Study on the Combustion Characteristics of Fuel Additive for Heavy Oil And Heavy Oil Residue

January 2003

Senior Research Scientist: Choo Su tae Ph.D TEL: 031-219-2679 FAX: 031-216-9125 CPI 011-823-8531

Plant Engineering Center of Institute for Advanced Engineering 1. Outline of Development Technique

1-1. Introduction

In aspects of recent worldwide environmental issue and safety insurance of energy demand and supply balance, oil which is mainly used as present energy should be energy source of other converted form for the future if there is no solution to environmental pollution and efficiency improvement of utilization technique. Also nations of the world has same understandings about alternative plan such as 'Alternative energy development' and 'Use clear fuel' for environmental issues, and has been driving research development program continuously under leadership of government. However, due to given conditions of economy, society, and technique, it is easy to forecast that oil will hold very large part of energy source field as usual.

Petroleum is used in various areas as variety form of fuel after refining process. Heavy oil is used widely for heating, power plant, industrial boiler and heavy oil residue is used for paving asphalt (Chu Dae Su (1975), Lee Woo hwan (1982)). In spite of its low price, prime cost of heavy oil has increased due to required after treatment section, which is needed for refining pollution elements such as reed, ash, and nitrogen in oil. Sulfur recovery unit, dust collector and other cleaning devices are those of after treatment sections and upkeep expenses of these utilities are fairly high throughout the entire progress.

Most of isolated power plant in Korea is using heavy oil and the cost of production per kWh is higher than other power plants using natural gas, coal, and atomic power. Actual circumstances of some heavy oil isolated power plants reached seasonal assistant source of electricity running deficit operation. In the long run, if management cost of existing after treatment section is not lowered or process of using cheaper fuel is not applied, operating remained isolated power plant will encounter difficulties. As an alternative proposal, operating isolated power plants using heavy oil residue, which is cheaper, or mixture of heavy oil and heavy oil residue will result in reduction of investment cost.

Heavy oil residue not suited for using directly in job-site unlike heavy oil because of its time difference according to temperature, which needs extra care for handling and applying. This is why heavy oil residue needs property and quality improvement similar to heavy oil as well as after treatment section. Specially, burner adjustment similar to heavy oil is possible by adding fuel additive for there is a critical point of combustion-burner improvement process. Technobio (Inc.), which is our client for this study, has experience in developing and commercializing fuel efficiency improvement material of heavy oil and

gasoline for many years in fuel improvement technology field. Accordingly, this study will examine the features of the fuel additive by combustion tester. Thermal treatment plant from Plant Engineering Center of Institute for Advanced Engineering will be used for this test and concentration of dust, NOx, CO will be compared with and without the fuel additive.

1-2. Status of Related Technology

Fuel additive research-development project and commercializing has been advanced for decades and is still being studied (Cooper (1984), Lynam etc. (1990), Matter etc. (1997), Duncan etc. (1997), Okada etc. (1997), Li etc. (2002)). Application range of fuel additive is vast from liquefied fuel of gasoline, light oil, heavy oil to solid fuel of bituminous coal. But result of scientific research or clear analytical research of the additives are only known as business secrets even though base of additives for each fuel has increased (Baek Min Soo etc. (1995), Cho Eun S ung etc. (1997), Yang Kwan Mo etc. (2000)). In addition fuel additives has lost technical credit because uncertified companies have been marketing similar products without actual proof recently. If so lets look around the technical status of additives today.

Fuel additives were required since when gasoline and light oil was first used for vehicles. Especially upon demands of the times pollution improvement and extension of engine life, multi-functional additives are in use now. Anti-knocking agent increases octane number of gasoline, which is used with Pb (CH3) 4 and 0.1% of aminophenol derivatives, or phenol derivatives are included as an anti-oxidant. Reaction activator (Amino-propane affiliated compound) and antifreeze mixture (aniline compound) is also being used with surface active agent which is included to remove sludge in vaporizer of internal combustion engine.

Diesel light oil is represented with cetane number, an index of compression ignition, and ignition improver is used to improve combustion efficiency and high numerical value maintenance. There is not much efficiency improvement compared to gasoline but still paraffin or Esther compound element are used. Light oil, which comes out from resolution process contains aromatic hydrocarbon more than paraffin hydrocarbon, which has higher cetane number. Therefore, additives are included to increase cetane number. Also additives are used as lubricity improver because light oil from low sulfur crude petroleum contains low melting point wax, which is used in cold areas. Reported effects of such fuel additives are fuel reduction (~10%), diminution of SOx, NOx discharge consistency, preventing corrosion, extending life of engine, and carbon sediment exclusion.

There is liquefied fuel called 'OrimulsionTM' which is manufactured by

combining bitumen with 30% water and 1% surface-active agent for power plant use. This liquefied fuel and developed by BP Company and PDVSA (Petroleos de Venezuela SA) who took local advantage of Venezuela, the country with more than half of world's bitumen reserve. Materials of bitumen have high viscosity, which is not fitted for power plant. So water and surface-active agent was needed to change property similar to heavy oil. Surface-active agent is used as additive for maintaining safe emulsion condition of water and heavy oil. Alcohol affiliated property of matter was used in early stage of development, but it is known that phenol affiliated ingredients are now being included.

Figure 1 is comparison of orimulsion and heavy oil with 1 coal as standard against pollution emitting factor. It is observed that elimination of SO2 and NOx has decreased by 50%. Principle of orimulsion is making corpuscle of fuel 10,000 times smaller than original, which makes more opportunity for oxygen to contact enabling complete combustion. Orimulsion is manufactures by setting impeller inside high-speed mixer for forced mixing. When fuel manufactured like this is sprayed in combustor by burner, water particle $(10-30 \neq \Box m)$ located inside of heavy oil particle $(30-150 \neq \Box m)$ evaporates and explodes and breaks up heavy oil particles.



Figure 1. Comparison of emissions from various fuels.

When we look into research results of heavy oil (Kim etc. (2002)), organic and inorganic compounds used combustion improver agent. Metal (Fe, Mg, Ca)-naphthenate, stearate, and solvents are used for organic compound and carbonate, nitrate compounds are used for inorganic compound. Small amount in range of 1~5wt% were used. Witzel (1995) tested reactivity of air and cenosphere form of heavy oil particles using cenosphere generator. At this time he compared reacting condition according to fuel additives (iron included organic compound). Decrease of particles over 60% in boiler test was observed and additives built cenos hpere structure well. There are about 10 small and medium-sized enterprises related in Korea and venture business for developing low-grade oil additive. Technobio, which is our client of this study, was recognized as leading enterprise by Korea government and made efforts in efficient use of petroleum related fuel for over 8 years with pro-environmental fuel conversion goals. Technobio also developed 'Power-Z Series' for vehicles and industrial boiler to save gasoline, light oil, heavy oil and reduce pollution element. Over 80 business including Samsung Engineering & Construction (Inc.), Kolon (Inc.), Hyundai Engineering & Construction (Inc.), H

using Technobio's products and shows reduction ratio for heavy oil boiler of 5~15%.

1-3. Anticipated Effects

Fuel additive, which will be developed in this project, is expected to solve combustion problem by improving property of low-grade oil and reducing density of pollution in waste gas. If heavy oil residue or improve heavy oil is used in industrial boiler and power plant, maintaining and mending cost profit can be expected due to current price of heavy oil residue which is about half of heavy oil. This fuel additive is also expected to show reduction in mixed fuel. For one example, vanadium or natrium is included in most of low-grade oil such as heavy oil and heavy oil residue with reed, which accelerates corrosion in high temperature part of boiler. Fuel additive has organic compound, which increases melting point and prevents high temperature corrosion caused by metal compounds of fuel melting point. When metal compounds, which creates corrosion turns white, heat absorption of brazier decreases and makes heat inclination of combustion chamber possible. Fuel additives also have Sox decrease effect, which could solve corrosion problems. And additives lower air necessity for combustion, which reduces air-polluting elements. The additives and mixed fuel could be applied to industrial boilers which uses heavy oil mostly and existing businesses where additives are already being used. The price of fuel additive will be applied in same level of existing ones, and investment cost will be saved if property improved heavy oil or heavy oil residue is used with this additive. Another applicable area could be power plants. Improved scale in year 2002 was about 30,000백만kWh, depending mostly on heavy oil. If fuel additive or heavy residue oil which is developed in this business can be used in power plant area, fixed investment cost will be saved and defraymen t of environment pollution factor in after treatment section will be minimized.

2. Experiment

2-1. Fuel

Heavy oil provided by Technobio (Inc.) and atmospheric residue is used in this study. Analyzed features of these fuels are shown at Table 1.

	공업분석 ¹⁾				원소분석 ²⁾						발열량4)
	MW(%)	VM(%)	Ash(%)	F-C(%)	C(%)	H(%)	N(%)	S(%)	O(%) ³⁾	Ash(%)	(kcal/kg)
중유 1	0.00	92.11	0.06	7.83	85.61	11.57	0.23	2.53	0.00	0.06	10195
중유 2	0.00	92.20	0.05	7.75	85.53	11.59	0.27	2.56	0.00	0.05	10221
잔사유	0.00	89.69	0.03	10.28	85.64	10.10	0.21	4.02	0.00	0.03	10210

Table 1. Characteristics of fuels employed in present study

주:1):As-received

2) : Moisture free basis

3): By-diff.

4) 중유 1 : 첨가제(power-z)를 포함한 oil

중유 2 : 첨가제(power-z)를 포함하지 않은 oil

잔사유 : 첨가제을 포함하지 않은 상압잔사유

Heavy oil, which we used, has 2.5% of reed included but analyzed value from industrial analysis and elementary analysis were almost same between additives included sample and not included sample. And effect caused by fuel additives in

caloric value wasnt observed. 4% of reed is included in atmospheric residue and has about half of ash compared to heavy oil. Caloric value of residue oil and heavy oil was about the same.

To find out the effects of fuel additive to oil residue, volume of additive was diluted by 1:1000. Additive added oil residue was manufactured with same process of additive included heavy oil. Preparation took over one week by mixing in temperature over 80 for 8 hours a day using stirrer. These additives increased liquidity of heavy oil and oil residue in normal temperature (10). And for oil residue viscosity increased also.

2-2. Testing instruments

Incinerator is used to test combustion features of fuel due to additives. This instrument is designed for stable, non-polluting, and quantity reducing process as purpose. Facility is consisted of 4 parts; pretreatment process, incineration-melting process, heat recovery process, and flue gas treatment process. Figure 2 is graphic display of main control, which shows entire structure of the facility.



Figure 2. Main control graphic display for melting furnace system.

The burner used in this study is product of Green Enertech(Inc.) GET101-T1, and is able to operate with 10~20kg of fuel for one hour. Air fan and oil pump for fuel absorption is designed as single body form, and air quantity is adjustable by damper. Supply line of fuel, which goes to the burner, is capable of adjusting nozzle temperature, which makes operating burner possible with heavy oil of high

viscosity (up to 300°C). Oil was poured into fixed heavy oil burner 8~12kg per hour and air was injected regularly with damper fixed. There was no change in fuel and air injection for each heavy oil and oil residue. Fuel was injected with temperature over 100°C from heating bucket located on top of balance and reserve oil was heated with same condition to prevent stoppage of fuel line. Supplying location of these fuels were above 50cm of entrance perpendicularly. Heavy oil burner was attached to flange located at the center of cap section (diameter 1200mm, length 200mm). Also observation window is attached at this part, which is upper cover of furnace for observing flame condition and features of combustion. Lower part of furnace, which is next to cap section, has upper section (diameter 500m, length 700m) and middle section (diameter 500m length 700m) with thermocouple attached for analyzing temperature grade of combustion. Pressure gauge is attached at center of upper section for observing pressure condition at the same time.

Inner pressure of incineration-furnace is adjusted to maintain about -10mmAq. This setting value of inner pressure could be adjusted with ID fan located at the very back of flue gas treatment process. Damper is automatically controlled based upon setting value and discharges combustion gas by maintaining steady pressure.

Stack sampler (Chung engineering (inc.), CE-221SM) from suitable range of secondary combustion chamber was used to analyze and compare the dust produced by combustion. Over 3 times average. And gas analyzer was used to analyze density of CO, CO2, SO2, NOx (x=1, 2) and O2. Observing measured value of these analyzed gas are available at on-line and is used as reference control variables with response speed of dust analysis and furnace pressure. V-cone was also used to measure the current speed between cyclone of flue gas treatment process and line of wet scrubber.

2-3. Examination method

Before injecting heavy oil and oil residue, LPG was used to heat incineration furnace to make normal operating condition. Test was started with inner temperature of furnace over 700. Assistant burner was also used other than preheating burner according to its need which used LPG also.

After the preheating, light oil was used as assistant fuel prior to heavy oil or residue oil to supply testing fuel smoothly. Only light oil was used at the first stage. And increased injecting amount of heavy oil slowly. Heavy oil or oil residue was put into burner at last. Amount of fuel and air injected in the burner was corrected before the test.

This study will focus mainly on the production of flue gas and dust while comparing additive mixed heavy oil and oil residue. Standard of the analysis will be confidence interval where operation variable of furnace facility system could be maintained stably. These territories will be compared in 1) territory with regular temperature grade of furnace 2) territory with regular gas production 3) territory with regular flue gas current speed, for 1 hour. In addition, dust analysis will be put in operation in same time zone where these territories are going on.

3. Test result and discussion

3-1. Combustion operation of Heavy oil combustion operation

8.1kg/h of both fuel additive included and excluded heavy oil was injected. Two fuels were stably injected and kept for one hour to burner where temperature about 200 was maintained. Figure 3 and 4 indicates flames of both additives included and excluded fuel. Flame form condition and length was about the same except for the flame color. Figure 3, which are heavy oil without fuel additive showed orange, color and light yellow for heavy oil with fuel additive could be observed. This result shows us that combustion conditions were improved by fuel additive.



Figure 3. Flame image of heavy oil without the additive.



Figure 4. Flame image of heavy oil with the additive.

Combustion condition improvement was also shown in temperature change. Inner temperature of heavy oil without additive was about 750~780, but heavy oil with additive was 780~820, which showed about 30~40iÉ increase. This fact concludes that fuel additive improves property of heavy oil to react with oxygen efficiently. Figure 5 and 6 shows production of waste gas from combustion according to fuel additives. It is observed that oxygen, carbon dioxide, and NO didn t have difference but 50~60ppm of CO decreased when additives were included.

Figure 5. Concentration profiles of heavy oil with respect to the additive for O2 and CO2.

Figure 6. Concentration profiles of heavy oil with respect to

the additive for CO, NO2, and NO.

Production of dust according to fuel additive was 16.5mg/Sm3 (fuel additive included) and 169.1mg/Sm3 (without fuel additive). To samples were compared in same condition, which shows combustion condition of heavy oil was increased vastly.

3-2. Combustion operation of Heavy oil residue

Fuel additive included heavy oil residue had orange flame for over 1 continuous hour stably as shown in Figure 7. Generally, it is difficult to operate gun type heavy oil burner because of grain size, even though inside of burner is heated in range of 250-300 However, in this examination, running heavy oil burner of residue oil was possible with fuel additive included heavy oil residue as shown in figure 7. Figure 7 also shows results when 12.3kg of heavy oil residue is injected in excess air condition. Conclusion is that fuel additives broke up particles of heavy oil residue smaller which increased combustion efficiency. Additional examination and grain size analysis of heavy oil residue is required to explain influence of fuel additive.



Figure 7. Flame image of heavy oil residue with the additive.



Figure 8. Flame image of heavy oil residue without the additive.

But as shown in Figure 8, heavy oil residue without fuel additive had difficulty in fuel injection and combustion operation. First of all, even though power of oil pump was same, injection quantity was only 6.4kg/h which is about half of fuel additive included heavy oil residue. At this time fuel injection line of heavy oil burner was maintained about 300. Because the temperature was about 120 for combustion operation test of heavy oil residue, it is difficult to compare production of waste gas and temperature change of furnace in same condition. However, operation feature difference due to fuel additive was confirmed. Compared to figure 7, length of flame shown in figure 8 was relatively short and closed to orange color. Maintaining regular flame was impossible for heavy oil without fuel additive.

heavy oil burner was maintained about 300. Because the temperature was about 120 for combustion operation test of heavy oil residue, it is difficult to compare production of waste gas and temperature change of furnace in same condition. However, operation feature difference due to fuel additive was confirmed. Compared to figure 7, length of flame shown in figure 8 was relatively short and closed to orange color. Maintaining regular flame was impossible for heavy oil without fuel additive.

Production of dust according to fuel additive was 800mg/Sm3 (with fuel additive) and 950mg/Sm3 (without fuel additive). Even though comparing two samples in same condition is difficult, this fact proves how effective fuel additives are for operating heavy oil residue burner. Figure 9 and 10 are pictures showing density of waste gas observed at the same time when dust was measured. NOx den sity of fuel additive included heavy oil residue was maintained low generally which

indicates operating condition improvement and density result of dust are corresponding.

Figure 9. Concentration profiles of nitric oxides of heavy oil residue by addition of the additive; 'add' in a parenthesis means an addition of the additive in the oil.

Figure 10. Concentration profiles of gases produced from heavy oil residue by addition of the additive; 'add' in a parenthesis means an addition of the additive in the oil.

4. Conclusion

Combustion operation test using heavy oil burner was held to carry combustion property and waste gas analysis experiment for additives of heavy oil and heavy oil residue. Temperature of heavy oil was increased over 30~40 when including additives and color of flame was light yellow which showed increase of combustion property. CO, dust, which originate from additives added heavy oil were maintained low. It is estimated that constituent of fuel has changed to react to air profitably due to additives. Viscosity was increased after adding additives to heavy oil residue and also had significant difference at combustion operation using heavy oil burner. Heavy oil residue was put in to 300 burner but compared to additives included heavy oil residue which temperature was maintained at 120, only half of sprayed fuel was burned. Also heavy oil residue without additives had bad combustion condition for great deal of NO, CO soot was produced and burner temperature was maintained low at 650. After all, the additives provided by Techno bio (Inc.) increased burner operation by changing property of heavy oil residue and decreased consistency of dust.

5. Reference

Min-Su Baek, Sang-Hun Oh, Experimental study on combustion features using jet-nozzle. The Korean Society of Mechanical Engineers Paper, 19(2) 548(1995).

Hyun-Dong Shin, Application and fundamental study of **Combustion Engineering**, **K** orea Society of Automotive Engineering Paper, 11(4), 13(1989).

Kwan-Mo Yang, Moo-Hwan Chun, Chil-Young Sun, In-Gahp Jang, Kil-Hong Jang, Experimental study on combustion features of spud type gas burner. The Korean Society of Mechanical Engineers, the great autumn meeting

Cooper, W.C., The health implications of increased manganese in the environment resulting from the combustion of fuel additives: a review of the

literature, J. Toxi. Env. Health, 14(1), 23(1984).

Duncan, M.P., Environmentally friendly production of polybutene amines for use as deposit control fuel additives, U.S.5583186 (1997).

Kim, Y. et al, Fuel additive composition for heavy oils; Wang, J., Composite heavy oil combustion improvers and their preparation, Fuel and Energy Abstracts, Jan. 2002, 19(2002).

Li, Y. et al, Manufacture of high efficiency multifunctional fuel oil additive, Fuel and Energy Abstracts, Jan. 2002, 24(2002).

Lynam, D.R., Pfeifer, G.D., Fort, B.F., and Gelbcke, A.A., Environmental assessment of MMT fuel additive, The Science of the Total Environment, 93, 107(1990).

Matter, U. and Siegmann, The influence of particle filter and fuel additives on turbo diesel engine exhaust, J. Aerosol Sci., 28(1), S51(1997).

Moszkowicz, P. and Witzel, L., Modelling of very fast pyrolysis of heavy fuel oil droplets, Chem. Eng. Sci., 51(17), 4075(1996).

Okada, M., Matsudaira, J., and Naruse, H., Effects of diesel fuel additives on engine performance and reliability, JSAE Review: Abstracts, 18, 185(1997).

Witzel, L., Moszkowicz, P., and Claust, G., Mechanism of particulate reduction in heavy fuel oil combustion, Fuel, 74(12), 1881(1995).