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学位授与の日付 **2015 年 3 月 31 日**

論文名 **Biodiesel fuel exhausted emission impacts on the atmospheric environment: ozone increment as secondary pollution and low molecular weight methyl ester emission**

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論文要旨

Fuel plays an important role in the development of every country in the world. In recent years, fossil fuels are depleting, and environmental issues by using fossil fuel are increasing. Therefore, there is a need to find new alternative fuels. Biodiesel fuels (BDFs) are expected to be the alternative fuel used to fulfill the energy demands of the world in the future because of their benefits such as eco-friendly, renewable and biodegradable. BDFs have been increasing interest in recent decades, and exhausted gas emitted from diesel engine by using BDFs has been also concerned when BDFs were used as replacement for diesel fuel.

Fuel combustions have long been recognized as one of the most important anthropogenic sources of atmospheric polycyclic aromatic hydrocarbons (PAHs) which are mutagenic and carcinogenic. BDFs have been demonstrated to decrease the PAHs emission. In order to evaluate an impact of BDF utilization, we should know an accurate background of the PAHs concentration in the atmosphere. Biodiesel fuel exhausted gas (BFEG) has been also reported to associate with increases of NO_x and non-methane hydrocarbon (NHMC) which are important ozone precursors. The ozone increment resulting as

secondary pollution from the uses of BDFs and diesel fuel have been estimated by computer simulation with a maximum increment activity of each carbonyl. Meanwhile, the reports on the ozone increment resulting by experiment have not been available. This study provides a better understanding of the ozone increment and focuses on the increment of ozone when BDFs are used instead of diesel fuel.

The status of regulated emission (NO_x, CO, and particulate matter) from BDFs combustion has been confirmed. However, unregulated emission such as carbonyl compounds, PAHs or unknown organic compounds is being investigated. Finding of a new pollutant group is needed, which helps us to understand more about characteristics of BFEG. We found low molecular weight - methyl ester (LMW-ME) group, which is more toxic than benzene. Thus, study on detailed chemical kinetics for thermal decomposition of LMW-ME becomes important to reduce LMW-ME emission in the future.

In the framework of this thesis, we focus on BFEG which has been continuing attention and discussion in recent years. This study is believed to have a significant contribution to BDF exhausted emission research field. The thesis is divided into six chapters with the structure as follows.

In Chapter 1, we provided some overviews of BDF exhausted emission profiles, BDF production methods, types of BDF and specifications of BDF. Furthermore, purposes of this thesis were also addressed.

In Chapter 2, new methods to collect PAHs in rain and snow were proposed. Benzene was added to a brown glass bottle before rain sampling, and a heated funnel combined with a brown glass bottle in which hexane was added for snow sampling in order to prevent decrease of PAHs during sampling and storage. Whether it is raining or not, the concentrations of $\Sigma 9$ PAHs in gas were always higher than those in particles. The ratios of the $\Sigma 9$ PAHs concentrations in the gaseous phase to those in the particulate phase were 3.51 and 1.99 during rain and no rain, respectively. The concentration of $\Sigma 9$ PAHs in rainwater ranged between 17.49 and 646.52 ng dm⁻³. The average ratio of these $\Sigma 9$ PAHs in gas versus [gas plus particles] was 77.9 % and 68.3 % during rain and no rain, respectively. Among 4, 5 and 6 rings PAHs in gas, particle, and rain, 4 rings were the highest contribution of PAHs. During the rain, the compositions of PAHs in the rain were similar to those in the particle but not those in the gas

phase. Small fraction of 4 rings PAHs in the gas phase were also incorporated in the rain, but the composition of PAHs in the gas phase was not affected by rain. The temperature and season were significantly related to PAHs concentration in the gas/particle/rain, and the concentrations of PAHs in the winter and spring were higher than those in summer and autumn.

In Chapter 3, ozone concentration increased with increasing amount of BFEG and diesel fuel exhausted gas (DFEG) emitted to the atmospheric environment because of increasing NO_x and NMHC. The ozone increment was conducted under both experimental conditions in chamber test with UV light and in the natural environment with sunlight. The ozone increment depends on radiation intensity and quality of ambient air. NMHC and NO_x are important factors that influence the trend of ozone formation. BFEG and DFEG were added to the separate air bags which were filled up by ambient air. With 30 cm³ of BFEG and DFEG were added to 18 dm³ of ambient air, the highest ratios of ozone increment from BFEG versus DFEG in Japan and Vietnam were 31.2 and 42.8 %, respectively, and the maximum ozone increment resulting from BFEG and DFEG compared to the ambient air in Japan were 17.4 and 26.4 ppb, respectively. The trends of ozone increments in Vietnam and Japan were difference: 1) ozone increment in Vietnam was higher and faster than Japan. 2) The ozone increment resulting from the use of BFEG in Vietnam was high compared to that from DFEG under all experimental conditions, but in Japan the opposite results were observed. We observed that the NO_x concentration decreased by the UV irradiation since NO_x reacted with OH radicals and volatile organic compounds (VOCs) to form HNO₃ and unknown organic nitrates.

In Chapter 4, formation of LMW-ME having one carbon-carbon double bond C_nH_{2n-2}O₂ (n=4-9) in BFEG was investigated. These compounds were generated from unsaturated fatty acid methyl esters by thermal cracking. LMW-ME was detected in WCO-BDF exhausted gas from a diesel electric power generator and in catfish-BDF exhausted gas from a mini truck. However, it was not detected in DFEG in both the power generator and mini truck test. The C₄ concentration which was observed with the highest concentration was 14.01 ± 1.07 mg m⁻³ (B100, 0 % load) and 2.22 ± 0.05 mg m⁻³ (B50, 0 km h⁻¹) from the power generator and mini truck, respectively. C₄ has an LD₅₀ value of 277 mg kg⁻¹ in rats via oral testing. This toxicity is 15 and 3 times higher than those of xylene and benzene, respectively. Therefore, LMW-ME emission is harmful and toxic for the environment and human beings. The concentration of LMW-ME increased with increasing

BDF ratios because the source of LMW-ME is BDF. However, the LMW-ME concentration decreased with increasing load or speed because of high temperature and combustion efficiency. The concentration of LMW-ME depends on types of engines and source of fuels. The concentration of LMW-ME with higher number carbon is smaller than lower number carbon except for C₈.

In Chapter 5, the detailed chemical kinetics for thermal decomposition of LMW-ME was investigated. Six standards of LMW-ME were used for thermal decomposition by a continuous flow reaction system. Kinetic data such as reaction orders, activation energies, and rate constants were calculated. The reaction orders of thermal decomposition reaction for each LMW-ME were 1.13, 0.96, 1.17, 0.80, 0.99, and 0.84 for C₄, C₅, C₆, C₇, C₈, and C₉, respectively. The reaction orders are not integer, which indicate that the decomposition of LMW-ME is complex not only involved the thermal reaction but also free radical reactions. Activation energies of each LMW-ME are 321.04, 117.37, 87.29, 62.94, 74.80, and 75.79 kJ mol⁻¹ for C₄, C₅, C₆, C₇, C₈, and C₉, respectively. From kinetic data, it can be explained why C₄ is the most abundant in the BFEG as being described in chapter 4. The decomposition of LMW-ME with higher carbon number was faster than LMW-ME with smaller carbon number except for C₈. Based on the observation of by-products from decomposition of each LMW-ME, it is suggested that from high number carbon methyl ester was not only decomposed to lower carbon number but also directly decomposed to C₄. This kinetic data will be applied to modeling study on BDFs decomposition, and engine technologies to reduce hazardous compounds emission.

In Chapter 6, the content of this thesis and future researches were summarized.

審査結果の要旨

本論文は、地球温暖化対策および軽油排ガスによる大気汚染負荷抑制のために利用拡大が期待されているバイオディーゼル燃料(BDF)を用いたときに排出される排気ガスの大気環境や人体、生態系へ影響を与える汚染物質の研究結果をまとめたものであり、次のような成果を得ている。

1) ディーゼル排ガスから放出される、発がん性の強い多環芳香族炭化水素類(PAHs)の雨および雪中の濃度を測るため、サンプリング中や保存中に PAHs が減少することを最大限抑えるサンプリング法を開発した。この方法を用いて大気環境中の気体、粒子、雨または雪中の PAHs を同時測定し、PAHs の除去過程を明らかにした。

2) BDF を用いた排ガスは、放出された環境大気の状態により、軽油を用いたときと比べオゾン濃度が高くなると、計算により予測されていた。本研究は実際にオゾン濃度の変化を実測し、NO_x が高く揮発性有機化合物濃度が比較的低い大阪の大気に BDF 排ガスが混入したときは、軽油のときよりもオゾン濃度は低く、NO_x が低く揮発性有機化合物濃度が比較的高いベトナムハノイの大気の場合は、軽油のときよりもオゾン濃度が高くなることを示した。

3) ベンゼンよりも毒性の強い低分子量不飽和メチルエステル(LMW-ME) が BDF 排ガス中に存在することを発見した。種々の原料からなる BDF および BDF と軽油の混合比を変化させた燃料を用いた発電機や軽トラックからの燃焼ガス中の炭素数 4 から 9 までの LMW-ME を測定し、軽油排ガスには LMW-ME は存在しないこと、BDF の混合比が増えると増加、負荷が増えると減少することなどを発見した。さらに炭素数 4 から 9 までの LMW-ME の熱分解の速度論を研究し、それぞれの化合物の反応速度定数や活性化エネルギーを求め、LMW-ME の削減対策の基礎データを蓄積した。

以上の諸成果は、BDF を用いたときに排出されることが予想される汚染物質の測定法を確立するとともに、利用拡大に伴い予想される新たな大気汚染問題を事前に予想し、警鐘を鳴らすものである。対策なしに利用拡大し、問題を深刻化させた従来の環境問題から人類が学び、利用拡大前にすべきことを示す重要な知見を示したものであり、人類の持続可能な発展に対して貢献するところ大である。また、申請者が自立して研究活動を行うのに必要な能力と学識を有することを示したものである。