C-3 Studies on the development of emission control techniques for acid-rain precursors in East Asia and on the methods of evaluation and promotion of them (Abstract of the Final Report)

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1. Introduction

With the serious air pollution, acidic precipitation and health threat caused by coal consumption in China and other developing countries, the development of cleaning-coal technology for low graded raw coal with high sulfur and ash is urgently required. However, since there are many problems to be solved, in this study, we carried out the development research on a new dry cleaning-coal technology. Now, there is a strong request about utilization research of dry cleaning-coal from the China side. Moreover, in order to spread bio-briquette technology with the actual result of the rationalization research to China through a wide area until now, it is necessary to study how the economical loss by damage to residents' health and corrosion of buildings or materials etc. is improved, and how the wastes after use of bio-briquette can be used effectively, and to aim at promotion of bio-briquette use. In addition, a new type diesel fuel made from vegetable oil was studied. From a point of view of the prevention of global warming, the use of biomass for getting energy is one of the most promising fields of technology.

2. Research Objective

The sub theme 1 aims at developing the dry coal cleaning technology using the static electricity. This technology can be possible to remove the inorganic sulfur and the ash from the raw coal without water. In this study, the dry cleaning-coal research equipment was developed. In order to improve the separating performance of coal cleaning machine and obtain the data for designing new coal cleaning machine, measurements of the characteristics of dynamic and electromagnetic behavior of ash component in the electric field as well as performance tests of the compounding electrodes were performed. The performance of the equipment was largely expanded aiming at effective use of sulfur and ash contained in the low grade coal produced in Chongqing City of China based on the know-how acquired by the basic development and measurement of the small dry cleaning coal equipment. The dry cleaning-coal technique of a drum-rotation type electrostatic system, whose possibility of practical use became clear in this research, is transferred to China, and local utilization is advanced. With the application of the data obtained from developing studies of the several testing machines, the parameters which contain the moisture, moving characteristics and electric characteristics of ash and coal component were determined, and the performance test of new multi-stage machine with the compound electrode were carried out. On the other hand,

it aims at developing the dry cleaning-coal technology which suited the needs of other developing countries.

In the sub theme 2 we evaluate the sulfur fixation efficiency and energy efficiency of a coal-biomass briquette in China. Rationalization of the production system for spreading coal-biomass briquette production technique in various regions of the northern and southern China and evaluation investigation of economical efficiency are conducted based on the combustion tests and aiming at the establishment of coal-biomass briquette technology. Another purpose in this investigation is the development of the utilization technique for combustion ash of coal-biomass briquette as a soil ameliorant from the viewpoint of high alkalinity of combustion ash. To show the improvement of health condition due to the reduction of sulfur dioxides by use of bio-briquette is also an important purpose of this study, because it can raise the incentives of citizens to use bio-briquettes.

In the sub theme 3 we aimed at preliminary studies on the synthesis of bio-diesel fuel and on the clarification of the characteristics of bio-diesel fuel. The most serious emission from diesel engines is the particulate matter. Ambient fine (less than 2.5μm) and ultra-fine (less than 100 nm) particles in diameter have a high probability to deposit deeply in the respiratory tract and cause respiratory diseases such as lung cancer. Due to increasing public concern about environmental pollution from emissions of diesel engines, alternative diesel fuels have received more attention in recent years. Bio-diesel fuels produced from such as soybean and rapeseed, and even used fryer oil from restaurants, become a good potential alternative fuel for diesel engines, because they are renewable sources of energy and virtually free of sulfur.

3. Experiments, Results, and Discussion

(1) Studies on development and generalization of dry coal-cleaning techniques

In this study, we carried out several experiments to obtain the data for the coal-cleaning-machine developing studies as follows.

i) Electric characteristics measurement of the coal and the mineral component.
ii) Numerical simulation of grains movement in high voltage electric field.
iii) Measurement of effect of moisture contained in grains on its movement.
iv) Measurements of the performance test of the compound electrode and multi-stage machine. 1.
v) Development of dry cleaning-coal technology of a drum rotation type electro-static system.

We obtained the dielectric constants of coal and some kinds of minerals Pyrite is easier to charge than coal since the dielectric constant is five times as high as that of coal. The experimental results in falling tests are coincident with movement of pyrite by the parallel plate electrodes. Thus it indicated that removal of pyrite from coal is easier by controlling strength of electrical field.

We studied effects of the coal grain size, density, and moisture content on the charging quantity. In case of constant weight samples, the charging quantity is proportional to the grain surface area and the charging quantity decreases as the grain size increases. Thus, larger grain size samples are more difficult to apply to coal cleaning by static electricity. The charging quantity of coal increases with the density. The charging quantity of the coal with high ash content (high density sample) is three times as high as that of the coal with low ash content (low density sample). The optimum moisture content of grain gives effective grains movement and high performance of coal cleaning efficiency.

We carried out the coal cleaning test by a compound electrode and multi-stage cleaning machine in Nan Dong coal mine. As the results, de-ashing and desulfurizing ratio rose up, which were 11% and 4%, respectively.

(2) Studies on technology transfer and popularization of coal-biomass briquette technique

1. Studies on the methods for technology transfer of coal-biomass briquette technique to the private sector

i) Coal-biomass briquette technology transfer:

i) Development of BB using the agricultural waste biomass and low grade and disposal pulverized coal
ii) Basic gasification experiment of BB fuel
iii) Combustion test using the local boiler
iv) Research on market and circulation in local areas

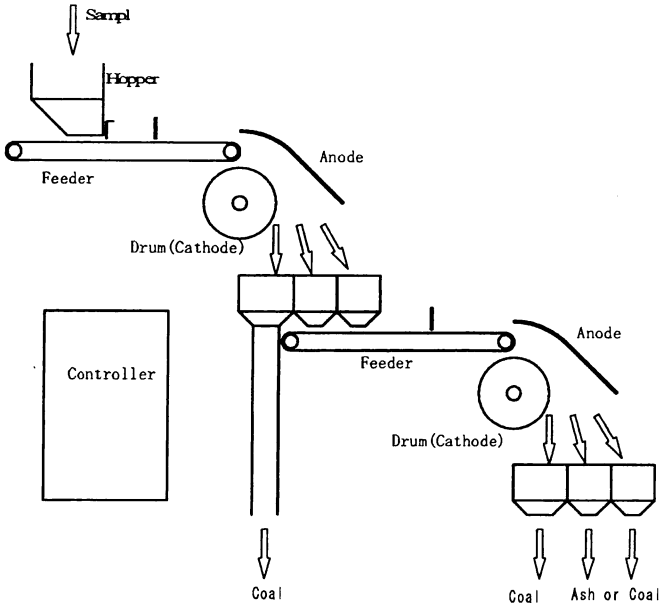

Fig. 1 Flow chart of two stage machine.

In our studies, the application of the coal-biomass briquette technology with desulfurization function was investigated for the physical or chemical characteristics of coals. Large amounts of pulverized coal discarded during coal mining, cleaning and preparation processes for resource producing were inefficiently used until now. In this study, instead of the raw coal, we developed BB with utilization of waste coal, and carried out several effective combustion tests in our laboratory or using the local boiler. This study suggested that BB produced from waste coal is available on their burning characteristics, which can lead to reduce production costs of BB. In addition, we also made an effort to gasify BB from waste coal and biomass to produce gas fuel. From these results, it was suggested that mixture of waste coal and biomass can be pyrolyzed efficiently and used for gaseous fuel better than individual raw coal or biomass.

In the each area, the market and circulation route of waste biomass and low grade and disposal pulverized coal were investigated. When calorific value of coal was > 3,000 kcal/kg, it was possible for the supply as coal materials to the BB manufacture enterprise. The kind of biomasses can differ with areas. In most cases straw is the most popular one. It can be distributed, and can collect in 40 ~ 100 yuans. When estimated the cost of BB manufacturing per ton. The order was Chongqing (250 Chinese yuan/ton), Anshan (190 yuan/ton), Wulumuqi (150 yuan/ton), and Datong (130 yuan/ton), respectively. The cost of circulation and transport can contribute 10 ~ 30% of local manufacturing cost.

ii) Utilization of ash from combustion of bio-briquette

Growth experiments were conducted to estimate the effects of the addition of BB ash to acidified soil (5wt% in the acidified soil) on the growth of radish plants and on the amounts of metals in plant tissue samples by using a growth chamber. The dry weight and length of plants were increased by the addition of BB ash to the soil, suggesting that plant growth was promoted because BB ash both neutralized acidified soil and contained much calcium, a plant nutrient. In addition, the addition of the BB ash inhibited the leaching of some phytotoxic metals (aluminum and manganese) from the BB ash and acidified soil and also inhibited the adsorption of the metals by plants. The BBs made of water plant such as reed, cattail, and water hyacinth had a high breaking strength and their combustion ash could be used as not

only soil neutralizing agent but also soil fertilizer.

Fundamental evaluation on the availability to the cheap non-calcinated bricks of BB combustion ashes was carried out, and then sufficient rise on the strength based on generation of ettringite was found. From the leaching experiment, the concentrations of most heavy metals in the leachate were below the environmental standards.

These results suggest that BB ash is suitable as an amelioration agent for acidic agricultural soils. In addition, it was estimated that the adverse effect in soil environment was small because the impact of heavy metal derived combustion ash was small. For the utilization of BB combustion ash as an alternative material of calcinated bricks, the further reduction of chromium (Cr(VI)) concentrations in the leachate are needed.

iii) Evaluation of damage to materials

The 16 sampling sites were situated at the heavily polluted areas in China: Chongqing, Shenyang, Ansyang; the urban sites in China: Beijing, Shanghai, Hong Kong; the South Korea sites: Daegu, Daejon; the urban sites in Vietnam: Hanoi, the highland site in Nepal: Kathmandu; the Japan Sea coastal site: Toyama; the urban sites in Japan: Osaka, Nagoya; the suburban sites in Japan: Kyoto, Fukuoka; the chilly site in Japan: Sapporo. The 2 types of test pieces, copper and steel, were exposed to dry and wet deposits under outdoor conditions, and exposed to dry deposits under indoor conditions. Environmental factors, such as meteorological conditions, dry and wet depositions, were simultaneously monitored during the exposure.

The concentration of SO_2 was inclined to decrease after 1997 at the Chongqing site. The trend seemed to be caused by the conversion of fuel from coal to natural gas after that year in Chongqing City. On the other hand, the amount of SO_4^{2-} in the rain indicated no change after 1997 at the Chongqing site. The total sulfur, emitted by the coal combustion, seemed to have no change in the southwest area of China around Chongqing City.

The total zinc loss, eluted from galvanized pylons, was evaluated to be 714 kg/y in 1997 in Chongqing. The economical loss would be estimated to be 27,440,000 yen.

2. Studies on the health effect of the popularization of bio-briquette

It is important to evaluate the improvement of health effects due the reduction of sulfur dioxides by using bio-briquette, instead of raw coals rich in sulfur dioxide emissions. We carried out the intervention on the influence of bio-briquette to population health in Chongqing and Anshan City, China.

In Chongqing, blood examination was carried out before and after using briquette for eighteen month. In Anshan, using bio-briquette group (43 female) and using raw-coal group (43 female) were selected and the intervention period continued for eighteen months. After the experiment, we interviewed the improvement of respiratory symptoms. Additionally, ten female were recruited the intervention research and they used raw coal for one week, and then used bio-briquette for following one week. A good trained physician checked their acute inflammatory findings one week before the experiment, and after the experiment.

In blood examination, reduction of DNA damage, acceleration of anti-oxidant function, and improvement of non-specific immunological function were observed.

Significant improvement of respiratory symptoms (cough, sputum, nasal discharge) was found in women of bio-briquette group. In contrast no women in raw-coal group answered recovery of their symptoms.

Besides, acute upper respiratory inflammatory findings induced by using raw coal for one week disappeared for almost all people after the use of bio-briquette for one week.

Indoor concentrations of sulfur dioxide and fluoride emitted from bio-briquette combustion were strictly decreased compared with those from raw coal combustion, though the level of

particle-bound polycyclic aromatic hydrocarbons or volatile organic compounds depended on the combustion condition.

A simple sampler for aerosols was developed and it became clear that the use of charged filter paper was very effective for sampling.

Two questionnaires studies carried out in China; one is for using bio-briquette and the other is on environmental conservation. Conclusions of this study are as follows: 1:Bio-briquettes are very good for residential fuel, 2:the need of environment conservation was well understood by Chinese students.

3. Introductory studies on development of low-pollution fuel

The most serious emission from diesel engines is the particulate matter. Ambient fine (less than 2.5μm) and ultra-fine (less than 100 nm) particles in diameter have a high probability to deposit deeply in the respiratory tract and cause respiratory diseases such a slung cancer. Due to increasing public concern about environmental pollution from emissions of diesel engines, alternative diesel fuels have received more attention in recent years. Biodiesel fuels (BDF) such as soybean oil rapeseed oil, and even used fryer oil from restaurants, become a good potential alternative fuel for diesel engines, because they are renewable sources of energy and virtually free of sulfur. However, it is worried much more emission of ultra-fine particles from diesel engines using BDF than that from petroleum-diesel fuels.

BDF is produced by the transesterification of vegetable oils and fats with short chain alcohols (methanol or ethanol). Since vegetable oils are produced from agricultural resources, BDF is a renewable and biodegradable form of energy. The aim of this study was to investigate the methanolysis of neat vegetable oil in the presence of low frequency ultrasound. The results of transesterification reaction under ultrasonic irradiation versus mechanical stirring under base-catalysis are presented.

The vegetable oils are mixtures of triglycerides of fatty acids. The transesterification reaction is a three-step consecutive equilibrium reaction. The overall reaction is:

Triglyceride +3ROH = 3 Methyl Esters + Glycerin

The test reactions with mechanical stirrer were carried at room temperature (25°C) with 1800rpm. The sonications were performed under the same conditions (25°C) in the ultrasonic fields of 28 and 40 kHz, respectively. The influence of low frequency ultrasound (28 and 40 kHz) versus mechanical stirring on the transesterification reaction of neat vegetable oil with methanol under base-catalysis was studied. It was found that the optimized variables 6:1 methanol/oil (mol/mol), 0.5% NaOH (wt./wt.), 40 kHz ultrasonic irradiation at 25°C for 20 minutes gave a maximum isolated ester yield of 98%. BDF is environmentally sound fuel from the point of carbon neutral for global warming gas and clean exhaust gas because exhaust gas from diesel engine of BDF contains less CO, HC, SO_2, particulates, and carcinogen such as poly-aromatic hydrocarbons (PAH) and nitro-compounds.

Emission characteristics of fine and ultra-fine particles from direct injection diesel engine (small power generator) using BDF derived from used fryer oil and pure rapeseed oil, and petroleum-diesel fuel were measured under different operation conditions. The results show the increasing tendency that elemental carbon and organic carbon in the emitted particles for both fuels are about the same. But when fueled with petroleum-diesel, the diesel engine can substantially increase emission of EC concentration with the increase of the engine-load. While, it was suggested the diesel engine with BDF emits smaller ultra-fine particles than that with petroleum-diesel from the observation of emitted particles with a scanning electron microscope and Scanning Mobility Particle Sizer.