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연구논문

Recovery of Clean Coal for the use of Synthetic Fuels from Anthracite by Froth Flotation

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Abstract : Coal generally contains numerous types of gangue minerals that produce different physical properties in the product. The aim of this study is to eliminate the impurities in coal by froth flotation to make it more suitable for use in synthetic fuels. In order to ensure optimum flotation conditions, the operational and physicochemical parameters of flotation need to be varied. According to the results, collector dosage and particle size had the most significant effect on the outcome. The results also suggest that the optimum conditions for the recovery of good quality clean coal are a particle size below 65 mesh (210 μm), using 1500 g/t kerosene as a collector; 1000 g/t sodium silicate as a depressant; and 100 g/t AF-65 as a frother. At this conditions, it is confirmed that clean coal can be recovered with a combustible recovery of over 85% and ash content below 12% by flotation.

Key words : Coal cleaning, Froth flotation, Coal flotation, Synthetic fuel

Introduction

Coal is the most widely distributed fossil energy source in the world. According to the reports, the total proved reserves of the world were 1.13 trillion tons at the end of 2016, and 326 million tons of those are in South Korea (British Petroleum P.L.C., 2017). With the emergence of petroleum products as a major commodity for transportation fuels and chemicals, coal's use has been mainly limited to power generation and steel manufacturing (World Coal Institute, 2009). However, a slowed growth in global oil production, combined with an increased environmental pressure to reduce greenhouse gas emissions from coal-fired power plants has led to renewed the interest in gasification as a clean-coal technology (Jin *et al*., 2014). In 2016, worldwide coal's share, as primary energy source, fell to 28.1%, the lowest share since 2004.

Gasification is a process used for converting any carbon-containing material into synthesis gas, commonly known as syngas, composed primarily of carbon monoxide and hydrogen. After gasification, the produced syngas can be converted into different products, such as hydrocarbon, alcohol, ether fuels, and other chemicals, using various catalysts. Coal gasification is the basis of coal conversion to liquid fuels cleanly and efficiently. Furthermore, among the processes that convert the syngas into hydrocarbons and other chemicals Fischer-Tropsch synthesis (FTS) is one of the most important processes (Wang, *et al*., 2009; Schulz, 1999; Steynberg, Espinoza, Jager, & Vosloo, 1999). Actually, in Korea, there have been several projects, some of them financed by the Government which want to increase new and renewable energy use in electric power generation (Kim, 2011). About that, The Korean government funded several R&D projects to find appropriate methods of cleaning anthracite. However, most of the coal mined in Korea are fine sized, making it difficult to clean (Yoon, Luttrell and Asmatulu, 2002). For the gasification process, coal with low ash content is economically and technically desirable. The increase of ash content in the coal, increases the oxygen consumption necessary to melt the ash, which affects gasification efficiency (Minchener, 2005). The minerals contributing for melting characteristics of the ash are silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), ferric oxide (Fe_2O_3), titanium oxide (TiO_2), phosphorus pentoxide (P_2O_5), calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na_2O), potassium oxide (K_2O), and sulphur trioxide (SO_3) (Wang & Massoudi, 2013). These minerals are often associated in Korean anthracite (Han, Kim, Kim,

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Table 1. Proximate analysis of Jang-Seong coal raw sample and chemical analysis of coal ash

Fixed carbon (%)		Volatile matter (%)		Ash content (%)			Moisture (%)	
43.09		7.24		49.34			4.24	
Chemical component (%)								
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	Loss on Ignition
54.33	31.61	4.36	1.79	0.83	3.31	0.12	1.35	2.3

Subasinghe and Park, 2014; Lee, *et al*., 2008; Choi Hong-Il, 2016). Hence, in order to use Korean anthracite efficiently in gasification, coal needs to be cleaned. There are many coal cleaning methods that have been developed to accomplish with the purposes and subsequent processing stages. One of the more suitable methods for cleaning fine coal is froth flotation (Sanders, 2007). According to Cho, *et al*., flotation is the best method of beneficiating Korean anthracite (1998). As the coal generally consists of many different types of minerals, having different physical properties, it is necessary to develop a specific technique to ensure required selectivity for the recovery of clean coal with varying the additions of flotation reagents. For this purpose, not only various factors but also proper reagent selection need to be tested (Urbina, 2003).Therefore, for the fulfillment of getting clean coal, several important factors in coal flotation technique should be examined: variations in reagents dosages, particle sizes, pH levels, pulp densities, and a number of cleaning flotation (Mainhood and Whelan, 1955; Whelan, 1953).

Experimental

Materials

A run-of-mine anthracite coal sample was received from the Jang-Seong coal mine, Gangwon province in Korea. After being crushed by jaw crusher and cone crusher the coal samples were dry ground by laboratory scale rod mill to various size fractions and used as per requirements of the flotations. The results of a proximate analysis of raw anthracite coal sample and chemical analysis of coal ash are presented in Table 1.

XRD analysis was carried out to identify coal-associated ash forming mineral phases present in coal sample. The XRD pattern of the flotation tailing sample using Cu Kα target is shown in Fig. 1. Diffractogram shows that the contents of the sample comprised of Quartz (SiO_2), Kaolinite ($Al_2Si_2O_5(OH)_4$), and Muscovite ($KAl_2(Si_3Al)O_{10}(OH)_2$, which could be separated by froth flotation techniques.

Flotation reagents used for the laboratory tests in this study are: sodium silicate, sodium hydroxide, and sodium carbonate as a depressant for gangue minerals; kerosene as collectors for coal particles; and methylisobutylcarbinol

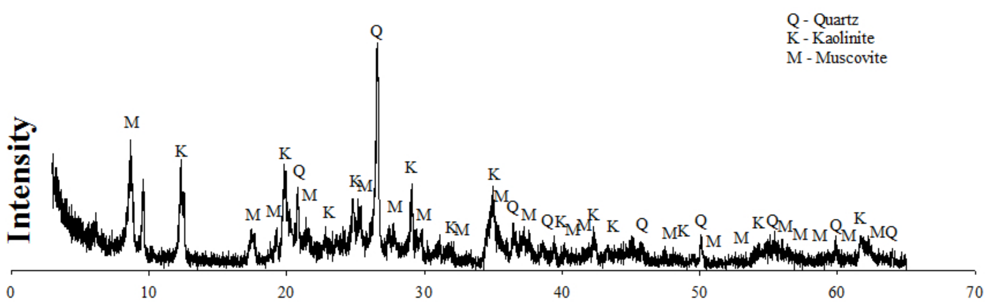

Fig. 1. XRD pattern of the raw anthracite sample.

(MIBC), Pine oil, and AeroFroth 65 (AF-65) as frothers (Jia, Harris and Fuerstenau, 2000). Additional reagents, such as sodium carbonate and sulphuric acid, were used as pH regulators in flotation.

Equipment and procedures

All flotation tests were conducted using Denver Sub-A flotation machine. Fig. 2 shows the flowsheet of the process in this research. In each test, except for the series where the alteration in pulp densities tested, 500 g sample was put in 2-liter stainless steel flotation cells with predetermined amounts of reagents added. Impeller speed of the flotation machine was set constant at 1500 rpm. The sample slurry was conditioned for 10 minutes after adding depressant, 4 minutes for the collector, and a minute for frother. Flotation time for the rougher stage is 5 minutes and 3 minutes for each subsequent cleaning stages. During rougher and cleaning flotation stages, water was added as needed to maintain sufficient level inside the cell. Each flotation products, concentrates, middlings, and tailings, were filtered, dried, and weighed before being analysed.

Laboratory flotation tests were conducted by Denver Sub-A flotation machine. And the ash content, volatile matter, moisture and fixed carbon of the flotation products were measured by TGA, using the TGA-701 (LECO Corp., USA). X-ray diffraction was recorded at 40 kV voltage and 40 mA current for a Cu-target tube. The analysis was conducted using X-ray diffractometer (D8 Advance, BRUKER Corp., USA).

Results and discussion

Combustible recovery is determined as (100-ash)% and is one of the key performance indicators of the flotation, which is calculated after determining the ash contents of the flotation process products. Masses of the flotation process products are expressed as F (mass of feed), C (mass of concentrate), and R (mass of reject). The mass of the feed is determined by the masses of the concentrate and reject (Sanders, 2007).

$$CR = \frac{(100-c)(f-r)}{(100-f)(c-r)} = Y\frac{(100-c)}{(100-f)};$$

Where, f, c, and r are the weight percentages of ash in the feed, coal concentrate, and reject; and Y is yield. By using this equation the yield and recoveries can be obtained from the proximate analysis data reporting ash contents of feed, product, and tailing products.

Collector dosage

Coal is hydrophobic by nature and the flotation of

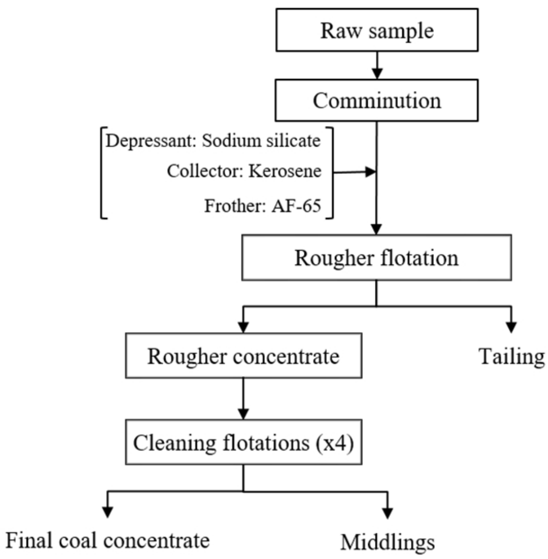

Fig. 2. Flotation flowsheet.

bituminous coal can be carried out using only frothers; however, anthracite is less hydrophobic, hence requires a collector, commonly emulsified kerosene or diesel oil (Gutierrez-Rodriguez, Purcell Jr., and Aplan, 1984; Boylu and Laskowski, 2007). Kerosene was used as a collector for the carbonaceous matter and the effects were tested from 0 up to 4000 g/ton, with an increment of 500 g/ton.

Fig. 3 shows that the collector dosage has a considerable influence on the combustible recovery and ash rejection of the flotation. Combustible recovery of the flotation concentrate was at the lowest point without the introduction of the collector. However, with the addition of collector dosage up to 2000 g/ton, combustible recoveries of flotation concentrates were in a relatively similar level, which suggests that the collector dosage is becoming excessive and the optimal dosage of the collector is around 1500 g/ton. Ash rejection in this series has also decreased gradually as the collector dosages increased; however, the overall decrease was not as steep as the increase in combustible recovery. Some authors coincide with oily collectors should be used sparingly since the oil also leads to the flotation of ash, forming minerals. This phenomenon could explain the gradual decline of ash rejection and an increase of ash content in the concentrate with the increase of collector dosages. Also, even its collecting purpose, the oil might block coal surface to adsorb the frothers (Leonard, 1991).

Particle size

For froth flotation to work efficiently, the coal needs to be ground to adequate particle size. Generally, coal flotations can be achieved from the -35 mesh size particles. however, due to he possibilities of entrainment or unliberation of gangue minerals in the carbonaceous matter, five different sizes (minus 200, 150, 100, 65, and 48 mesh) were put through flotation tests. Fig. 4 shows that the ash content of the flotation concentrate at finer particle size fractions (-200, -150 and -100 mesh size) are lower than that of coarser (-65 and -48 mesh size) fractions. Nevertheless, in terms of the combustible recoveries, the results are high at -48 and -65 mesh size fractions. According to some studies, the flotation of coarse particles significantly reduces when the amount of ultrafine coal is increased. It is due to the factor that ultrafine particles catch the majority of the collector (Firth, Swanson and Nicol, 1978; Fuerstenau, Jameson, and Yoon, 2007). Results on Fig. 8 show that the optimal particle size for flotation is minus 65 mesh fraction.

Depressant dosage

Generally, the depressant has an effective function to inhibit the collector adsorption onto unwanted minerals without affecting the flotability of the minerals intended to float. Adsorption of an effective depressant also makes the

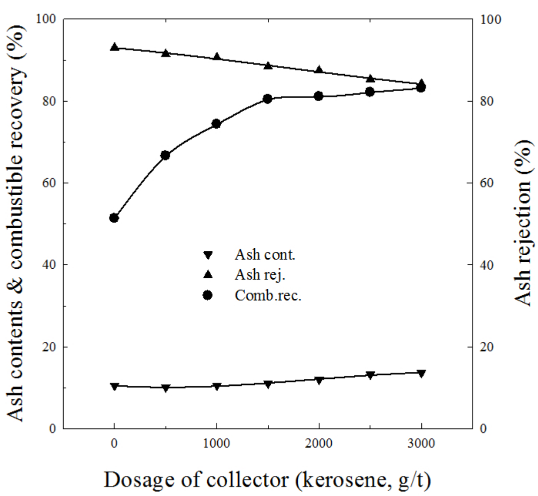

Fig. 3. Effects of collector dosage on combustible recovery and ash content (Depressant: Sodium silicate, 1000 g/t; Frother: AF-65, 500 g/t).

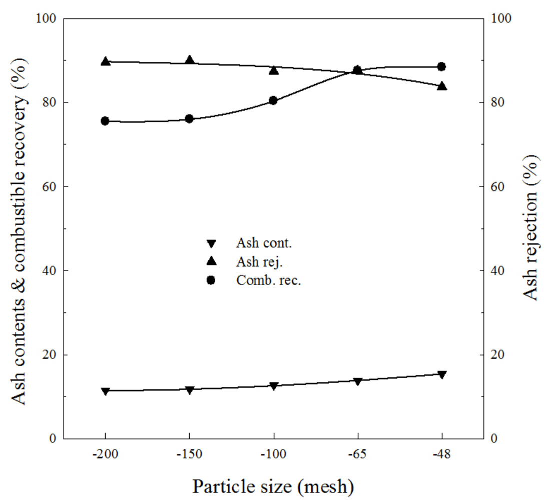

Fig. 4. Effects of particle size variation on combustible recovery and ash content (Depressant: Sodium silicate, 1000 g/t; Collector: Kerosene, 1500 g/t; Frother: AF-65, 500 g/t).

mineral surface more hydrophilic. In flotation, one of the essential tasks is to depress gangue minerals by creating a hydrophilic layer on the surface with depressing agents (Urbina, 2003). It is common that quartz, as the main gangue mineral in coal sample, should be depressed by silica-based sodium silicate (Na_2SiO_3). It was made test without the use of depressants, in order to examine the effects of depressing agents in coal flotation, it was first performed without using depressant. Then in subsequent flotation tests, the depressant dosages were increased by

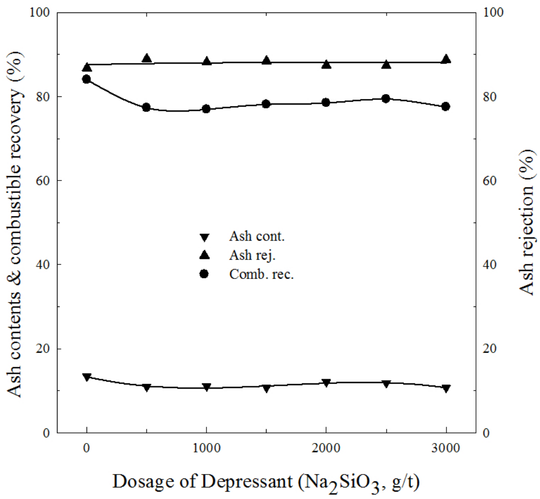

Fig. 5. Effects of depressant dosage on combustible recovery and ash content (Collector: Kerosene, 1500 g/t; Frother: AF-65, 500 g/t).

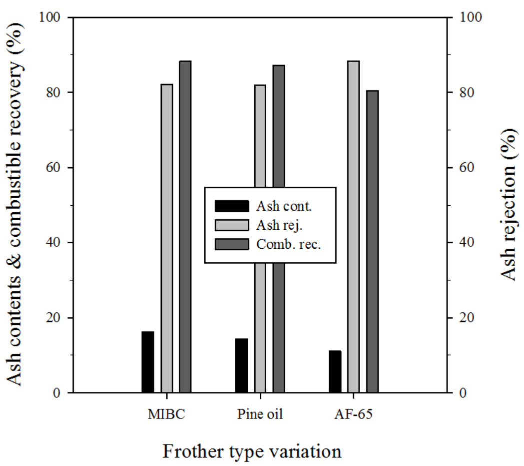

Fig. 6. Effects of frother type on combustible recovery and ash content (Collector: Kerosene, 1500 g/t).

500 g/ton in each test. The results, showed in Fig. 5, pointed that even the dosages of depressant may affect the outcome of flotation, the further increase in dosages does not necessarily affect positively to the combustible recovery and ash rejection of flotation concentrates.

Frother type

The most common frothers used for coal flotation are MIBC and pine oil (Urbina, 2003). However, considering the dissimilar nature of coal compositions, there is a need to test different types of frothers. Effects of frother types were tested using three commonly used types of frothers MIBC, pine oil, and AF-65. The results are showed in Fig. 6. At the same amounts of frothers in the flotation, the uses of MIBC and pine oil shows relatively higher ash content in the concentrate than the targeted ash content. But the same amount of AF-65 shows good result.

pH

The surface chemistry of most minerals is affected by the pH. In order to discover the effects of the pH levels of the slurry to the outcome of flotation, a series of tests were conducted. Slurries with five levels of pH were produced, before adding flotation reagents, using regulating agents. Natural pH of the flotation slurry averaged at around 8.6. Results shown in Fig. 7 displays that combustible

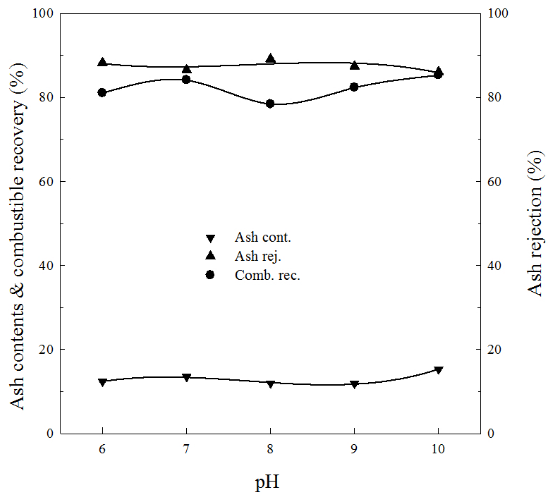

Fig. 7. Effects of pH variation on combustible recovery and ash content (Depressant: Sodium silicate, 1000 g/t; Collector: Kerosene, 1500 g/t; Frother: AF-65, 500 g/t).

recovery, ash rejection and ash contents of the flotation concentrates aren't fluctuating with the change of pH, which suggests pH does not seem to affect the flotation outcomes greatly. The result of the pH effect agreed with earlier study, where proved that the flotation recovery of coal decrease at low and high pH values with the maximum recovery being obtained at or near neutral pH (Zimmerman, 1948). This is further studied in another research, where it's concluded that pH does not appreciably affect the flotation recovery of clean coal in tap water and in the absence of clay slimes in the range pH 3.5-9 (Arnold & Aplan, 1986).

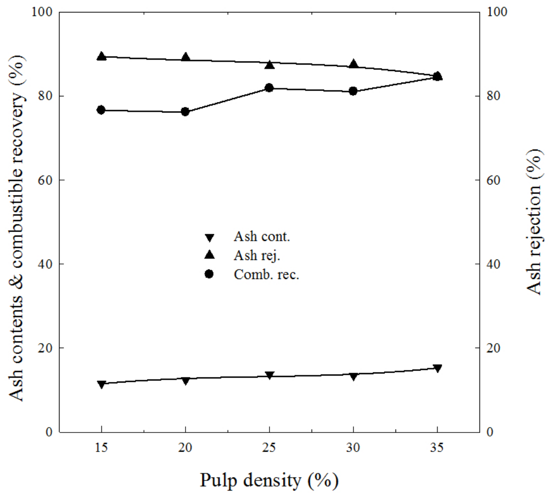

Fig. 8. Effects of pulp density variation on combustible recovery and ash content (Depressant: Sodium silicate, 1000 g/t; Collector: Kerosene, 1500 g/t; Frother: AF-65, 500 g/t).

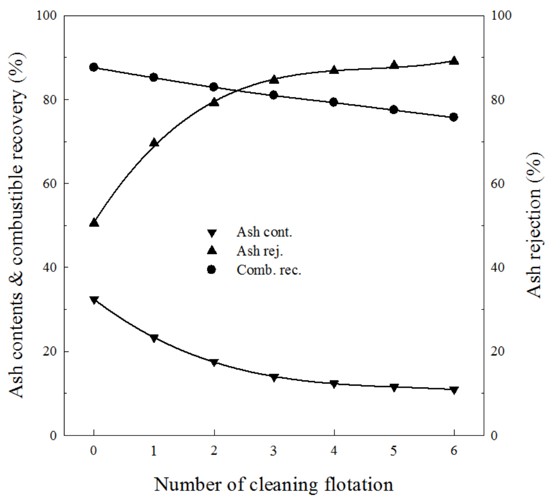

Fig. 9. Effects of a number of cleaning flotation on combustible recovery and ash content (Depressant: Sodium silicate, 1000 g/t; Collector: Kerosene, 1500 g/t; Frother: AF-65, 500 g/t).

Pulp density

The percentage of solids in the pulp is one of the most significant variables of coal flotation. It directly affects the economic aspects of the process. If the pulp density is high, the production capacity will increase; however, the separation efficiency of flotation might decrease. So the decision of proper pulp density of flotation pulp must be important. Based on the results shown in Fig. 8, the optimal pulp density for Jangseong coal flotation is 20% solids.

Number of cleaning in flotation

After the rougher flotation, the gangue minerals are still likely to be entrained in the float products, which should be removed by cleaning flotations. In order to determine the required number of cleaning flotation this series of flotation was carried out and the results pointed in Fig. 9. This Results proved that the single rougher flotation is not sufficient with yielding over 30% of ash content. Ash content was further decreased after each cleaning flotation until the ash content is just above 10% by the sixth cleaning flotation. However, by the sixth time combustible recovery is well below the required level, which prompts the optimal number of cleaning flotation to be lower than six times. Therefore, based on the results shown in Fig 9, the optimal number of cleaning flotation for the Jangseong anthracite coal is four times.

Conclusions

With the ever-increasing calls for the environmentally friendly source of fuel and coal production, the current trends for replacing conventional coal and oil production methods are increasing. Amid these new approaches, the coal gasification process and the Fischer-Tropsch process are commonly considered as the leading candidates. In Korea, there have been many studies about using synthetic fuels extracted from coal and other biomass. The current study is centred on a clean coal preparation technique for the coal gasification process.

(1) The sample used for the study is an anthracite provided by the Jangseong coal mine. Proximate analysis of the raw coal sample shows that it contains volatile matter 7.24%, moisture 4.24%, ash content 49.34%, and fixed carbon 43.09%.

(2) Various factors have been tested with varying values. And according to the results, the most significant effects on the outcome of the flotation results were observed on the collector dosage and particle size variation test series.

(3) pH does not have a considerable effect. On the other hand, the most influential factors were observed to be dosages of reagents, alterations of particle sizes and pulp density.

(4) The results also suggest that the optimum conditions of the flotation for the recovery of good quality clean coal are as follows; minus 65 mesh particle size grinding, the dosages of reagents: 1500 g/t kerosene, as a collector, 1000 g/t sodium silicate, as a depressant, and 100 g/t AF-65 as a frother. In this condition, the flotation produces a coal concentrate with the combustible recovery of over 85% and ash content below 12%.

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