Combustion Characteristics and Pollution Minimum Technology for VR (Vacuum Residue) Fired Boiler*

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An experimental study on the combustion of extra heavy oil has been performed using a cylindrical test furnace. Recently, light oil such as gasoline is almost exclusively demanded as liquid fuel made from petroleum. In order to produce light oil in a high yield, extra heavy oil, which is called as VR (Vacuum Residue), remains after refinement under reduced pressure. VR features extremely high viscosity, as well as high percentages of sulfur, nitrogen, heavy metals, and resident carbon in fuel. Regarding the use of VR as a fuel for actual commercial boilers, a number of serious problems must be overcome. These include high- and low-temperature corrosion of metal materials, and the need to meet environmental regulations calling for low NO_x and a low unburned carbon ratio in exhaust gas. In the present study, accordingly, a firing test has been conducted to accumulate the basic characteristics of VR combustion. From the test results, stable ignitability was ascertained, and both NO_x emission and the unburned carbon ratio in exhaust gas were found to be at the same level as for bituminous coal combustion. Also, the reactivity and the carbon structure of the sampled soot and char were chemically examined in detail, and the reaction rate with oxygen was formulated. Furthermore, numerical simulation of combustion in one-dimensional furnace was conducted, and the calculated results were compared with the experimental data.

Key Words: Fossil Fuel Fired Power Generation, Liquid Fuel, Boiler, Combustion Product, Combustion

1. Introduction

As liquid fuel made from petroleum, light oil such as gasoline is exclusively demanded recently. Accordingly, the trend for heavy oil remaining after distillation to be used as the fuel for commercial boilers has been rising. In recent years, refinement of petroleum has been conducted under reduced pressure, and the oil remaining after this process becomes heavier. This extra heavy oil is called as VR (Vacuum Residue), and is characterized by high percentages of the resident carbon, sulfur, nitrogen, and heavy metals, as

well as by viscosity that is much higher than that for asphalt which has been the typical heavy oil heretofore.

Since the oil crisis, dependence upon heavy oil as an important energy source has been proceeding, and our company has constructed commercial boilers for heavy oil such as asphalt at more than twenty locations^{(1),(2)}. Although technology for the combustion of heavy oil has essentially been established, VR is more difficult to utilize in actual commercial boilers, due to its high viscosity and high percentages of resident carbon and metals, while environmental standards for pollutant emission become increasingly strict.

Generally, if the value of excess oxygen in exhaust gas is permitted to be high, the soot and char contained in exhaust gas can be reduced to some degree, while the conversion from SO_2 to more corrosive SO_3 promotes, as well as the combustion

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Table 1 Properties of VR(Vacuum Residue)and C-heavy oil

Item \ Unit		Fuel	VR (Vacuum Residue)			Heavy Oil (Rank C)
			A	B	C	
Proximate Analysis	Calorific Value (HHV)	kcal/ kg	9950	9650	9720	10300
	Specific Gravity (15/ 4 °C)	—	—	1.081	1.092	0.95
	Viscosity	cP	5000 (110 °C)	30000 (110 °C)	10000 (110 °C)	22 (100 °C)
	Ash	wt %	0.05	0.06	0.08	0.01
	Water	wt %	< 0.01	< 0.01	0.12	< 0.1
	Resident Carbon	wt %	28	37.7	38	11
Ultimate Analysis	S	wt %	5.56	4.8	3.04	3
	N	wt %	0.47	0.43	0.92	0.2
	V	ppm	135	159	334	80
	Ni	ppm	43.2	72	118	10
	Na	ppm	66.1	26.6	55	30

Fig. 1 Dependence of viscosity of heavy oil on temperature, represented in loglog(viscosity)-log(temperature) diagram

efficiency declines. In the present paper, therefore, VR firing tests have been conducted to accumulate the knowledge on combustion, and an appropriate distribution of combustion air was identified. Also, the structure of char in exhaust gas was chemically analyzed in detail and its reactivity is discussed.

2. Features of VR

Chemical analyses for four typical kinds of VR are shown in Table 1, with analyses of C-heavy oil and asphalt for references. Also, the dependence of viscosity on temperature is shown in Fig. 1, according to ASME procedures^{(3),(4)}. The horizontal and vertical coordinates in Fig. 1 are calibrated as the logarithm of temperature and twice the logarithm of viscosity, respectively. When a high viscosity oil is measured using the capillary method, it is known that the viscosity-temperature curve can be well arranged in these special coordinates. Compared with C-heavy oil, which is the most popular fuel for oil-fired boilers, the features of VR are summarized as follows.

(1) Very high viscosity

Since VR is solid at room temperature, it must be heated in order to atomize with a burner. Even at 100°C, which is the typical temperature for C-heavy oil atomization, the viscosity of VR is greater than 5 000 cP. At 250 - 300°C, viscosity becomes 20 - 30 cP, which is the ideal value for atomization with a two-fluid-type burner assisted by steam or air.

(2) High percentage of nitrogen in fuel

The value of nitrogen contained in VR is generally 0.4 - 0.9 wt%, which is approximately twice as large as that of C-heavy oil. Accordingly, low NO_x burners and de-NO_x equipment for exhaust gas should be provided to satisfy environmental regulations.

(3) High percentage of sulfur in fuel

The value of sulfur contained in VR is generally 3 - 6 wt%, two to three times as high as that in C-heavy oil. Generally, the conversion factor from sulfur in fuel to SO_x in exhaust gas is nearly 100%. Therefore, chemical compounds such as magnesium should be provided to prevent the corrosion of metals exposed to high-temperatures, such as burner ports (due to light metal-sulfur compounds). Further, to prevent low-temperature corrosion of metals (due to SO₃ produced from the reaction of SO₂ with water) such as the rotating metal drum in the air preheating equipment where heat is exchanged between exhaust gas and the combustion air supplied to the burner, the temperature level of metal surface in the exhaust gas line should be controlled so as not to condense water.

(4) High percentage of resident carbon

The value of resident carbon in VR is 20 - 40 wt%, two to four times as high as that in C-heavy oil. Here, the percentage of resident carbon is defined as the residual weight of carbon after keeping the fuel at 850°C in inert gas, and this index shows the nature of carbon polymerization when fuel is heated. The high

value for VR means that the carbon in VR is long-chained. Generally, when the percentage of resident carbon in fuel increases, dust in exhaust gas tends to increase. Accordingly, the most important problem to overcome for the VR firing is to maintain a high combustion efficiency (low unburned carbon ratio), and this is deeply related to low NO_x and low SO_3 technologies. This point is discussed later in more detail.

3. Experimental Apparatus and Procedure

For the VR firing test, the cylindrical furnace shown in Fig. 2 was used, with an inner diameter of 2.2 m and an inner length of 7.5 m. The inner wall is coated with fireproof ceramics 10 cm thick, and the outer wall is surrounded by a water jacket. The system flow of the experimental apparatus is shown in Fig. 3.

Solid VR (VR-A in Table 1) was first crushed with a hammer crusher and melted in the fuel tank, the temperature of which was maintained at 250–300°C

Fig. 2 Photograph of the test furnace (inner diameter : 2.2 m, inner length : 7.5 m)

by an electric heater. Double-annular tubes were used for all the VR piping with steam running through the gap between the inner and outer tubes. Prior to VR firing, C-heavy oil was supplied and the experimental apparatus was preheated. The exhaust gas sampled from the sampling port was analyzed using gas-chromatography and the particles contained in exhaust gas were collected in a cylindrical filter.

4. Soot and Char Contained in Exhaust Gas

4.1 Reactivity of resident carbon

A typical photograph of particles sampled from exhaust gas is shown in Fig. 4. It is found that the sampled particles consist of a mixture of two kinds of particles; one is relatively large (20–50 μm) with a rigid surface, and the other is relatively small (1–10 μm) with a smooth surface. The large particles are considered to have originated in the resident carbon, because of its rigid surface, while the small are thought to be the soot produced in the gas phase through hydrocarbon polymerizing. These large

Fig. 4 Photograph of soot sampled from exhaust gas of VR (Vacuum Residue) firing

Fig. 3 System flow of experimental apparatus for VR (Vacuum Residue) firing test

particles of unburned carbon are frequently referred to as cenosur.

The reactivity of sampled particles was examined using a thermo-gravimetric analyzer. The change of weight when the temperature of sample was programmed to increase (T-G curve), is shown in Fig. 5. The rate of temperature increase was set at 10 deg/min somewhat low, in order to realize the reaction to be controlled by the reaction between particle surface and gas, but by the diffusion of gas adjacent to particle surface. The mechanism of oxidation reaction at the particle surface should be complex⁽⁵⁾, but attempts were made to correlate the reaction rate with the Arrhenius form of the simple first-order expression:

$$-dX/dt = A_a P_{O_2}^n (1-X) \exp(-E_a/RT)$$

where X , A_a , E_a , P_{O_2} , and T represent the reaction ratio at time t , the apparent frequency factor, the activation energy, the oxidant partial pressure, and the particle temperature, respectively. The T-G curve was converted to the Arrhenius expression using the following equation⁽⁶⁾:

$$\log \left\{ \frac{\log(1-X)}{2.303 T^2} \right\} = \log \frac{A_a R}{f E_a} \left(1 - \frac{2RT}{E_a} \right) - \frac{E_a}{2.303 RT}$$

where, f represents the rate of temperature increase in T-G measurement, and the power n of oxidant partial pressure is assumed to be 1.0.

Furthermore, particle structure was examined by means of X-ray diffraction pattern, and the typical chart measured is shown in Fig. 6. The absence of sharp peaks indicates that the particle has a random structure of carbon. A broad peak can be seen around $2\theta = 27$ deg, which corresponds to the 002 diffraction surface of carbon as defined in the Miller index. The

Fig. 5 Representative chart of results generated by thermo-gravimetric analyzer (T-G curve) for the soot of VR (Vacuum Residue) firing (oxygen: 5 vol%)

average diameter (L_c) of crystallized carbon can be estimated from Fig. 6⁽⁷⁾.

The derived values of A_a , E_a , and L_c are summarized in Table 2, compared with the values for typical bituminous coal char that was devolatilized during three seconds in nitrogen at 1 200°C. From Table 2, the value of E_a for VR char is found to be about 10% greater than that for coal char. This means that, for VR combustion, the dependence of the reaction rate on temperature is more significant and that the temperature should be increased in order to reduce the unburned carbon, while A_a , which is the proportional coefficient of reaction rate, is approximately one-half of that for coal char. Furthermore, the value of L_c for VR char is larger than that for coal char and the crystallization of carbon proceeds to a greater extent than coal char. These results imply that the reactivity of VR char tends to be lower than that for bituminous coal char.

4.2 Numerical simulation of one-dimensional furnace

The computer program used in the study was composed by expanding the combustion model for single particle^{(8),(9)}, and the reaction rate of particle with oxygen was given by the derived equation in Arrhenius form. In the modeling of VR combustion, the weight percentage of resident carbon contained in VR was assumed to change to the char shown in Table 2 after the combustion of vaporized

Table 2 Characteristic values for the soot of VR and the char of bituminous coal, representative of reactivity and carbon crystallization

Sample	E_a/R (Activation energy)	A_a (Pre-exponential factor)	Crystal diameter of 002 surface carbon
VR (vacuum residue) char	16350 K	845 s ⁻¹ atm ⁻¹	28.8 Å
Bituminous coal char	14950 K	1526 s ⁻¹ atm ⁻¹	15.9 Å

Fig. 6 XRD (X-Ray Diffractometer) pattern for the soot of VR (Vacuum Residue) firing

components. About the modeling of droplet vaporization and the coal combustion, refer to the Refs. (5), (8), and (9).

VR droplets atomized from a burner react along an one-dimensional gas stream (x -coordinate), the temperature, composition, and velocity of which are determined from the mass and energy balances that hold true within each calculating cell (Fig. 7). In this simulation, the mean value of oxygen concentration at the cross section of flame was used as the value of oxygen concentration in each calculating cell, and the diffusion pattern along x -coordinate, which depends on the burner type and the angle or velocity of secondary combustion air, was assumed according to the empirical equation derived from accumulated data.

4.3 Comparison between firing test and calculated results

In Fig. 8, the relationship between unburned carbon and excess oxygen in exhaust gas is shown for VR and a typical bituminous coal, where symbols and solid lines represent the experimental and calculated results, respectively. The proximate analysis of coal calculated here is as follows: water; 7.7, carbon; 57.6,

Fig. 7 Heat balance between control volumes (calculating meshes) in the one-dimensional furnace

Fig. 8 Experimental and calculated results of the dependence of the unburned carbon ratio on excess oxygen concentration in exhaust gas

volatile matter; 26.5, ash; 8.2 wt%, and calorific value; 6 370 kcal/kg. In the calculation, for the distribution of particle diameter just atomized, measured atomization data were used as the initial condition.

For VR firing, when the values of excess oxygen are 0.5, 1.0, and 2.0%, the unburned carbon ratios are 0.46, 0.39, and 0.29%, respectively. These levels are approximately two to three times as large as those for C-heavy oil, and a little higher than those for bituminous coal. When excess oxygen is greater than 2%, the gradient of the curve for VR tends to become flatter than that of coal, while the gradient for the experimental data of VR shown with dotted line in Fig. 8 is steeper than that of calculated. Since the reaction data of carbon were obtained using the unburned carbon sampled from exhaust gas, this carbon should have a decreased reactivity due to the influence of carbon crystallization shown in Fig. 6 and Table 2. Compared the experimental results with the calculated, the structure of carbon must be changing with the reactivity of oxidization decreasing during the combustion process.

Since VR contains a high percentage of sulfur, excess oxygen should be reduced as much as possible, in order to prevent low-temperature corrosion due to SO_3 . It could be found that the unburned carbon ratio for VR is at almost the same level as with coal firing when low-excess oxygen operation is adopted.

5. NO_x Emission from VR Combustion

The relationships between excess oxygen and NO_x emission, and between OFA (Overfire Air) distribution and NO_x emission are shown in Figs. 9(a) and 9(b), respectively. Here, OFA was introduced 5 m downstream from the burner port. With the increase of excess oxygen or the decrease of OFA distribution, NO_x emission in exhaust gas increases, and the absolute level of NO_x emission for VR is 15–25% greater than C-heavy oil, while the weight percentage of nitrogen in fuel differs by more than two times.

Fig. 9(c) shows the relationship between nitrogen weight percentage and NO_x emission for various fuels. Since these experiments were conducted using the same experimental apparatus and the temperature distribution in the furnace was almost the same, the NO_x emission level obtained by extrapolating the nitrogen percentage in fuel toward zero represents the level of thermal NO_x (produced from the oxidation of nitrogen in combustion air). The gradient of curve (0.3–0.4) in Fig. 9(c) may represent the conversion factor from nitrogen in fuel to NO_x . Since the experimental results for VR tend to be plotted a little under the correlation line in Fig. 9(c), the conversion ratio for VR appears to be lower than that for coal.

Fig. 9 Characteristics of NO_x emission in exhaust gas of VR (Vacuum Residue) firing test (absolute NO_x values are converted to values for 4% excess oxygen)

6. Summary

In the present study, firing tests for VR (Vacuum Residue) have been conducted using a cylindrical test furnace and the following results were obtained.

1) Since the viscosity of VR is extremely high, the temperature should be increased in order to atomize with a burner. At 250 - 300°C, viscosity becomes 20 - 30 cP, which is the ideal value for atomization with a two-fluid-type burner.

2) When the values of excess oxygen in exhaust gas were 0.5, 1.0, and 2.0%, the unburned carbon ratios were 0.46, 0.39, and 0.29%, respectively. These values were a little higher than those for typical bituminous coal.

3) The NO_x emission in exhaust gas was approximately 110 ppm, with 4% excess oxygen and 5% OFA (Overfire Air). Although the weight ratio of nitrogen in VR was about twice as large as that for C-heavy oil, the NO_x emission level was only 15 - 20% higher. The form of nitrogen bonding among the carbon chain of fuel will bring about the difference in fuel-N to NO_x conversion ratio. This is an important subject to be clarified in the next step.

4) The reactivity and carbon structure of dust sampled from exhaust gas were chemically examined, and the rate of reaction with oxygen was derived as Arrhenius expression. One-dimensional numerical simulation of VR combustion was conducted applying the derived equation of reaction rate, and the experimental and calculated results for the relationship between excess oxygen and unburned carbon ratio were found to agree fairly well.

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