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에멀존 연료의 연소 배출가스특성 및 연소 효율에 관한 분석평가

박현미 · 어연우 · 백승우 · 박일룡 · 팽기정* · 김영만 · 이강봉★
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An Analytical Evaluation on the flue Gas and Combustion Efficiency of Emulsion Fuel

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요 약 : 중유 및 물이 혼합된 에멀젼 연료의 연소 특성이 평가되어졌다. 에멀젼 연료의 연소 가스 중 SO_x의 농도는 순수한 중유 연소가스의 57%로 감소되었으며, 에멀젼 연료의 연소 가스 중 NOx의 농도는 순수한 중유 연소가스의 67%로 감소되었다. 에멀젼 연료 연소가스에서의 SO_x의 감소는 에멀젼 연료 중 포함되어있는 계면 활성제중의 salt와의 반응에 기인하는 것으로 사료된다. 또한, 에멀젼 연료의 연소 효율은 순수한 중유보다 약 6% 정도 더 높은 것으로 평가되었다.

Abstract : The combustion behavior of heavy oil and its emulsion with water was evaluated. The concentration of SO_x in the combustion gas of emulsion oil was reduced to 57% with respect to that of the combustion gas from neat heavy oil. Also, the concentration of NO_x in the combustion gas of emulsion oil was reduced to 67% with respect to that of the combustion gas of neat heavy oil. These reductions of SO_x in the combustion gas of emulsion oil seems to be due to the reaction with salts included in surfactant of emulsion oil. Also, the combustion efficiency of emulsion oil is evaluated to be about 6% higher than that of neat heavy oil.

Key words : emulsion oil, combustion, SO_x , NO_x

1. Introduction

With the enhancement of the living level and attaching importance to the environment, air pollution is becoming very serious. The uses of fuels bring us not only power, but also serious environmental pollution. The pollutants from fuels include mainly particulates, NO_x, SO_x, CO_2, acid rain and so on, which are harmful to people's health. Although many of those pollutants are from the emission of cars, the heavy oil used in the thermal power plant and huge burner in

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factory are one of the main source of those pollutants. Therefore, the way to use the limited fuels efficiently and cleanly is an extremely urgent problem.[1-2]

The emulsified fuels have been known to have some advantages in the reduction of pollutants and the combustion efficiency. They can enhance the transformation efficiency of fuels, and more importantly they can reduce NO_x emission and particulates.[3-5] This is because evaporation of water in the combustion process reduces the oxygen concentration and burning temperature to reduce NO_x emission notably and secondary atomization is beneficial to heavy oil to enhance the combustion efficiency. Water vapor reacts with carbon particulates to produce CO and H_2 in the region lacking in oxygen, so both the particulate and the equivalence ratio will be reduced. So it can not only reduce the pollutants but also reduce the exhaust loss and enhance the thermal efficiency. The work of Kozinski on heavy oil combustion demonstrated that the formation of polycyclic aromatics in the emulsion flame was significantly reduced.[6] Data on the emission of NO_x are scarce. No differences in NO_x emissions between neat oil and oil-water emulsion flames have been encountered in some studies.[7] Ahmad and Gollahali reported some variations, but they were unrelated to the presence of water and were probably connected with the nature of the surfactant.[5] Cunnunggham *et al.* measured a decrease of about 10 % in the emission of NO_x when burning heavy oil-water emulsions.[8] This change was attributed to the lower flame temperature due to the additional water. Some results suggest a possible influence of the added water on the NO_x formation through the increase in the OH radical pool, leading to a reduction in oxygen atom concentration and hence in NO formation.[9] However, they did not demonstrate any report that the emulsion fuels would reduce the emission of SO_x.

BimixKorea, Inc, a venture company in Korea has recently developed a new surfactant to form a stable microemulsion of water and heavy oil used in boilers. This microemulsion oil is a preatomized water-in oil type of emulsion and consists of 30% water, 68% heavy oil and 2% surfactant in volume. The newly developed surfactant allows water and fuel to mix and remains stably in this state for ca. six months.

The aim of this paper is to evaluate the reduction of SO_x and NO_x concentration in the flue gas and the combustion heat efficiency of this microemulsion oil with regard to those of neat heavy oil.

2. Experimental

2.1. The flue gas sampling of heavy and emulsion oils

The boiler to combust neat heavy oil and emulsion oil was manufactured in Bimix Korea, Ltd. to test the characteristics of neat heavy and emulsion oils. This boiler is the very much same in comparison to that available commercially. The combustion gases for neat heavy oil and emulsion oil burned in the boiler were sampled using portable air sampler (Xontech, Van Nuys, CA, USA). The input sampling tubing of air sampler was put into the chimney and the its output tubing was connected with 6 liter SUMMA electropolished canister (Scientific Instrumentation Specialists, Moscow, ID, USA) and the canister was confirmed to be cleaned by Gas chromatography before it was filled with flue gas. The canisters were filled with the flue gas of two atms.[10]

2.2 Analytical evaluation of SO_x in the flue gas of heavy oil and emulsion oil

Analysis of SO_x (SO_2 + SO_3) in the combustion gas was performed by Arsenazo III [2, 7 - Bis (azo-2) phenylarsono - 1, 8 - dihydroxynaphthalene - 3, 6 - disulfonic acid] method. The flue gas collected in the canister was absorbed in hydrogen peroxide solution, and this solution is reacted with bariumacetate ($(CH_3COO)_2Ba \cdot H_2O$). The excess barium ion is reacted with Arsenazo III, which gives a Ba [Asenazo III] with blue color. This method was used for the concentration range of 50 - 700 ppm of SO_x.[11]

2.3. Analytical evaluation of NO_x in the flue gas of heavy and emulsion oils

The NO_x (NO + NO_2) in the combustion gas was analyzed using phenol disulfonic acid method. The combustion gas collected in the canister was passed through hydrogen peroxide and water solution, and added with phenol disulfonic acid. The absorbance of this solution was measured with optical spectrometer. This method is useful to measure the concentration range of 10 - 1,000 V/V ppm.[12]

2.4. XRD analytical evaluation of bottom ashes of neat heavy and emulsion oils

The XRD data for the ash were collected on a RINT/DMAX 2500 model of Rigaku (The Woodlands, Texas, USA) with four circles diffractometer using Cu $K\alpha_1$ radiation from a rotating anode source. A triple axis system, in which Ge (1 1 1) reflection was used for both monochromatizing the incident beam and analyzing the diffracted beam, was used to collect the diffraction data.[13]

2.5. Ion chromatographic evaluation of bottom ashes of neat heavy and emulsion oils

The bottom ashes of heavy and emulsion oils was dissolved in distilled water. The amount of sulfate anions in ash were analyzed using a Metrohm (Herisau, Switzerland) ion chromatography with Modular Dual Channel System.[14] The ion chromatographic parameters were summarized in *Table* 1.

Table 1. Single column ion chromatographic parameters of the simultaneous determination system

Eluent	1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$
Flow rate	1 ml min^{-1}
Separator column	4.0 x 250 mm Metrosep A Supp4
Guard column	4.0 x 10 mm Metrosep A Supp4/5 Guard
Injection volume	20 $\mu\ell$
Detector	Metrohm 732 IC Detector (Suppressed conductivity)

2.6. Measurement of the combustion efficiency of heavy and emulsion oils

The combustion heat of neat heavy and emulsion oils have been measured using 1266 bomb calorimeter (Parr Instrument, Moline, Illinois, USA). Since the commercial calorimeter has been usually used to measure the amount of calories of oil produced when it is burned under high pressure of oxygen.[15], we have manufactured the home - built calorimeter to measure the combustion efficiency of heavy and emulsion oils in practical condition of atmospheric pressure (not shown). This home - built calorimeter was manufactured in the same way with that available commercially except that the oil is burned in atmospheric pressure.

3. Results and Discussion

3.1. The concentration of SO_x and NO_x in the flue gas of heavy and emulsion oils.

The concentrations of SO_x and NO_x in the flue gases of heavy and emulsion oils have been measured using Arsenazo method and phenol disulfonic acid method, respectively. We have measured three times for each gas samples, and their concentrations in the flue gas of neat heavy and emulsion oils were displayed in *Table* 2 and 3.

Table 2. Analytical Result of SO_X in the flue gas of heavy and emulsion oils

unit : v/v ppm

	1st	2nd	3rd	Average
Neat Heavy oil	382.6	366.7	354.8	368.0 (100%)
Emulsion oil	208.4	206.7	213.9	209.7 (57%)

Table 3. Analytical Result of NO_x in the flue gas of heavy and emulsion oils

unit : v/v ppm

	1st	2nd	3rd	Average
Neat Heavy oil	178.8	160.2	164.2	171.6 (100%)
Emulsion oil	133.0	122.0	99.4	114.8 (67%)

As seen in *Table* 2, the concentration of SO_x in the flue gas of emulsion oil was reduced to 57% with respect to that of the flue gas from neat heavy oil. Also, the concentration of NO_x in the flue gas of emulsion oil was reduced to 67% with respect to that of the flue gas of neat heavy oil as displayed in *Table* 3. These low concentrations of SO_x and NO_x in the flue gas of emulsion oil in comparison to those of neat heavy oil are particularly attractive in the aspect of the environment. Therefore it is important to understand the reason why the concentrations of SO_x and NO_x in the flue gas of emulsion oil is lower than those in the flue gas of neat heavy oil.

3.2. The XRD analysis of ash remained in the burner after the combustion of neat heavy and emulsion oils.

The XRD spectrum for the bottom ashes of emulsion oil is shown in *Fig.* 1. The XRD spectrum of the bottom ashes for neat heavy oil does not show any significant signals representing any salt forms(not shown), but the XRD pattern of the as - received ashes for emulsion oil exhibits reflections of Na_2SO_4 and $CaSO_4$ as shown in *Fig.* 1. These salts seem to be produced by the reaction of sulfur compounds contained in oil and Na^+ ion (or Ca^{2+} ion) included in surfactant during oil combustion process. Therefore, these reaction products such as Na_2SO_4 and $CaSO_4$ make reduce the exhaustion of SOx compounds in the combustion of emulsion oil.

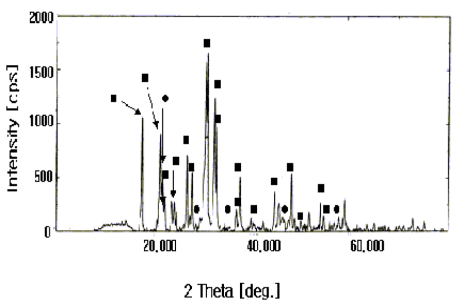

Fig. 1. Typical X-ray Diffractogram of the bottom ashes of emulsion oil (■, Na_2SO_4 ; ●, Ca SO_4). The X - ray Diffractogram for the bottom ashes of neat emulsion oil do not give any peaks (not shown)

We have expected the existence of nitrate salts as well as sulfate salts in ash remained after the combustion of emulsion oil as a cause for the reduction of NO_x in the combustion gas of emulsion oil. However, the XRD spectrum for the bottom ashes of emulsion oil does not show any nitrate salt form. Although the ash includes nitrate salts, these salts could exist as a totally amorphous state, which does not show any signals in the XRD spectrum. Therefore, the existence of these nitrate salts were confirmed by ion chromatography after the ash was dissolved in water (see below).

3.3. The ion chromatographic analysis of ashes dissolved in water.

Since the existence of nitrate salts was not monitored by the XRD spectrum, the ion chromatography was utilized to identify NO_3^- or NO_2^- ion. The bottom ashes of neat heavy and emulsion oils were dissolved in water. The ion chromatogram for the bottom ashes of emulsion oil was shown in *Fig.* 2.

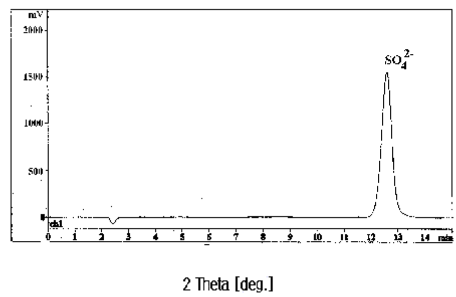

Fig. 2. Typical ion chromatogram of the bottom ashes of emulsion oil. The ash dissolved in water was filtered and the solutions were injected to ion chromatography. The SO_4^{2-} ion signal with the retention time of 12.6 min. is showed in ion chromatogram. The IC chromatogram for the bottom ashes of neat emulsion oil do give a trace of SO_4^{2-} ion signal (not shown)

It indicates that the ash from the combustion of microemulsion oil does not include any nitrate salts. The ion chromatogram for the ash from neat heavy oil does not show any sulfate or nitrate anion signal (not shown), which suggested that the origin for the reduction of NO_x in the combustion gas of the emulsion oil is totally different from that for the reduction of SO_x in the combustion gas of the emulsion oil. Therefore, the reduction of NO_x in the combustion gas of emulsion oil would be due to the lower flame temperature by added water as suggested earlier.

3.4. The combustion energy efficiency in heavy and emulsion oils.

Table 4 shows the combustion energies produced when neat heavy and emulsion oils are burned in the bomb filled with 40 atm oxygen gas using the bomb calorimeter. Although the energy produced from emulsion oil corresponds to 70.3% of that produced from neat heavy oil, there is no combustion energy difference between two oils within experimental error since the amount of neat heavy oil contained in emulsion oil is about to be 68%. However, since the energy showing in calorimeter does not represent the combustion energy under real condition, we have manufactured the home-built burner to measure the energy efficiency in real condition (not shown). The combustion energies for neat heavy and emulsion oils were displayed in *Table* 5. When the amount of neat heavy oil in emulsion oil included about 68% in volume, the combustion energy efficiency of emulsion oil is 6% higher than that of neat heavy oil. This result is consistent with the combustion energy efficiency of emulsion oil measured earlier and this better efficiency seems to be due to easier atomization of emulsion oil by added water.[15]

Table 4. Heat of combustion for neat heavy and emulsion oils measured in commercial calorimeter

unit : calories/gram

	1st	2nd	3rd	Average
Neat Heavy oil	10,150	10,100	10,050	10,100 (100.0%)
Emulsion oil	7,040	7,170	7,100	7,103.3 (70.3%)

Table 5. Heat of combustion for neat heavy and emulsion oils measured in home-built calorimeter

unit: calories/gram

Oils	Measurement	Combustion energy	Average
Heavy oil	1st	2,377	2,684
	2nd	2,675	
	3rd	2,806	
	4th	2,876	
Emulsion oil	1st	2,174	1,942
	2nd	1,943	
	3rd	1,796	
	4th	1,745	
	5th	2,050	

4. Conclusions

The combustion gas of emulsion oil was evaluated in comparison to that of neat heavy oil. The concentrations of SO_x and NO_x in the combustion gas of emulsion oil were reduced to 57 and 67% with respect to those of the combustion gas of neat heavy oil, respectively. The reduction of SO_x concentration in the combustion gas of emulsion oil seems to be due to reaction of SO_x with salts included in surfactant of emulsion oil. Also, the combustion efficiency of emulsion oil is evaluated to be about 6% higher than that of neat heavy oil.

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