RESEARCH AND DEVELOPMENT ON A PETROLEUM COKE-WATER SLURRY AS A FUEL

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INTRODUCTION

A coal-water mixture fuel and a coal-oil mixture fuel have been developed to compensate defects of solid fuels which are difficult to handle, cause air pollution problems around a storage yard and so on. But these fuels have defects in that they have a high ash content and they are inferior to fuel oil economically at present. To compensate these defects we intended to develop a petroleum coke-water slurry fuel. However a petroleum coke-water slurry fuel is less combustible than a coal water slurry, because a petroleum coke has a lower volatile matter content than a coal. We overcame this fault by adding the catalyst to the petroleum coke-water slurry to promote combustion.

EXPERIMENTAL

A small batch reactor was used to determine relationship between feedstock properties and product coke quality. Twenty milliliters of a feedstock oil was charged to the reactor and heated at 465 degree C for twelve hours. Around 30 weight percent conversion to coke was obtained, and its properties were compared with the feedstock properties. Maya vacuum residue and hydrotreated middle east vacuum residue were tested as the feedstocks.

Property targets were set in terms of stability in storage and ease of handling.
They are as follows:
(1) Phase separation does not occur for two months and
(2) Viscosity is less than 1,000 mPas.

Two kinds of dispersion reagent were studied (additive(a)-polyolefin, additive(b)-polyacrylate). Sodium hydroxide was used as a pH controller, and a certain clay as a stabilizer. The petroleum coke was crushed to be smaller than 3 millimeters. And it was put into a ball mill with water, a dispersion reagent, sodium hydroxide, and a stabilizer. More than 98 percent of the petroleum coke was ground under 150μm in the ball mill and a petroleum coke-water slurry was obtained. The slurry content was measured by vaporizing water in a dryer at 107 degree C. Viscosity was measured with a rotary viscometer. A 100 ml glass sample tube containing the petroleum coke-water slurry was vibrated at 20 mm amplitude for 5 minutes at 90Hz. Stability of the slurry was evaluated by observing deposits at the bottom of the sample tube.

Twenty two kinds of catalysts were examined as combustion promoter. They were organic acid metals and inorganic acid metals which were considered to have an ability to promote combustion. Petroleum coke was crushed under 500μm, and sieved to its 88~105μm portion. Volatile matter was removed from coke flour of the 88~105 μm portion by heating at 900 degree C for 7 minutes. Four weight percent of combustion catalyst as metal was added to the char by diluting with water or toluene. Then solvent was vaporized by heating. As a result catalyst added char was prepared. This char was put into a reactor(10mm diameter quartz tube) which was kept at 800 degree C under nitrogen flow. Then nitrogen was switched to oxygen flow. Carbon dioxide concentration in flue gas was detected with infrared analyzer. Combustion rate was determined by the trend of carbon concentration.

A petroleum coke-water slurry to which combustion catalyst B, C, or E was added was burned at a small boiler(steam generation 2 tons/hour). Combustion efficiency was defined as the ratio of fuel quantity burnt against fuel quantity supplied to the boiler.

RESULTS AND DISCUSSION

We planned to produce two kinds of cokes which have different sulfur contents. They are 5~6 weight percent(coke A) and 6~7 weight percent(coke B). The blend ratio of the feedstocks was changed to get desired coke sulfur content. The relation between the concentration of petroleum coke in the slurry and viscosity varies according to the content of a stabilizing reagent. In the case of 0.1 percent stabilizing reagent, the slurry concentration is 75 weight percent to get 1,000 mPas of slurry viscosity. In the case of 0.2 weight percent stabilizing reagent, it is 74 weight percent. When 0.3weight percent of stabilizing reagent is added, the slurry concentration is 72.5 weight percent. No difference can be seen in petroleum coke A and B. Dispersion reagent (a) gives a high slurry concentration than reagent (b) to get the same slurry viscosity. Judging from the relationship between the addition ratio of the dispersion reagent and viscosity, 0.3 weight percent of the dispersion reagent seems optimal. Viscosity and pH increase with an increase of the ratio of sodium hydroxide. When petroleum coke A and B are compared, petroleum coke B shows higher pH and viscosity. A lower sodium hydroxide ratio is preferable to get a higher slurry concentration. But, considering the stability of slurry, 0.1 weight percent addition is the optimum.

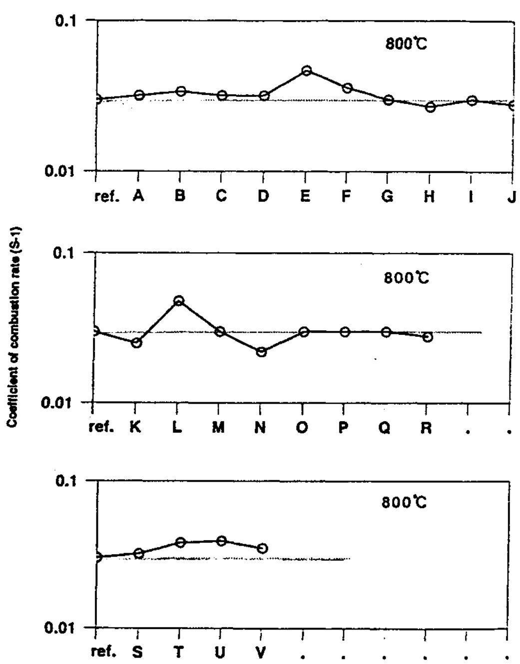

Fig.1 Effect of combustion catalysts

Stabilizing reagents have the affect of increasing the viscosity. 0.2 weight percent of stabilizer content is considered good.

Figure 1 summarizes the screening results of twenty two combustion catalysts. Combustion catalysts A, B, C, E, F, L, S, T, U,and V show the effect of promotion of com-bustion. Catalysts A and B are organic rare earth metal compounds, and catalys C is an inorganic rare earth metal compound. Catalyst E is copper naphthenate, F is iron naphthenate, and L is potassium naphthenate. Catalyst S is copper sulfate, T is copper acetate, U is copper neocaprate,and V is copper caprylate.

Figure 2 shows the results of the boiler combustion test. Fifty weight ppm(as metal) of catalyst addition shows significant affect on increasing the combustion efficiency. Two hundred weight ppm of catalyst addition shows remarkable affect of promoting combustion. Catalyst E and L shows the remarkable affect among tested catalysts. The combination of catalyst B and E shows synergetic effect on promoting combustion.

CONCLUSIONS

When the dispersion reagent is 0.3 weight percent, pH controller is 0.1 weight percent, and the stabilizer is 0.2 weight percent, a stable petroleum coke-water slurry was obtained. By adding 200 weight ppm of copper naphthenate or potassium naphthenate as a combustion promoter catalyst, combustion efficiency improved. As a result, a more economical and less polluting slurry fuel was developed.

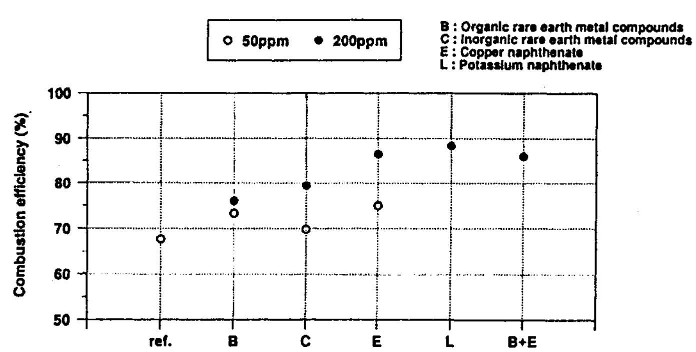

Fig.2 Results of boiler combustion tests