmental Engineering, and [2.]Dioxin Research Center ,
Pukyong National University, 599-1 Daeyon 3 dong, Namgu, Busan, 608-737, Korea

Abstract

The Korean traditional house heating system is called On-dol and it is the most common way of heating house. Longtime ago, the fuels used to produce a heat in On-dol were timbers and other agricultural remnants materials. However, after the industrialization, the materials based on coal called briquettes are being used. Recently, the oil and LNG are utilized for the house heating system. This research had done the combustion experiment of dioxins that are not included in the categories of main sources and it is necessary to estimate the Briquette as one of the new sources of dioxin.
In case of briquette, the average concentration of ∑PCDD/DFs produced from the exhaust combustion gas was 160.79 ng/Nm^3, and ∑ PCDFs took 95% of homologue concentration. Average concentration of TEQ was observed as 2.81ng WHO- TEQ/Nm^3, and TEQ- ∑ PCDFs were accounted for 82%. Likewise an ignition briquette, the total WHO_{98}-TEQ concentration was dominated by 2, 3, 4, 7, 8 – PeCDFs.
In the calculated result by the 2005 year base, annual air emission of PCDD/DFs and DLPCBs were estimated 20.168g WHO-TEQ/yr from house heating by using fuel of briquette.

Introduction

By Stockholm Convention and the European POP Regulation, PCDD/DFs and dioxin-like PCBs(DLPCBs) were identified as an unintentionally produced substances that releases persistent organic pollutants.[1] PCDD/DFs and dioxin-like PCBs(DLPCBs) are persistent organic pollutants(POPs) that is one of the chemicals produced by the industrialization. The dioxins are known to be caused by various reasons such as a combustion process of fuels, waste combustion and other sources released to the environment.[2-4] Currently the sources of dioxins such as formation mechanism and control technology are reported, and furthermore, the sources' emission inventories are continuously reported from the various countries.
The Ministry of environment of Republic of Korea had been developed the emission inventory methods of dioxins and had done the investigation for the sources' emission inventory by classifying the sources into the eight main categories.[6-7] The energy system was included in one of the main categories in emission inventory of dioxins. Non-point sources were also included in the main categories for the house heating system and as the subcategory, the gas-boiler and oil-boiler were included. However, the briquette by coal base was not included in this sub-category and as a result it was not calculated for the air emission to the dioxins.
In case of Korea, Koreans used the house heating system called On-dol for a very long time. On-dol is the heating system that was generated by the agricultural remnants materials, timbers and other materials. However, after the industrialization; 1960 till the present, the coal based material called Briquette was used to run the heating system of the houses. Also, the Oil, LNG and other materials are used as a fuel for the house heating system.
This research had done the combustion experiment of briquette that are not included in the categories of main sources and it is necessary to estimate the Briquette as one of the new sources of dioxin. Therefore, this study reports the air emission concentration and the load of air emission of dioxins inventory produced by the combustion of briquette.

Materials and Methods

Manufacturing of briquette follows the fundamental regulation of industrial standard (KSE3731 coal briquette, KSE 3732 coal briquette method of examination). The regulation defines that caloric value of household briquette must be more than 4,600kcal, and the weight has to be 3.6kg when it is first imprinted. When the briquette dries, it has to weigh more than 3.3kg. The Fig. 1 shows the briquette and the Ignition briquette.

The briquette used in this research had the weight of 3.4kg, the diameter of 14.5cm, and the height of 16cm. In case of Ignition Briquette, the average weight was 200g, the diameter was 14.5 cm, and height was 5 cm. The main raw material of the briquette is anthracite and is also consists of cokes, charcoal powder and etc. In other hand, the ignition briquette is composed of carbonized sawdust, chaff (rice hulls) and waste wood scrap and etc., to be ignited easily. These compositions of materials are the reason for the differences in weight between briquette and ignition briquette.

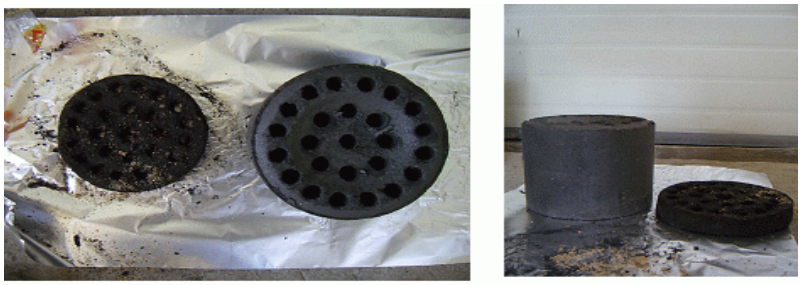

Fig.1. Ignition Briquette and Briquette used as a fuel for the house heating.

The sampling of the flue gas was carried out by the stack gas sampling method of isokinetic. The setting of the sampler was ordered as following; probe, thimble filter, water 100ml impinger 2ea, XAD-2 Trap, Diethylene glycol 100ml impinger, empty impinger, pump and gas meter. The release velocity of exhaust gas by burning the briquette was 0.5 m/s in average. The time needed for the combustion test of one briquette and one ignition briquette was respectively four hours and thirty minutes. Furthermore, the combustion experiments were carried out 5 times each.

The sample pretreatment was carried out by the EPA 1613 method and the samples cleanup had gone through multi layer silica gel (Merck Co., 70-230 mesh) column chromatography and alumina column chromatography by the aluminum activated at 600℃ for 24 hours (Activation Rate I, Merck Co., 70-230 mesh). The samples were analyzed according to congener group of the PCDD/DFs by HRGC/HRMS(HP 6890 GC coupled to a JEOL JMS-700D HRMS).[5]

Results and Discussion

Content Level of PCDD/DFs and DLPCBs in Briquette and Ignition-Briquette

In case of Ignition briquette, the average content concentration of the homologous ΣPCDD/DFs was 973.35 pg/g, and the average content concentrations of WHO-TEQ was 34.14 pg WHO-TEQ/g. The homologous of content profile for the Ignition Briquette's PCDD/DFs had a high content concentration of low chlorinated compounds while the high chlorinated compounds showed characteristics of low content concentration. Furthermore, in case of toxicity equivalence of an isomer, 2,3,7,8,-TeCDD and 1,2,3,7,8,-PeCDD were dominant in PCDDs, while 2,3,4,7,8,-PeCDF showed the highest content ratio between PCDFs.

In case of briquette, average content concentration of ΣPCDD/DFs homologous was 36.55 pg/g, while the average content concentration of WHO-TEQ was 1.54 pg WHO-TWQ/g. The content profile of homologous for the PCD/DFs in briquette showed dominance by content concentration of High chlorinated compounds such as HeCDD/DFs and OCDD/DF than the low chlorinated compounds. As a result, content profile was appeared that there is a great different characteristic between Briquettes and Ignition briquettes. Thus a great difference of PCDD/DFs profile are considered because of the chlorination effect by physical element such as temperature, pressure and forming time in forming process of the Briquette and Ignition Briquette.

Also, comparing the content concentration of PCDD/DFs with ignition briquette and briquette, PCDD/DFs concentration of ignition was higher. Also, likewise the average content concentration of total organic carbon (TOC) has higher in the ignition briquette than briquette. Average concentration of TOC was observed that Ignition briquette and briquette were 71.41% and 59.93%, respectively.

Therefore, the reason of differences in the content concentration of PCDD/DFs of Ignition briquette and

briquette is considered to be the high content concentration of one of the materials added in the Ignition briquette that was used to make the flame liable.

Concentration Level of Combustion Flue Gas

The average concentrations of Σ PCDD/DFs from the exhaust gas by the combustion of ignition briquette were observed as 24.14ng/Nm3. Especially homologous concentration by ∑ PCDFs were 76% of the concentration levels of Σ PCDD/DFs. Also, the average TEQ concentration showed 0.47ng WHO- TEQ/Nm^3, and TEQ- ∑ PCDFs were 70% of TEQ. 2, 3, 4, 7, 8 - PeCDFs were determined to be the dominant congener of the exhaust gas of ignition briquette. Also, the average concentration of ∑ DLPCBs from exhaust combustion gas of ignition briquette was 0.03ng WHO- TEQ/Nm^3. The average concentration of 3, 3 '4, 4', 5 - PeCB(PCB 126) was 0.029ng WHO - TEQ/Nm^3 which is 97% of DLPCB's average concentration.

In case of briquette, the average concentration of ∑PCDD/DFs produced from the exhaust combustion gas was 160.79 ng/Nm^3, and ∑ PCDFs took 95% of homologue concentration. Average concentration of TEQ was observed as 2.81ng WHO- TEQ/Nm^3, and TEQ- ∑ PCDFs were accounted for 82%. Likewise an ignition briquette, the total WHO_{98}-TEQ concentration was dominated by 2, 3, 4, 7, 8 – PeCDFs. Also, in the case of ∑ DLPCBs, average concentration of combustion exhaust gas was 0.2ng WHO- TEQ/Nm3, and the average concentration of 3, 3 '4, 4', 5 – PeCB (PCB 126) among DLPCB congeners were 0.194ng WHO - TEQ/Nm^3. This concentration result was 95% of the average concentration of Total-DLPCB.

When the briquette and the ignition briquettes are combusted together, the average concentration of Σ PCDD/DFs from the exhaust gas was 41.24ng/Nm^3 and Σ PCDFs took 98% of homologous concentration. The average TEQ concentration was 1.36ng WHO-TEQ/Nm^3 and TEQ- Σ PCDFs was 83% of the average total TEQ concentration. Likewise an ignition briquette and briquette, 2,3,4,7,8-PeCDFs was found to be dominant.

Furthermore, the average concentration of ∑DLPCBs, was 0.262ng WHO- TEQ/Nm3, and the average concentration of 3, 3 '4, 4', 5 – PeCB (PCB 126) was 0.254ng WHO - TEQ/Nm^3. It was accounted for 97% to the average concentration of total DLPCBs.

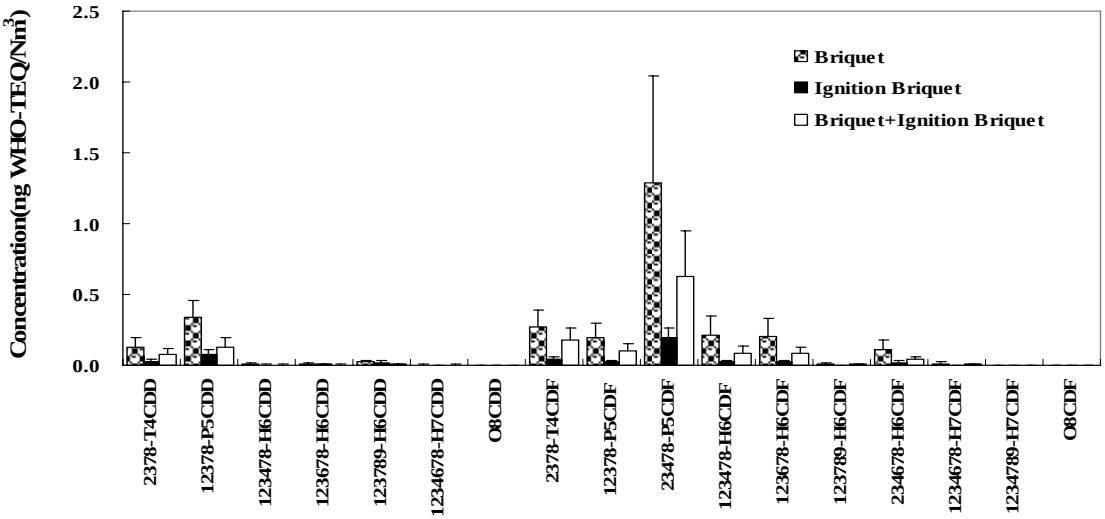

Fig. 2. Profiles of PCDD/DFs WHO_{98}-TEQ concentration in exhaust gas by combustion of Briquettes.

As the result of this study, the average concentration of exhaust gas was sequenced as combustion of briquette >combustion of ignition briquette + briquette > combustion of ignition briquette. Following differences were considered to be caused by the relationship between the temperature of combustion chamber and the time required to continue the high temperature in the chamber.

These results are exhibited that the time required to persist the high combustion temperature can be interrelated with temperature of needed for the combustion. The study suggests that the temperature and the time is the key parameter that decides the result. Also, result of contained quantity analysis of chloride (Cl) element that concentration of ignition briquette and briquette were 0.27% and 0.02%, respectively. Therefore, exist of

chloride element as role of a precursor was suggested that can be sufficient condition to the dioxins formation by inclusion of only a few trace % levels. Fig. 2 shows compare with the profile of PCDD/DFs WHO_{98}-TEQ concentration to the respective combustion in exhaust gas.

Air Emission of PCDD/DFs and DLPCBs

In the calculated result by the 2005 year base, annual air emission of PCDD/DFs and DLPCBs were estimated 20.168g WHO-TEQ/yr from house heating by using fuel of briquette. Fig.3 shows the estimating temporal trend of air emission of PCDD/DFs and DLPCBs by briquette combustion.

This results estimated that emission amounts of PCDD/DFs from briquette were calculated more than 100g WHO-TEQ/yr from 1970 to 1992, and it was increased in addition to the using of briquette from beginning 1972 to 1986 year, and maximum emission was 248g WHO-TEQ/yr in 1986 year. Since 1987 year, amount of dioxins air emission show a tendency to decrease by decline in consumption of briquette.

Korea dioxins inventory were classified including waste combustion by eight main categories, and air emission of dioxins were calculated about 1,219 - 1,250 g WHO-TEQ/yr to base in 2001. [6-7]

When dioxins air emission of this result and including the dioxins emission by briquette combustion of house heating, it is estimated that air emission of dioxins were increased about 1,239 - 1,270 g WHO-TEQ/yr in Korea.

Also, when the compare with others main sources, air emissions rates of dioxins exhibited that followed the sequence waste combustion (about 1,079 ; 87.5%) > steel industry (about 113.6 250g WHO-TEQ/yr ; 9%) > house heating by briquette combustion (about 20.168 ; 2%) ≥ nonferrous metal (about 19.8g WHO-TEQ/yr ; 2%) > energy industry combustion (about 11g WHO-TEQ/yr ; 1%) > etc., and house heating by combustion of briquette was evaluated as one of main sources.

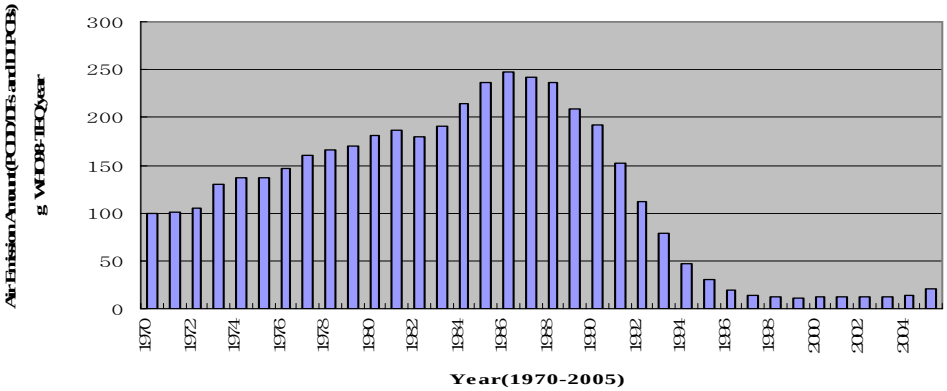

Fig. 3. Estimating temporal trend of air emission of PCDD/DFs and DLPCBs by briquette combustion

References

1. UNEP, *Stockholm convention on persistent organic pollutants* 2001.
2. Fiedler, H. *Chemosphere* 1996; 32:55.
3. Fiedler H. et al., *Study on behalf of the European Commission, DG Environment, Final Report* 2000.
4. U.S.EPA, *PCDD and PCDF:Reduction Options, Great Lakes National Program Office*, 2000.
5. Ok, G, Ji S.H, Kim S.J, Kim Y.K, Park J.H, Kim Y.S, Han Y.H. *Chemosphere* 2002; 46:1351.
6. Ok G. Comparison study inventory of dioxins with Korea and Japan- In case of Korea, 2005' Joint meeting proceeding; The ministry of environment of the republic of Korea and the ministry of the environment of Japan on joint research and cooperation concerning endocrine disrupting chemicals, dioxins, furans and polychlorinated biphenyls. 2005.
7. The ministry of environment of the republic of Korea; Development of dioxins inventory method. 2002.