*Physicochem. Probl. Miner. Process., 55(1), 2019, 49-57*

http://www.journalssystem.com/ppmp

Physicochemical Problems of Mineral Processing

ISSN 1643-1049



*Received January 20, 2018; reviewed; accepted April 10, 2018*

# Enhancing low-rank coal flotation using a mixture of dodecane and n-valeraldehyde as a collector

**Zechen Liu, Yinfei Liao, Maoyan An, Qingteng Lai, Longfei Ma, Yuliang Qiu**

Key Laboratory of Coal Processing and Efficient Utilization of Ministry of Education, School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou Jiangsu, 221116, China

Corresponding author: e-mail: ruiyin@126.com (Yinfei Liao)

**Abstract:** Low-rank coals are difficult to float using common hydrocarbon oily collectors, such as dodecane and diesel. In this investigation, a mixture of dodecane and n-valeraldehyde was used as a collector to enhance low-rank coal flotation. The changes of the contact angle and surface functional groups of low-rank coal were measured before and after different collectors' adsorption to indicate its absorption mechanism. Surface tension of different collectors was also measured to identify its spreading performance. The results showed that the flotation performance using the mixture as a collector was much better than that using dodecane or n-valeraldehyde solely. When used the mixture of dodecane and n-valeraldehyde as collector, dodecane primarily covers the hydrophobic sites while n-valeraldehyde primarily covered the hydrophilic sites by hydrogen bond promoting adsorption of dodecane at these sites. There existed synergistic effect between dodecane and n-valeraldehyde. Additionally, n-valeraldehyde can reduce the surface tensions to improve the spreading performance of mixed collector on low-rank coal surface. The improvement both in adsorption and spreading was responsible for the enhancement of low-rank coal flotation by using the mixture.

***Keywords:*** mixed collector, oxygen-containing functional groups, adsorption mechanism, low-rank coal, flotation

## 1. Introduction

Coal flotation is a progress in which fine coal particles are separated selectively from associated minerals in water slurries by attaching to rising air bubbles. Coal rank has a great effect on the flotation of fine coals (Tian et al., 2017). It is generally known that low-rank coals are difficult to float using common hydrocarbon oily collectors, such as dodecane and diesel. This is mainly due to the surface of low-rank coal has many oxygen-containing functional groups that are hydrophilic (such as hydroxyl, carboxyl, methoxyl, and carbonyl). Hydrophilic functional groups can be bonded with water by hydrogen bonds. As a result, the hydration film on the surface of low-rank coal is very thick. This thick hydration film prevents the adsorption of the collectors on the coal surface as well as the attachment of coal particles on the bubbles (Xia et al., 2015).

In recent years, the flotation performances were improved by using surfactant to finish the surface modification of coal. Harris et al. (1995) pointed out that nonionic surfactant tetrahydrofuran is an effective collector for lignite flotation. Jia et al. (2000) used Tetrahydrofuran (THF) esters [C4H7O–CH2–OOC–R] to improve the floatability of low-rank/oxidized coals on the basis of Harris' paper (Harris et al., 1995). They found that the reagents containing oxygen functional groups and benzene rings were better collectors for low-rank coals. Bustamante and Woods (Bustamante et al., 1984) showed that the hydrophobicity of composite grains, which consisted of coals and surfactants, was decided by the adsorption of cationic dodecyl ammonium. As a whole, the surfactants can enhance flotation performance, but the process of synthesizing surfactants is difficult and expensive, which is not suitable for industrial production. In addition, it is necessary to emphasize that the benzene ring containing the

DOI: 10.5277/ppmp18109

pharmaceutical will pollute the environment.

Mixed collectors have also been proven to be more effective, have a lower cost, and use a fewer dosage in many industrial applications (Gao et al., 2015; Mcfadzean et al., 2012). In previous researches, Drzymala et al. (2005) applied a mixture of 4-dodecylphenol (DDP) and hexadecane (HXD) as a new collector for the removal of unburned carbon from fly ash. Xia et al. (2015) successfully investigated a mixture of 4-dodecylphenol (DDP) and dodecane to improve the performance of lignite in the flotation. Using the mixture of DDP and dodecane as the collector, the dodecane primarily covered the hydrophobic sites on the lignite surface while the DDP primarily covered the hydrophilic sites on the lignite surface. In order to improve the flotation efficiency of low-rank coal, Tian et al. (2017) used mixtures of diesel oil (hydrocarbon) and oxygenated chemicals (aldehyde, ketone, and carboxylic acid) as non-conventional flotation reagents. The results indicated that the reagents containing oxygen-functional groups, with their increased bonding energy, were much better collectors than diesel oil for the flotation of low-rank coals. These mixed collectors can be prepared only by simple blend. The raw materials are common chemical products which have mature, fast and easier access trading market. And these flotation reagents are common organic oil collectors. The organic polar oxygen-containing functional groups mainly include carboxyl, hydroxyl, keto, aldehyde, ether etc. Low-rank coal collectors usually contain one or more organic compounds corresponding to these groups.

It was common sense that polar groups of the collector can interact with the oxygenated functional groups on the coal surface by hydrogen bonding, thereby improving the flotability of low-rank coals or oxidized coals (Jia et al., 2000; Jia et al., 2002). The aldehyde group is one of the organic polar oxygen-containing functional groups. There is no hydrogen bond and association phenomenon between the aldehyde groups. And aldehydes can be dissolved in organic solvents very well. However, collector containing aldehyde group for the flotation of low-rank coals has not been systematically used and studied.

In this investigation, a mixture of dodecane and n-valeraldehyde as collector was conducted in the flotation of low-rank coal. Throughout this article, some measurements, such as XRD, XPS, FTIR and contact angle measurement, were used to indicate the properties of low-rank coal and make explanations for flotation responses. The mechanism of improvements in the flotation performance of low-rank coal using the mixture of Dodecane and n-valeraldehyde was fully discussed.

## 2. Experiments and methods

### 2.1. Samples and reagents preparation

The low-rank clean coal sample with size >13 mm was obtained from the Shangwan coal preparation plant located in the city of Ordos, China. First, the clean coal was broken to size<6mm then separated by a heavy liquid with density of 1.36 $g·cm^{-3}$. The heavy liquid was prepared by mixing $ZnCl_2$ (31% w/w) with deionized water. The float product was washed with deionized water. Second, the float product, i.e., ultra-low ash coal, was dried for 3 h at 70 °C, and dry-ground by a porcelain ball mill (QHJM-2) for 10 min at 200 rpm, 45% filling rate (Zou et al., 2016), the ash content was 2.75%.

The dodecane and n-valeraldehyde were provided by Aladdin biochemical technology co. LTD of Shanghai, China. The mixture of dodecane and n-valeraldehyde used in this investigation was obtained by mixing dodecane and n-valeraldehyde in a 1:1 proportion. The constitutional formulas of dodecane and n-valeraldehyde are shown in Fig. 1.

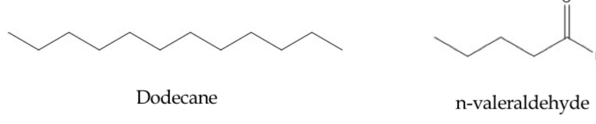


Fig. 1. The constitutional formulas of dodecane and n-valeraldehyde

### 2.2. The physicochemical properties of coal samples

For the indication of surface properties of the ultra-low ash coal, the size distribution analysis of coal samples was conducted on a laser particle size analyzer (Microtrac S3500, America). X-ray diffraction has been used extensively for determining mineral composition analysis, and mineral matter generally represents a significant proportion of coal composition (XRD, Germany). The coal surfaces functional groups were identified using XPS. The XPS experiment was conducted at room temperature in an ultra-high vacuum (UHV) system with the surface analysis system (ESCALAB 250Xi, America). The base pressure of the analysis chamber during the measurement was lower than 1.0 × 10-9 mbar. Al Kα radiation from a monochromatized X-ray source was used for XPS, and for all analyses, the take-off angle of the photoelectrons was 90º and the spot size was 900 μm. The spectra of survey scan were recorded with the pass energy of 100 eV; the energy step size was 1.00 eV. High-resolution spectra were recorded with the pass energy of 20 eV, and the energy step size was 0.05 eV. The data processing (peak fitting) was performed with XPS Peak fit software. The binding energies were corrected by setting the C1s hydrocarbon peak at 284.6 eV (Tian et al., 2017).

### 2.3. Flotation tests

The dodecane, n-valeraldehyde, and the mixture were used as collectors separately. 2-Octanol was used as a frother. The flotation procedure was designed as follows, the flotation tests were conducted in a 0.5 $dm^3$ XFD flotation cell using 30 g of coal. The impeller speed of the flotation machine was 1900 rpm and the airflow rate was 4.2 $dm^3$/min. The collector dosage varied from 0.6, 1, 2, 3, 4 and 5 kg/Mg. The frother dosage (0.3 kg/Mg) was kept constant. For each test, the pulp was first agitated in the flotation cell for 2 min, after which the collector was added and agitated for an additional 3-min period. The frother was then added and the pulp was conditioned for 30 seconds. Flotation products were collected at an interval period of 4 min. Flotation concentrate was analyzed by index: clean coal of flotation yield.

### 2.4. Contact angle measurements

Contact angle (θ) is a measurable quantity that can reflect wettability of mineral surfaces. Low water contact angles indicate hydrophilicity, whereas higher angles are measured on surfaces that are more hydrophobic (less hydrophilic) in nature (Crawford R J and Mainwaring D E, 2001). The ultra-low ash coal was conditioned with different collectors (dosage of 5 kg/Mg) for 3 min. After the conditioning processes, the coal samples were filtered and dried at a low temperature of 40ºC. Four ultra-low ash coal samples were obtained as follows: (1) original ultra-low ash coal, (2) ultra-low ash coal conditioned with dodecane, (3) ultra-low ash coal conditioned with n-valeraldehyde, and (4) ultra-low ash coal conditioned with a mixture of n-valeraldehyde and dodecane. For contact angle measurements, four processed ultra-low ash coal samples were firstly pressed into the plates, then the plates of coal were measured using water contact angle analyzer (DSA100, Germany), such as a water droplet on the surface of coal plate in air.

### 2.5. Fourier transformation infrared spectroscopy (FTIR) measurements

Four ultra-low ash coal samples as the same as the contact angle measurements, FTIR spectrums of the coal samples were obtained with KBr pellets, prepared with four different coal samples and analytical grade KBr. A Perkin Elmer Spectrum 2000 model spectrometer was used for the FTIR analyses, and the spectrum was obtained at 2 cm−1 resolution between 4000 and 400 cm−1.

### 1.6. Surface tension measurements

An automatic surface tension meter (K100, Germany) was used to measure the surface tension of the test solution. To make the measurements feasible, the solution only contained tap water and the flotation collectors (dodecane, n-valeraldehyde, and the mixture) used in the flotation tests, the surface tension of water is used as a contrast at the same time. The concentrations of the reagents were also the same as the contact angle measurements.

## 3. Results and discussion

### 3.1. The characterization of coal

Fig. 2 shows the particle size fractions. The ground ultra-low ash coal contains 94.86% particles below 125 μm, which indicating that the coal sample can be used as a flotation feed. X-ray diffraction pattern shows that the main gangue minerals in coal sample are quartz and kaolinite in Fig. 3, but the content of gangue minerals are rare. Thus, these minerals have little negative effect on flotation performance when using polar reagents as collectors.

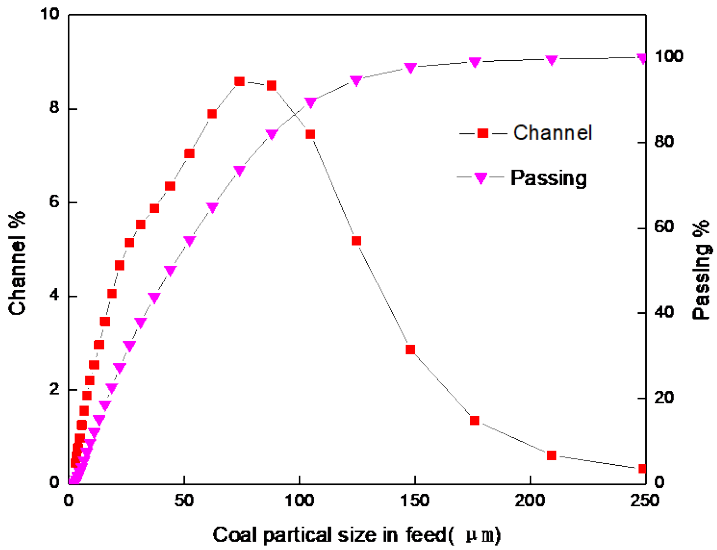


Fig. 2. Size distribution of coal sample

The C1s peaks are fitted as shown in Fig. 4, and the relative contents of carbon forms on the surface of low-rank coal are presented in Table 1. It is well known that C-C and C-H groups are the primary hydrophobic functional groups, while C-O, C=O, and O=C-C groups are the primary hydrophilic functional groups on the coal surface (Bolat et al., 1998; Wang et al., 2013). The XPS results showed that there were many hydrophilic functional groups, such as C-O-C (19.04%), C-O (7.91%), and C=O (2.47%), on the surface of the coal. The ratio of hydrophobic functional groups to hydrophilic functional groups usually determines the hydrophobicity of the coal surface. Apparently, hydrophilic functional groups were more on the surface of low-rank coal. This indicates that the surface of low-rank coal will be covered by a thick hydration shell when the coal is prewet because these hydrophilic functional groups can be bonded with the water by hydrogen bond. Thus, it is hard to float low-rank coal in the presence of traditional collectors. Under this condition, collector containing polar groups may be more suitable for low-rank coal flotation because these polar groups in collector may be able to be bonded with polar groups on the coal surface, thereby enhancing the hydrophobicity of low-rank coal.

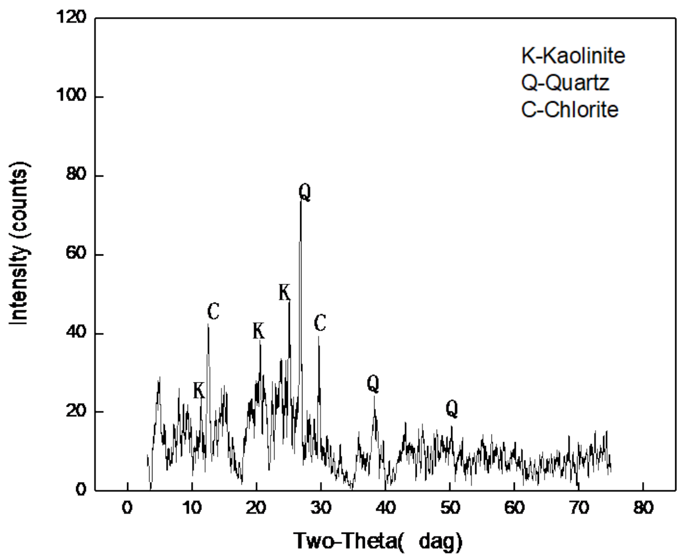


Fig. 3. C1s peaks of low-rank coal

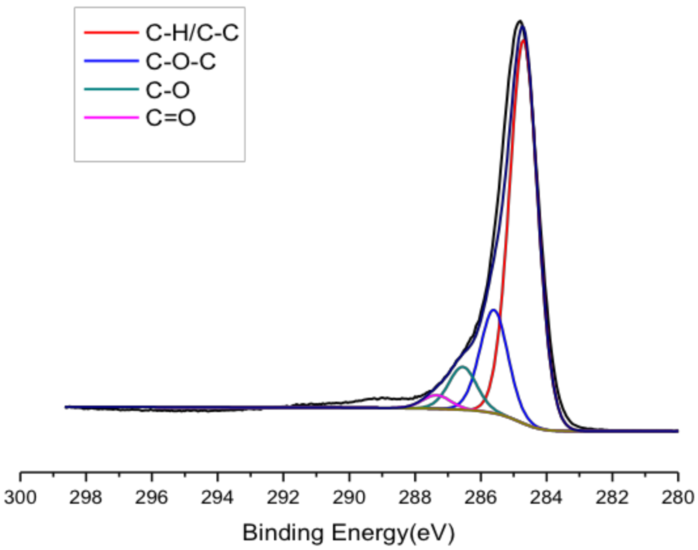


Fig. 4. C1s peaks of low-rank coal

Table 1. Relative contents of carbon forms on low-rank coal surface

| Types | C-C/C-H | C-O-C | C-O | C=O |
|---|---|---|---|---|
| Contents (%) | 70.58 | 19.04 | 7.91 | 2.47 |

### 3.2. Flotation results

The flotation responses of low-rank coal using different collectors are shown in Fig. 5, the results given in the Fig. present that the flotation clean coal yield increases with the increase of the collector dosage. The flotation clean coal yield is highest when uses the mixed collector at the same dosage. It is also found that the flotation clean coal yield using n-valeraldehyde as collector is a little higher than that using dodecane as the collector. The flotation clean coal yield at the mixture dosage of 3 kg/Mg is about 90%, while using dodecane as the collector is 56% and n-valeraldehyde is 59%, which is much higher than that using n-valeraldehyde or dodecane as a solo collector. And the flotation clean coal yield even at the mixture dosage of 5 kg/Mg is about 97%. The mixture of n-valeraldehyde and dodecane as the collector enhances the flotation recovery of ultra-low ash coal and shows a good separation performance of coal.

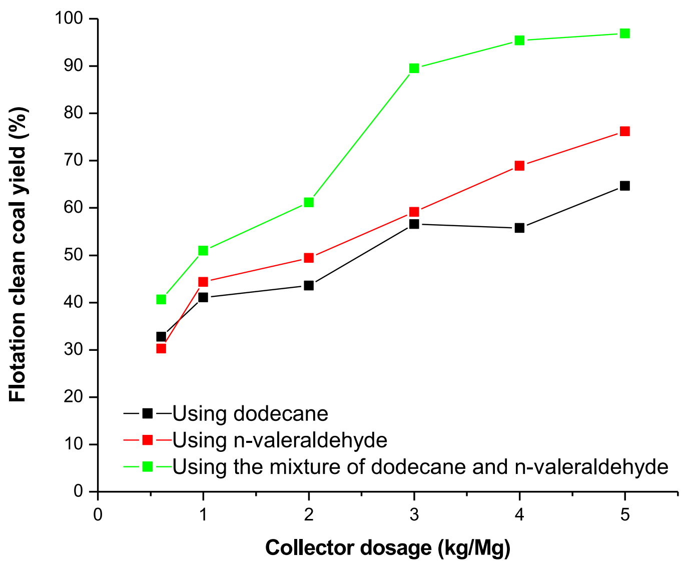


Fig. 5. Flotation results using different collectors

### 3.3. Contact angle results

The contact angle of raw coal is 60.2º by measurement, which is low and also directly illustrate poor floatability of low-rank coal. Fig. 6 shows the contact angles of coal sample after conditioning with different collectors. The result shows that after conditioned with mixed collector, the contact angle of coal is higher than that conditioned with a solo collector (n-valeraldehyde or dodecane), and the contact angle of the original coal sample conditioned without collectors is the smallest. As a result, the coal surface hydrophobicity is enhanced using the mixture of dodecane and n-valeraldehyde as collector, in other words, the contact angle of conditioning with mixed collector is 20.7° larger than the original coal sample.

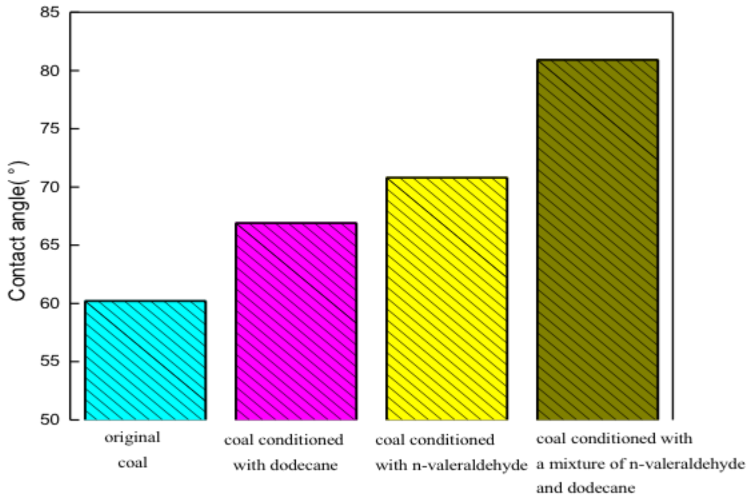


Fig. 6. Contact angles of coal slime after conditioning with different collectors

### 3.4. FTIR analysis

As shown in Fig. 7, FTIR spectrums of ultra-low ash coal before and after conditioning with different collectors are presented. The functional groups corresponding to appropriate peaks in the coal samples as follows (Hong et al., 2001; Çınar 2009), the absorption peak at 3500 $cm^{-1}$ to 3000 $cm^{-1}$ represents the intramolecular hydroxyl (-OH), the absorption peak at 1700 $cm^{-1}$ to 1600 $cm^{-1}$ represents the group of carbonyl (C=O) or carboxyl (COOH), and the characteristic absorption peaks at approximately 1184 $cm^{-1}$ are the stretching vibration of carbonyl. These analyses indicate that the existence of hydrophilic functional groups (C-OH, C=O, COOH) is the material causing poor flotation of low rank coal.

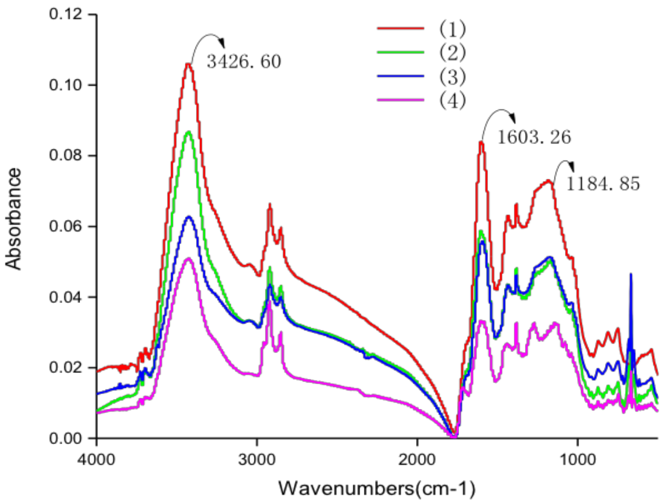


Fig. 7. FTIR spectrums of low-rank coal before and after conditioning with collectors: (1) original ultra-low ash coal, (2) ultra-low ash coal conditioned with dodecane, (3) ultra-low ash coal conditioned with n-valeraldehyde, (4) ultra-low ash coal conditioned with a mixture of n-valeraldehyde and dodecane

It can be clearly seen that the peaks for the hydrophilic groups in coal are weakened due to the conditioning with collector from the Fig. 7. However, it should be observed that the peak areas of the hydrophilic groups are decreased by the conditioning with a solo collector (n-valeraldehyde or dodecane), and the peak areas of hydrophilic groups by the conditioning with dodecane are a little more than by the conditioning with n-valeraldehyde. It indicates that a solo collector (n-valeraldehyde or dodecane) can increase the floatability of low-rank coal, and n-valeraldehyde is better than dodecane. However, the peak areas of the hydrophilic groups are little decreased by the conditioning with a solo collector (n-valeraldehyde or dodecane) while greatly decreased by the conditioning with a mixture of n-valeraldehyde and dodecane, and the floatability of low-rank coal is enhanced a lot. Because the surface of coal consists of inherently hydrophilic areas and sites containing oxygenated moieties, such as carboxyl, carbonyl, phenolic, and ester group (Xing, Y et al., 2016). Therefore, the mechanism of interaction between the mixed collector and the coal surface appears to be through the polar group of the n-valeraldehyde interacting with the oxygenated functional group on the coal surface by hydrogen bond (Jia et al., 2000). Dodecane primarily covers the hydrophobic sites while n-valeraldehyde primarily covers the hydrophilic sites (Xia et al., 2015) by hydrogen bond promoting adsorption of dodecane at these sites, that is, there existed synergistic effect between dodecane and n-valeraldehyde. Thus, the flotation performance is improved, and the interaction mechanism is illustrated schematically in Fig. 8.

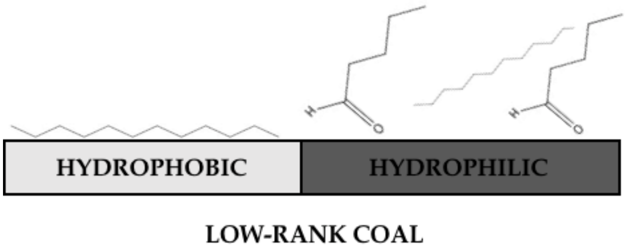


Fig. 8. Schematic representation of interaction between surfactant molecules and coal surface

It is worth noting that the ultra-low ash coal with rare gangue minerals was used in our study. The gangue minerals had little negative effect on flotation performance when using polar reagents as collectors, so we just considered the interaction between reagent functional groups and coal surface sites. The interaction between reagents and gangue minerals should also be considered in the future industrial applications. We can eliminate the effect as much as possible by adjusting the proportion of the mixed collector, or we can achieve better dispersion of coal and its associated clays by adjusting the pH value (Kelebek et al., 2008).

### 3.5. Surface property of flotation solution analysis

The effects of collectors on the surface tension of the flotation solution and water as the contrast sample of the surface tension are shown in Fig. 8. Tap water had a surface tension of 73.5mN/m, the order of the surface tension in the three types of collectors was the mixture of n-valeraldehyde and dodecane (49.1mN/m) < n-valeraldehyde (50.7mN/m) < dodecane (58.4mN/m). The decrease of surface tension facilitates the spreading of collector oils, increase the probability of collector-coal particle collision and ultimately improve flotation performance. In other words, the lower the surface tension of a flotation solution, the better the flotation performance. The lower surface tension values for the mixed collector than that of dodecane and n-valeraldehyde solely, the fact that mixed collector has a lower surface tension value implied that the mixed collector should spread faster on solid surfaces immersed in water than dodecane or n-valeraldehyde, and the mixture showed a good separation performance of flotation test. That's probably because the n-valeraldehyde can adsorb on the interface between the dodecane and water phases and, consequently, decrease the interfacial tension of dodecane with water (Ding L P, 2010). That is to say, n-valeraldehyde as a accelerator, it can reduce the interfacial tension of dodecane with water, therefore, the surface tension of the flotation solution containing the mixture of dodecane and n-valeraldehyde is least. And the interaction schematic diagram between mixed collector and low-rank coal surface is shown in Fig. 10. These results are also in very good agreement with the flotation test results.

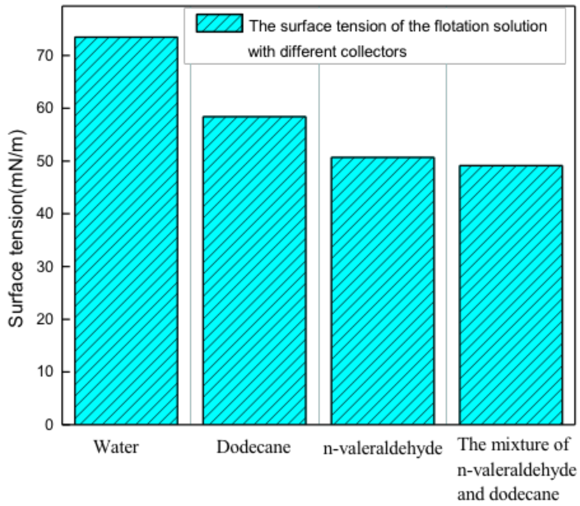


Fig. 9. The surface tension of the flotation solution with different collectors

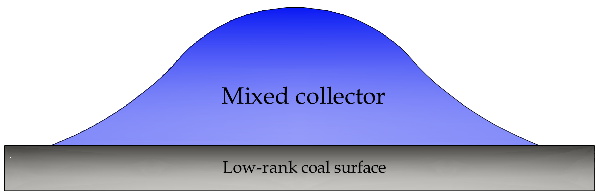


Fig. 10. The interaction schematic diagram between mixed collectors and low-rank coal surfaces

## 4. Conclusions

In the present study, the physical and chemical properties of coal sample were characterized by size distribution, XRD, XPS, and water contact angle measurements. XPS results showed that there were many hydrophilic functional groups including C-O-C (19.04%), C-O (7.91%), and C=O (2.47%) on the surface of low-rank coal and the contact angle of raw coal was 60.2°. These measurement results revealed poor flotability of low-rank coal.

The flotation results showed that better flotation performance was obtained using the mixture of n-valeraldehyde and dodecane as collector. The coal contact angle after mixed collector adsorption was higher than that after solo collector adsorption. FTIR results showed that the peak areas of the hydrophilic groups were little decreased by a solo collector while the peak areas of hydrophilic groups were greatly decreased by a mixture of n-valeraldehyde and dodecane. When used the mixture of dodecane and n-valeraldehyde as collector, dodecane primarily covered the hydrophobic sites while n-valeraldehyde primarily covered the hydrophilic sites by hydrogen bond promoting adsorption of dodecane at these sites. There existed synergistic effect between dodecane and n-valeraldehyde. On the other hand, the order of the surface tension for these collectors was the mixture of n-valeraldehyde and dodecane (49.1mN/m) < n-valeraldehyde (50.7mN/m) < dodecane (58.4mN/m). It indicated that n-valeraldehyde could reduce the surface tensions to improve the spreading performance mixed collector on low-rank coal surface. Therefore, the improvement both in adsorption and spreading was responsible for the enhancement of low-rank coal flotation by using the mixed collector.

## Acknowledgements

This research was supported by the Fundamental Research Funds for the Central Universities (2017CXNL04).

## References

BOLAT, E., S. SALAM, S. PISKIN, 1998. *The effect of oxidation on the flotation properties of a Turkish bituminous coal.*

Fuel Processing Technology. 55: 101–105.
BUSTAMANTE, H., WOODS G., 1984. *Interaction of dodecylamine and sodium dodecyl sulphate with a low-rank bituminous coal*, J. Colloids & Surfaces. 12(3-4):381-399.
ÇINAR, M., 2009. *Floatability and desulfurization of a low-rank (Turkish) coal by low-temperature heat treatment*, Fuel Processing Technology 90(10):1300-1304.
CRAWFORD, R. J., MAINWARING, D. E., 2001. *The influence of surfactant adsorption on the surface characterisation of Australian coals*, Fuel. 80(3):313-320.
DING, L. P., 2010. *Effect of Collector Interfacial Tension on Coal Flotation of Different Particle Sizes*, Industrial & Engineering Chemistry Research. 49(8):3769-3775.
DRZYMALA, J, GORKE, J. T., WHEELOCK, T. D., 2005. *A flotation collector for the separation of unburned carbon from fly ash*, Coal Preparation. 25(2):67-80.
GAO, Z., BAI, D., SUN, W., CAO, X., HU, Y., 2015. *Selective flotation of scheelite from calcite and fluorite using a collector mixture*, Minerals Engineering. 72:23-26.
HARRIS, G. H., DIA, J., FURSTENAU, D.W., 1995. *Coal flotation with nonionic surfactants*, Coal Preparation. 37(2): 135-147.
HONG Z., HU, L. I., ZE, O. U., 2001. *Study on Surface Modification of Different Rank Coals by Using FTIR*, Journal of China University of Mining & Technology.
JIA, R. HARRIS G. H., FURSTENAU, D. W., 2000. *An improved class of universal collectors for the flotation of oxidized and/or low-rank coal*, International Journal of Mineral Processing. 58(1): 99-118.
JIA, R. HARRIS G. H., FURSTENAU, D. W., 2002. *Chemical Reagents for Enhanced Coal Flotation*, J. Coal Preparation. 22(3):123-149.
KELEBEK, S., DEMIR, U., SAHBAZ, O., UCAR, A., CINAR, M., KARAGUZEL, C., 2008. *The effects of dodecylamine, kerosene and pH on batch flotation of Turkey's Tuncbilek coal*, International Journal of Mineral Processing. 88(3–4):65-71.
MCFADZEAN, B., CASTELYN, D. G., O'CONNOR, C. T., 2012. *The effect of mixed thiol collectors on the flotation of galena*, Minerals Engineering. 36-38(10):211-218.
TIAN, Q., WANG, Y., LI, G., 2017. *Application of special collectors and flotation column for beneficiation low rank coal slimes*, Physicochemical Problems of Mineral Processing. 53(1): 553-568.
TIAN, Q., ZHANG, Y., LI, G., WANG, Y., 2017. *Application of Carboxylic Acid in Low Rank Coal Flotation*, International Journal of Coal Preparation & Utilization. (2).
WANG, B., PENG, Y., VINK, S., 2013. *Diagnosis of the surface chemistry effects on fine coal flotation using saline water*. Energy Fuel 27: 4869–4874.
XIA, W., NI, C., XIE, G., 2015. *Effective Flotation of Lignite Using a Mixture of Dodecane and 4-Dodecylphenol (DDP) as a Collector*, International Journal of Coal Preparation & Utilization, 262-271.
XING, Y., GUI, X., CAO, Y., WANG, Y., XU, M., WANG, D., LI, C., 2016. *Effect of compound collector and blending frother on froth stability and flotation performance of oxidized coal*. Powder Technology. 306: 166–173.
ZHOU, W., CAO, Y., SUN, C., 2017. *Adsorption of anionic polyacrylamide onto coal and kaolinite: Changes of surface free energy components*, Particulate Science & Technology, 35, 233-238.