Study on coal recovery technology from waste fine Chinese coals by a vegetable oil agglomeration process

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Abstract

Nowadays, coal production increases continuously due to an increase in mechanization in coal mining and demand in its related fields of application worldwide. Coal production in China is especially an increasing trend and a large amount of waste fine coal is produced. Waste fine coals usually contain large amounts of ash and inorganic sulfur due to non-selective coal mining of the coal. Therefore, waste fine coals are available as a resource and cause spontaneous combustion leading in turn to air pollution because of their coal contents and small particle sizes which increases the surface area liable to be wet and oxidized, and the disposal site of waste fine coals cause land occupation, soil pollution and water contamination.

In this study, a vegetable oil agglomeration process was performed for coal recovery from Chongqing Nantong waste fine coals in China. The oil agglomeration process has been used to mineral oil of exhaustible resource. Therefore, in this study, several kinds of vegetable oils are selected as oil agglutinative agents because the vegetable oils which are renewable, available and less-pollutant energy resources. The effects of the parameters including particle sizes, agitation conditions, chemical structure and viscosity of vegetable oils were investigated based on the combustible matter recovery, ash reduction and efficiency index. It was concluded that particle sizes of waste fine coal, agitation rate and agitation time will influence on the recovery efficiency of combustible matter from its original waste coal by the colza oil agglomeration. Furthermore, a wide range of vegetable oil alteration grades including prepared waste vegetable oil samples and therefore, of oil properties, such as chemical

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structural changes and unsaturated carbonaceous functional groups by the oxidation processes in the used waste vegetable oils have to be achieved.

Keywords: waste fine coal, vegetable oil, oil agglomeration, combustible matter recovery, China.

1 Introduction

The primary energy consumption expands, because it is thought to be an increase in the future by improving the living standard in the world [1]. The recoverable coal reserves are estimated to be about 847.5 billion tons [2] and the prediction of reserve coal production is 133 years [2]. It is thought that coal will be an important energy source because it is excellent in the stability of supply and the economy, more than other fossil fuels, because there is no eccentrically-located source. However, a large amount of waste fine coal (< 500 μm) is produced by mechanizing the coal preparation process and mining. Because of the pulverized coal with the small particle sizes in diameter, the handling of waste fine coals is difficult, which contained a lot of minerals and the calorific value is low [3, 4]. The utility value as an energy resource is scarce, thus the a lot waste fine coals have been discarding. However, combustible matter is still contained in waste fine coals, it discards risk of spontaneous combustion, additionally it causes air pollution, water contamination and land occupation. Waste fine coal of production, especially in China, has grown in quantity and this problem has become aggravated. Then, coal clean technology is needed in order that recovery of combustible matter from waste fine coals for reduction of environmental burdens and application of unused resources.

There are dry processes and wet processes in clean coal technologies. For example, our previous attempts at air pollution abatement have involved the use of coal-biomass briquettes (BBs) (also called biobriquettes (Wang *et al.* [5])), which are prepared under high pressure from mixtures of low-rank coal (70–85 wt%), biomass (15–30 wt%), and a sulfur-fixing agent such as slaked lime molar ratio of calcium to total sulfur content of coal. Laboratory combustion experiments have shown that SO_2 emissions are reduced by 75–95% during the combustion of BBs as compared with low-rank coal, owing to the following reactions of SO_2 with $Ca(OH)_2$ and CaO to form $CaSO_4$ [6]. Beside of these methods, oil agglomeration in wet processes has been also found to be one approach of the effective methods for separating organic matter (coal) from mineral matter (ash).

The oil agglomeration processes apply the different surface properties of combustible organic matter and mineral matter in raw coals to coal cleaning technique, separation of coal from mineral matter is achieved due to differences in the surface hydrophobic properties of the organic coal and inorganic ash contents of coal samples. The organic constituents are hydrophobic, while the mineral matter is generally hydrophilic. A suspension of finely ground coal in water is very fast agitated with a small amount of bridging oil. Intense agitation

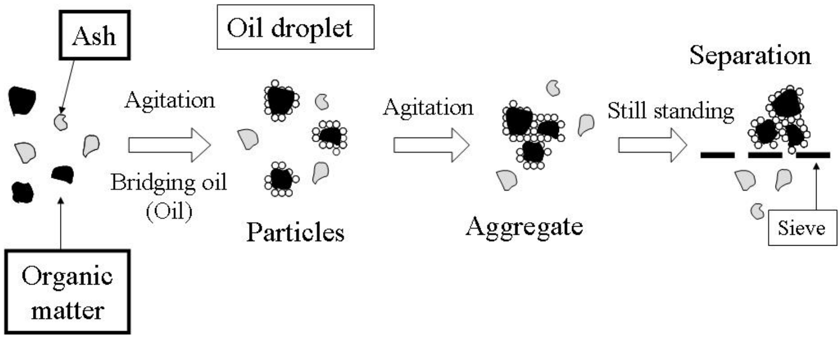

Figure 1: Principle and concept of oil agglomeration for coal cleaning.

breaks the bridging oil into fine spherical droplets and allows the hydrophobic coal particles to form agglomerates of oil-coated particles bonded to other oil-coated particles, leaving the hydrophilic mineral particles behind in the water phase. The agglomerates of combustible organic matter can be separated by screening (figure 1) with a sieve from the mineral matter of original waste fine coal.

In the past, mineral oil (kerosene) has used oil agglomeration, however, vegetable oils are selected as oil agglutinative agents in this study because the vegetable oils are renewable, available and a less-polluting energy resource.

The main object of this work is to recover combustible matter more efficiency by a vegetable oil agglomeration, thus chemical structure and property of vegetable oil, agitation conditions and particle sizes of waste fine coal in China were investigated. The waste fine coal was agglomerated with the used vegetable oil such as colza oil samples heated at the certain frying temperature in the interval times within several days. Thus, a wide range of oil alteration grades and therefore, of oil properties, such as viscosity and unsaturated carbonaceous bonds by the oxidation processes in the used waste vegetable oils were investigated. Structural changes and unsaturated carbonaceous functional groups in the colza oils were monitored by a Fourier-transform infrared (FTIR) technology. Oil agglomeration efficiencies were evaluated by measuring the recovery of combustible matter, ash reduction and efficiency index.

2 Materials and experimental methods

2.1 Waste fine coal samples

In this study, the samples of waste fine coals were selected and collected from Chongqing Nantong coal mining in the south-eastern China. Before our experiments, the coal samples were ground to pass through a 75 μm sieve. The proximate and ultimate analyses of coal samples were measurement according to the Japanese industrial standard (JIS) method of JIS-M8812.

From proximate analysis and ultimate analysis of waste fine coal (<75 μm), it is revealed that coal contained high ash and sulfur shown in table 1. We also found that there are very good relationship between ash and total sulfur content. Therefore, it is possible that ash and sulfur maybe separated together from this coal sample by the oil agglomeration process.

Table 1: Results of proximate analysis and ultimate analysis (particle sizes of waste coal: <75 μm).

	Air dried	Dry basis
Proximate analysis (wt%)		
Ash	61.3	63.2
Moisture	2.9	-
Volatile matter	18.3	19.3
Fixed carbon	17.8	17.5
Ultimate analysis (%)		
Carbon	-	18.1
Hydrogen	-	1.7
Nitrogen	-	0.4
Total sulfur	9.4	9.6
Oxygen	-	7.0

2.2 Experiment of oil agglomeration for coal cleaning

Schematic diagram of a procedure of oil agglomeration is given in figure 2, and experimental conditions are shown in table 2. The oil agglomeration experiments were carried out in a 500 mL beaker. The products of the two simultaneous agglomeration experiments were poured into the beaker and mixed, followed by the separation of the agglomerates as clean coals. The agglomerates were filtered, dried overnight at the room temperature, washed with ethanol to extract the residual oil, dried at 50°C, and analyzed for ash content in each clean coal. As the results, the resultant agglomeration products were separated from the mineral matter (ash) in waste fine coals below 75 μm. Actually, on the industrial application, we should say that the solvent washing step of the agglomerates would not be necessary and the coal/vegetable oil agglomerates could be used directly as fuel because of the less-pollutants in the waste vegetable oils.

2.3 Preparation of simulated waste vegetable oil samples

With a point of view for effective utilization of waste vegetable oil, it was necessary to use waste vegetable oil in the experiment of oil agglomeration. Therefore, A prepared simulated waste vegetable oil of viscosity, chemical structures changed with the different conditions in heated-treated times.

In the case of heated-treated oil, carbonyl compound and carboxylic acid degraded product of oil are advanced produce. These products are hydrophilic

Table 2: Experimental conditions of oil agglomeration.

Item	Conditions
Coal	15.0 g
Particle size	<75, 75~150, 150~212, 212~300 μm
Water	200 mL
Oil concentration	4.0 g
Agitation ①	2000 rpm, 3min
Agitation ②	Time: 5, 10, 15, 20, 25 min
	Speed: 1000, 1500, 2000, 2500 rpm
Standing time	3 min

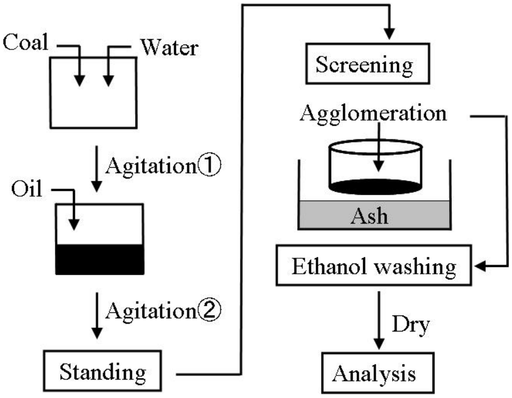

Figure 2: Schematic diagram of coal cleaning procedure of oil agglomeration.

behavior, as the result, there may be an adverse effect for efficiency of clean coal by of oil agglomeration, because these products are effective like cross-linker between combustible matter and ash contents.

Therefore, for preparing the simulated waste vegetable oil, a commercial colza sample oil was poured into metallic pot about 1.0 L and heated at 180°C for 30 min day^{-1} by a gas moveable cooking stove during 7 days heating experiment period. These samples in different heated-treated days were used as the coal agglomerating agents in this work to check the availableness and capability of the waste vegetable oil agglomeration. The sample oil heated each day was cooled in the room temperature and restored till experiments of oil agglomeration.

2.4 Identification for chemical structure of waste vegetable oil by a FT-IR

In order to find changes in chemical structure of waste vegetable oil samples mentioned in section 2.3 based on the Fourier-transform infrared (FTIR) technology, the infrared spectra were recorded using a Model IR-6100 (JASCO Corporation, Japan) interfaced to a personal computer operating with Windows-based Spectra manager (Version 2). A film of the oil sample was placed between two disks of NaCl. This study is used disk pathlength of NaCl cells of 0.1 mm. The spectra were recorded from 4000 to 400 cm^{-1}, the number of scans being 256 at a resolution of 4 cm^{-1}. The infrared absorption frequencies characteristic of functional groups for the chemical structural elucidation of waste vegetable oil and its original oil were especially observed from the frequencies of 900 to 2000 cm^{-1}.

2.5 Viscosity measurement of simulated waste vegetable oil samples

A viscometer (Model VT-04F, RION Co. Ltd., Japan) was used to measure the viscosity of the oils. In this procedure, a disk/spindle is submerged in the oil and the force which is necessary to overcome the resistance of the viscosity to the rotation is measured. The viscosity value (dPas) is automatically calculated on the basis of the speed and the geometry of the spindle. According to previous vegetable oil viscosity values which were determined basing on the Japanese industrial standard (JIS) method of JIS-Z8803, a spindle speed of 62.5 rpm was chosen in this work to carry out the measurements.

2.6 Evaluation of coal cleaning efficiencies by the waste vegetable oil agglomeration

The efficiencies of coal cleaning were calculated by the percentages (wt%) of combustible matter recovery (CMR), ash reduction (AR) and efficiency index (EI) from ash content in clean coal [7]. These parameters can be calculated as the following equations (1)–(3).

$$CMR = 100 \times \frac{CM_{agglom}(wt\%) \times wt_{agglom}(g)}{CM_{feed}(wt\%) \times wt_{feed}(g)} \quad (1)$$

$$AR = 100 \times \left[1 - \frac{Ash_{agglom}(wt\%) \times Ash_{agglom}(g)}{CM_{feed}(wt\%) \times wt_{feed}(g)} \right] \quad (2)$$

$$EI = CMR + AR \quad (3)$$

Where CM (combustible matter) is calculated as 100-(ash contents), agglom is the weight of agglomeration, feed is the weight of coal sample, and wt gives as the weight unit (g), respectively.

3 Results and discussions

Before the evaluation of coal cleaning efficiencies by the waste vegetable oil agglomeration, we have obtained some results from basic experiments for the agglomeration condition decision of particle sizes, agitation rate and time.

3.1 Effect of waste coal sizes in oil agglomeration

Figure 3 shows effect of waste coal sizes. As can be seen, CMR is increased with decreasing particle size of waste coal and EI is also shown the same tendency with CMR. These results have possibilities that a lot of coal particles presented in ash, or combustible matter. A high ash content waste coal is mixed and dispersed combustible and mineral matter containing in large coal particles, on the other hand, small coal particles are of combustible matter and less ash. As this reason, we have selected waste fine coal (<75 μm) as the waste coal sample.

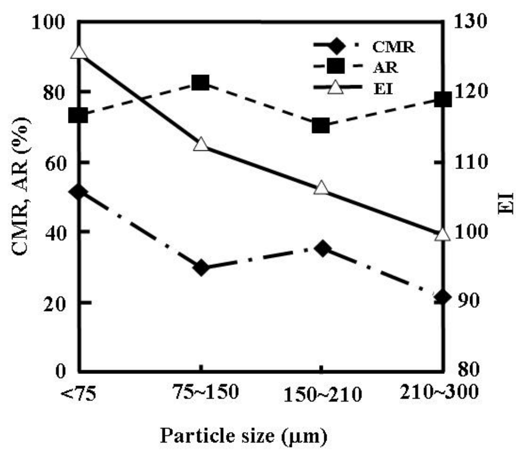

Figure 3: Effect of particle sizes of waste coal on the oil agglomeration performance.

3.2 Effect of agitation rate in oil agglomeration

Figure 4 shows effect of agitation rate. As can be seen, when the agitation rate accelerates, the increased agitation rate considered to enable more coal particles to stick to colza oil droplets due to increase in the possibility of contact between coal and colza oil. However, further increase in agitation rate to 2000 rpm, resulted in a decrease in ash reduction adversely affecting the selectivity.

This may be due to the trap of mineral particles into the agglomerates as a consequence of excessive turbulence induced in the system [8, 9]. In addition, increase in 2500 rpm may be due to break of aggregates to contact an increase with the aggregates and stirring blade, because the increment of agitation rate may also increase the collision chances of granulated aggregates with each other.

3.3 Effect of agitation time in oil agglomeration

The impact on coal efficiency of agitation time is investigated. This result shown in figure 5. As can be seen, in the case increasing agitation time than one, CMR is slightly increased, AR is not shown a huge shift was observed.

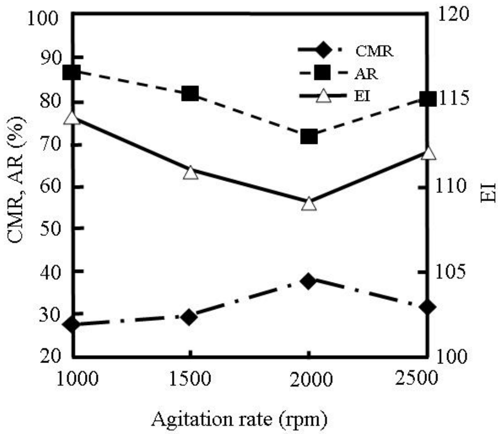

Figure 4: Effect of agitation rate on the performance of oil agglomeration process (agitation time: 5 min).

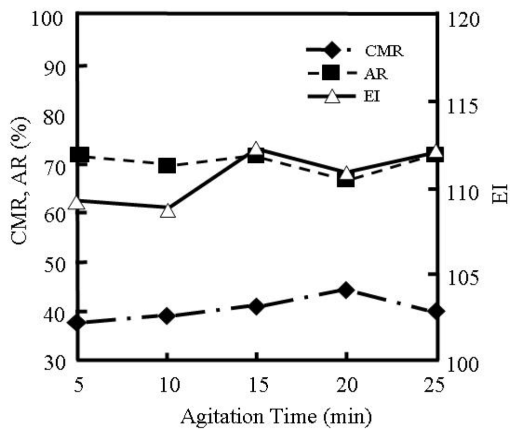

Figure 5: Effect of agitation time on the performance of agglomeration process (agitation 5–25 min).

CMR was increased, because of between aggregate particles and coal to increase the agitation time, due to an increase in collisions between oil droplets and coal particles, which may be considered that stimulated the growth of particles [8, 9].

3.4 Viscosity investigation of simulated waste vegetable oil

The tendency of coal cleaning efficiencies influenced by colza waste oil viscosity was investigated. The result is shown in figure 6. The viscosities of the different waste oil samples increased slightly with increasing the heated-treated time period because some of antioxidant was contained in the original commercial colza sample oil.

The other authors reported that increment of heated time of waste vegetable oil could to extremely increase the oil viscosities [10] and there are correlations between oil agglomeration capability and the oil viscosity as well [11]. Therefore, the heated-treated time in this study may be shorter than other studies, in which we can consider that oxidation in the oil was not prompted so much. As the results, CMR, AR and EI as the coal cleaning efficiencies were not influenced and changed obviously in these experiments.

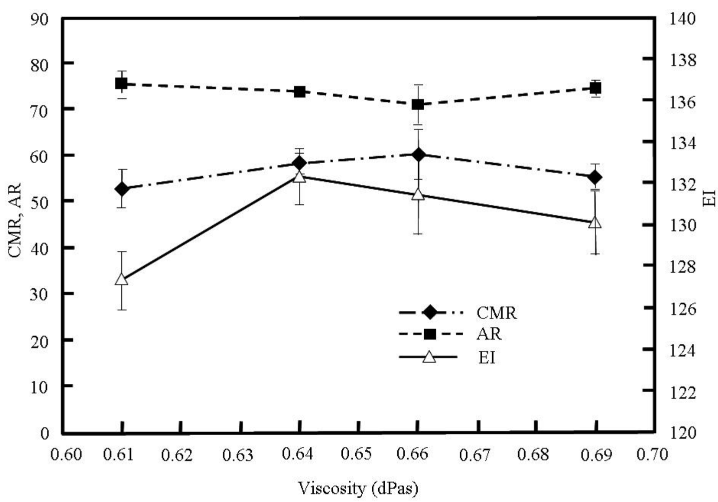

Figure 6: Viscosity influence on the performance of agglomeration process (agitation rate: 2000 rpm, 5 min).

3.5 Changes in chemical structure of simulated waste vegetable oil samples based on FT-IR spectra

The Fourier-transform infrared (FTIR) technology has been commonly used for the structural identification or qualitative determination of the fingerprint of organic compounds, because some groups of atoms display the specific characteristic vibrational absorption frequencies in this infrared region of the electromagnetic spectrum [12]. Spectra in the mid-infrared region have well resolved bands that can be assigned to functional groups of the components of the oil samples. The exact location of the corresponding bands depends on the influence of the rest of the molecule. The infrared absorption frequencies

Table 3: Functional groups and modes of vibration in the FT-IR of oil samples.

Frequency (cm^{-1})	Functional group assignment
3008	C-H stretching vibration of the cis-double bond (=CH)
2928 and 2856	asymmetric and symmetric stretching vibration of the aliphatic CH_2 group
1738	Ester carbonyl functional group of the triglycerides
1463	Bending vibrations of the CH_2 and CH_3 aliphatic groups
1235 and 1166	Stretching vibration of the C-O ester groups
723	Overlapping of the CH_2 rocking vibration and the out-of-plane vibration of cis-disubstituted olefins

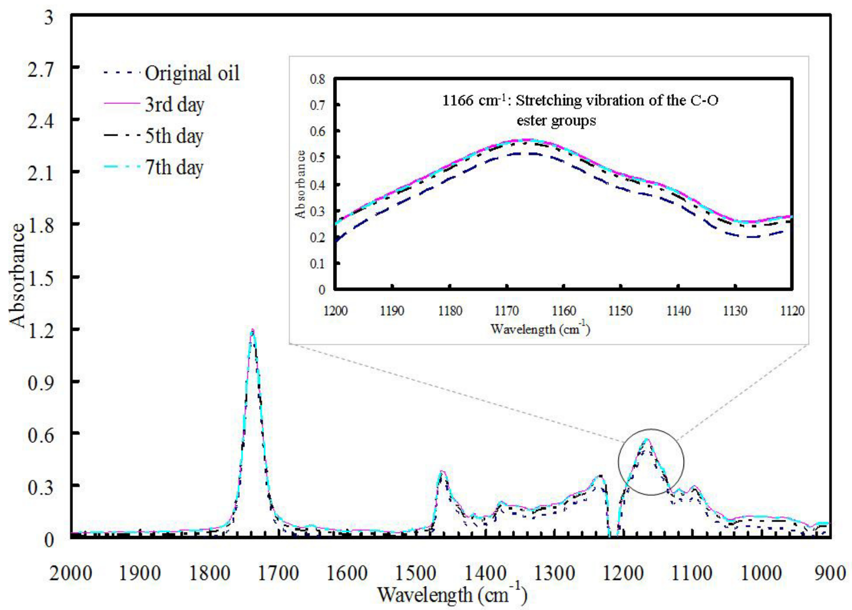

Figure 7: FT-IR spectra of simulated waste vegetable oil samples.

characteristic of functional groups afford a useful and valuable tool for the chemical structural elucidation of waste vegetable oil was investigated by a FT-IR. The analytical evaluation of the colza oil spectra is given table 3.

Figure 7 shows spectra of oil samples stretching vibration of the C-O ester groups at 1166 cm^{-1}. As can be seen the infrared absorbance of spectra was inconsiderably increased when sample oil was heated-treated. In this case, heated-treated temperature of 180°C, the heated oil is more oxidized than original oil, the oxidation of sample oil was slightly undergoing evolution. The aggregating effect may be attenuated as agglomerating agent of vegetable oil, because of these products may have amphipathic property. However, CMR and AR of coal cleaning efficiencies did not change much effectively. However, the other author was reported that there are correlations between oil agglomeration capability and chemical structural of waste vegetable oil [10]. In this study, waste vegetable oil of experimental condition can be considered to be used as an aggregating agent of oil agglomeration for waste fine Chinese coal cleaning.

4 Conclusion

In this study, effect of agitation rate, agitation time, oil property for clean coal efficiencies on the vegetable oil agglomeration to recover combustible matter more efficiently from waste fine coal was investigated.

The agitation rate and agitation time were indicated to affect clean coal efficiency. These conditions needed optimization in order that efficiently oil agglomeration technology conducted.

Investigation of efficiency of oil property was used that the oil preparation poured a commercial colza oil into metallic pot and heated sample oil at 180°C for 30 min day^{-1} by a gas moveable cooking stove during 7 days heating experiment period. The heated-treated time considered that oxidation was only slightly facilitated by the analysis of FT-IR in this study. The viscosity and chemical structural in waste sample oil did not show much effect about the CMR, AR and EI as well. This result can indicated that waste vegetable oil may be used as an aggregating agent for oil agglomeration, which just to pass the preprocess filtration of food residue.

However, in fact, used waste oil on the industrial process is longer term, thus there are the future subjects, heated-treated time to vegetable oil is extended and a wide variety of oils are used on our further applicable experiments for waste fine Chinese coal cleaning.

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