Pyrolytic Oils in Coal Flotation

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Summary

The aim of this article was the research of new flotation reagents, which were formed through pyrolysis of different types of waste. Potential new flotation reagents are liquid organic phase pyrolysis of tires, plastic and wooden materials. Another goal is to achieve the coal flotation ash content quality below 10%.

The results imply that it is possible to produce flotation collectors from various types of waste, which may be applicabe in black coal flotation. Producing and application of a suitable collector, which would be ecologically as well as economically interesting, makes an inseparable part of the flotation process.

Keywords: pyrolytic oils, flotation, black coal, new flotation reagents

Introduction

Coal is one of nonrenewable energy sources. It has mined for different purpose of many industrial branches such as power-engineering, chemistry, metallurgy and many others. The level of waste in the coal mining is depends on applied tehnological processes. The question that arises is how to deal with slump in coal mining. One possibility is a perfect preparation of coal and maximum utilization of its combustible component. In that purpose froth flotatation is widely used particle separation process. However, its high performance is limited to narrow particle size range between approximately 50 to 600 µm for coal and 10 to 100 µm for minerals. Beyond this range, the efficiency of froth flotation decreases significantly, especially for difficult to float particles of weak hydrophobicity. (Sobhy et al. 2013)

Coal flotation deals with cleaning the finest fractions of coal that originated due to abrasion or desintegration in the course of coal mining preparation. In the flotation process, very fine fractions get separated, which would otherwise transfer into waste. Utilization of new flotation collectors, which would be ecologically as well as economicaly interesting, makes an inseparable part of the flotation process. (Fečko et al. 2011)

Many diferent flotation reagents such as Triton x-100 ($C_{34}H_{62}O_{11}$), Brij-35 ($C_{58}H_{11}8O_{24}$), MIBC ($C_6H_{14}O$), SDS ($C_{12}H_{25}NaO_4S$) were used in flotation of Turkish bituminous coal (Erol et al. 2002). Pine oil as a frother and Oleic Acid, Fuel Oil and kerosene as collectors were used in flotation of fine rich tailings coal, i.e. 54.8% ash with 60% of the sample passing through a 46 microns screen. These collectors were used industrially in coal cleaning (Abdelrahman. 1988). For all types of coals hydrocarbons such as kerosene, diesel oil and fuel oil have long been used in flotation process. Their dosage increase as the rank decreases or the oxidation level of coal surfaces increases. Sub - bituminous and lignite coals might require 5 kg/t of fuel oil and in some cases this level can increase up to 50 kg/t (Kelebek et al. 2008).

Non-ionic reagent Triton x-405 (p-tert-octyphenoxy-poly-ethoxyethanol), $C_{14}H_{21}(OCH_2CH_2)_{40}$ avgOH) were used in flotation of low-rank British coal from British Coal Bickershaw collery (Banford and Aktas.2004).

For coal flotation from Kailuan mine in China (Xiahui, et al. 2013) were used diesel fuel as a collector. In that purpose different collector dosages (120 g/t, 270 g/t and 320 g/t) with frother dosages of (75 g/t, 110 g/t, and 145 g/t) were applied. The majority of 48.32% coal yield exists in the size range of (−0.246 mm+0.124 mm).

Materials and methods

For flotation experiments were used coal samples Lazy from mine Karviná that belongs Ostrava- Karviná coal basin. In our research we tested pyrolytic oils P550, KOPD (9), KOPD (11) and Montanol (551+Vipírací oil) as flotation collectors. These oils are liquid pyrolysis products of various types of wastes such as tyres and wooden residues. Following methods were used for Lazy coal treatment: Petrographic analysis on Laits DMLP microscope, Sieve analysis on Ritsch sieves, Infra- red spectrometry analysis of pyrolysis oils on FTIR spectrometer Nicolet NEXUS 470 company Thermo Fisher Scientific USA, and flotation tests on device VRF-1 of producer RD Příbram.

Petrographic analysis of coal sample Lazy

Micropetrographic testing of coal sample Lazy were carried out on products that are made from coal grit up to 1 mm without screening. Qualitative and quantitative analysis of macerals was preformed on microscope (Laits DMLP) at faculty of Mining and Geology, University of Belgrade. Determination of macerals and minerals was performed according to the standards of the International ommittee of the petrology of coal and organic petrology (International Committee for Coal and Organic Petrology-ICCP1998; ICCP2004 Taylor et al., 1998).

Results of micropetrographic verifications of the coal samples are shown in Table 1, and a distinctive look macerals is shown in (Figure 1.). The investigated coal samples have the following microscopic features:

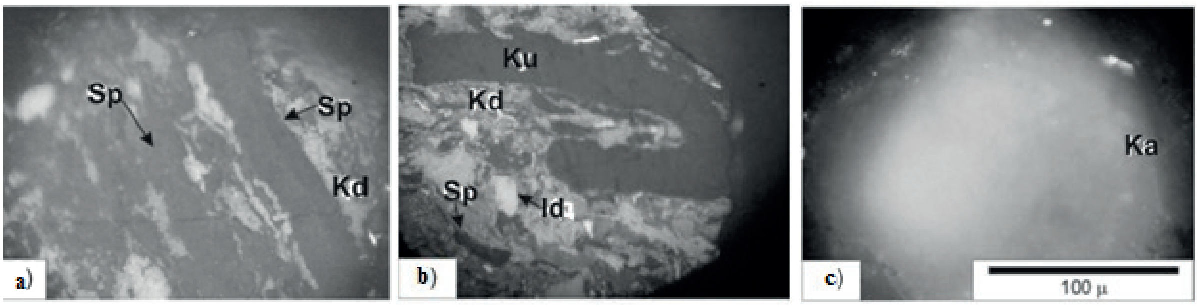

Fig. 1 Macerals for coal sample Lazy (a,b,c) Kd-Kolodetrinit, Sp-Sporinit, Ku-Kutinit, Id-inortodetrinit, Ka-Karbonaty

Rys. 1 Macerały węgla z kopalni Lazy (a, b, c), Kd-Kolodetrinit, Sp-Sporinit, Ku-Kutinit, Id-inortodetrinit, Ka-Karbonaty

Tab. 1 Micropetrographic composition of the coal samples from Lazy, Czech Republic

Tab. 1 Skład mikropetrograficzny próbki węgla z Lazy, Czechy

Macerals and minerals, vol %	Lazy	Lazy without mineral matter
Telinite	2.0	2.4
Kolotelinite	32.4	40.0
Vitodetrinite	1.3	1.6
Kolodetrinite	18.4	22.6
Gelinite	0.8	1.0
Korpogelinite	0.7	0.8
VITRINITES	55.6	68.4
Sporinite	7.8	9.6
Kutinite	1.1	1.4
Rezinite	0.7	0.8
Suberinite	0.2	0.2
Alginite	-	-
Liptodetrinite	1.6	2.0
Bituminite	-	-
LIPTINITE	11.4	14.0
Fuzinite	6.4	8.0
Semifuzinite	4.1	5.0
Makrinite	0.2	0.2
Funginite	0.3	0.4
Inertodetrinite	3.3	4.0
Micrinite	-	-
INERTINITE	14.3	17.6
Sum of Coal	81.3	100.0
Clay	4.5	
Pyrites	0.8	
Carbonates	13.2	
Others	0.2	
MINERAL MATERS	18.7	

The sample lies micropetrographic terms can be defined as trimacerit with 55.6 % vitrinite (Table. 1), high content liptinita (11.4%) and inertinite (14.3%) and a relatively low content of minerals (18.7%). The most common macerals of vitrinite groups is kolotelinite 32.4% and from 18.4% kolodetrinit (Fig 1. a,b) .Telinite and vitrodetrinite occur in low concentrations (1.3 - 2.0%), while gelinite and korpogelinite present in very low concentrations (< 1%). Within the group liptinite predominant maceral is sporinit (7.8%) (Fig 1. a,b), while liptodetrinite (1.6%) and kutinite (1.1%) Fig 1. b) occur in low concentrations.

Rezinite and suberinite occurs in very low concentrations (< 1%). From inertinite group of maceral fuzinite is most common (6.4%), semifuzinite (4.1%) and inertodetrinite (3.3%) Fig 1. b), while very low concentrations occur in funginite and makrinite. Macerai liptinite and inertinite groups usually occur in kolodetrinite. The most common minerals are carbonates (13.2%) and clay (4.5%) (Table 1), while the pyrite content is very low.

Sieve analysis

The fly ash distrubution was determinated using standard (Retsch) sieves for dry sieving. The ash particles mean diameter for coal sample Lazy $d_{(50\%)}$= 0.36 mm.

On the other hand from the lowest ash content of 23.45% on sieve (+1.0 mm) and recovery of 0.76% were achieved in the coal sample Lazy. On the other hand, the highest ash content in coal sample Lazy of 55.61% on sieve (−0.1 mm+0.063 mm) with recovery 5.81% (Table 2).

Infra Red spectrometer of pyrolysis oils

The characteristics of new flotation reagents were analysed on department of laboratory research on geomaterials (Science Academy of Czech republic- Institut of Geonics) on the unit FTIR spectrometer Nicolet NEXUS 470, company Thermo Fisher Scientific, USA.

The spectrum of the flotation collector (Montanol 551+Vypírací oil) is apparently high proportion of a mixture of aliphatic hydrocarbons (2956 cm^{-1}, 2922 cm^{-1},2870 cm^{-1}, 2854cm^{-1}). Here prevail non branched chain of aliphatic hydrocarbons. Belt 2922 cm^{-1} belonging to a functional group CH_2, is more intense than belt 2956 cm^{-1}, belonging to a functional group CH_3. The peak 1550 cm^{-1} suggest about representation of NO_2 compound wih is contain only in (Montanol 551+Vypírací oil) (Fig. 2).

The spectrum of flotation collector (P550) is apparently represented of aliphatic mixture hydrocarbons. As opposed to spectrum (Montanol 551+Vypírací oil), collector (P550) is represented by the presence of aromatic aldehydes or ketons. There is a great simularity with (Montanol 551+Vypírací oil) in the value of 1734 cm^{-1} and in value 1704 cm^{-1} for (P550) in unsaturated or aromatic ketone groups. Also in collector (P550) is a significant presence of aromatic rings (1599 cm^{-1}, 1493 cm^{-1}, 1309 cm^{-1}), which exceed the value of the CH_3 and CH_2 deformation groups (1448 cm^{-1}, 1375 cm^{-1}). Very significant peak is 2921 cm^{-1} with functional group CH_3, which is most intense. (Fig. 2). Spectra of collectors KOPD (9) and KOPD (11) is showed a mean medium content of impurities of inorganic materials. About (110 cm^{-1}) and low moisture content (3200-3500 cm^{-1}). A significant proportion of both collectors KOPD hold a mixture of aliphatic hydrocarbons (2959 cm^{-1}, 2929 cm^{-1}, 2872 cm^{-1}) are dominant non branched chain. In this collectors there are no evidence of symmetric valence vibration CH2 groups (Fig. 2).

Flotation tests

These tests were carried out in the laboratory of the Institute of Environmental Engineering VSB Technical University in Ostrava on flotation device VRF-1of producer RD Příbram. The coal concentrate and the coal tailings are filtered through a 240mm diameter filter paper and dried in a laboratory oven at 105°C. After drying, samples were weighted, homogenized and treated by chemical analysis of the ash content and yield. Flotation conditions were:
sample density: 150 g/l;
collector dosage: 250 g/t ; 375g/t ; 500g/t;
flotation time 5 min and agitation timr 1 min.

Results and discussion

Using pyrolysis oil (P550) at a concentration of 500 g/t, flotation concentration was obtained 56.61% of the mass fraction of concentrate, with the lowest ash content of 9.32% (Tab.3). It is interesting to note that the ash content is almost the same in the collector spending of 500 g/t and 250 g/t with a concentration recovery rate of 56.61% and 36.87% respectively (Fig. 3).Using the pyrolysis oil KOPD (9) at concentration of 250 g/t was achieved the lowest ash

Tab. 2 Size distribution of coal sample Lazy

Tab. 2 Rozkład wielkości ziaren próbek węgla Lazy

Sieve size range (mm)	W_t (%)	Ash content (%)	Cumulative undersize ΣM (%)↓	Cumulative oversize ΣM(%)↑
+1.0 1	.20	23.45	1.2	100
−1.0+0.5	24.72	29.87	25.92	98.8
−0.5+0.3	36.35	33.45	62.27	74.08
−0.3+0.2	18.24 4	2.09 8	0.51 3	7.73
−0.2+0.1	13.01	47.22 9	3.52 1	9.49
−0.1+0.063	3.88 5	5.61 9	7.4 6	.48
−0.063+0.0	2.60 5	0.07 1	00 2	.6
Σ 1	00 3	7.11 -	-	

content of 8.85% and the recovery of 54.81% (Fig. 4). With the increasing consumption of collector comes to a strong increase in ash content in the concentrate and increase efficiency (Table 3).

Using flotation collector (Montanol 551+Vipírací oil) at the concentration of 250 g/t was achieved the ash concentrate of 9.53% with recovery 55.37% (Fig. 3) and (Fig. 4). It is interesting to note that with the increase of spending the collector (Montanol 551+Vipírací oil) of 250 g/t respectively 500 g/t there is a gradual increase in recovery of 55.37% to 71.33% (Table 3).

Using the flotation pyrolysis oil KOPD (11) at the concentration of 375 g/t was obtained the ash content of 13.7 and the recovery of 29.6% (Fig. 3) and (Fig. 4). It is interesting to note that with the increase of spending the collector KOPD (11) of 250 g/t respectively 500 g/t there is a gradual decrease in utilization of concentrate of 74.84% respectively 67.68% (Table 3).

Conclusion

In this paper we were carring out with the flotation of black coal Lazy from mine Karviná. Various types of waste such as old tires and wooden remains can be processed by pyrolysis process. New flotation reagents (pyrolysis oils) P 550, KOPD (9), KOPD (11) and Montanol (551+Vypírací oil) were successfully applied. This confirms the fact of achieving the ash content of the concentrate below 10%. The lowest ash content in the concentrate of 8.85% and

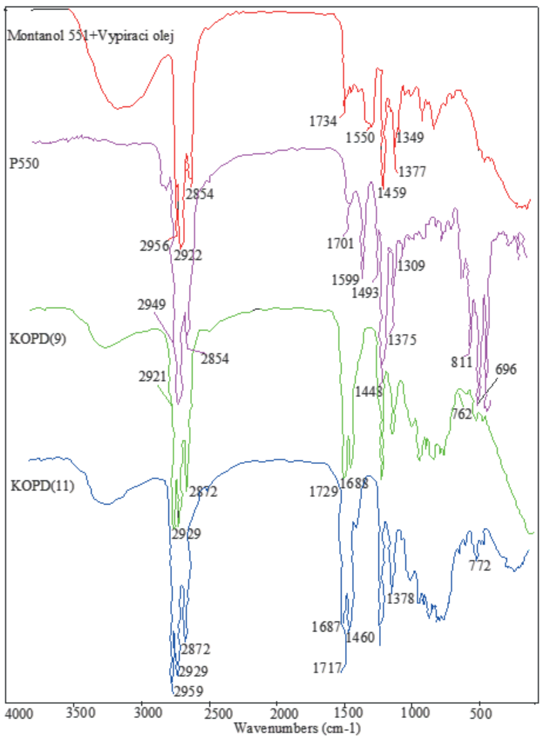

Fig. 2 IR spectra of flotation reagents: (Montanol 551+Vypírací oil, P550, KOPD (9), KOPD (11))

Rys. 2 Widmo IR odczynników flotacyjnych: (Montanol 551+Vypírací oil, P550, KOPD (9), KOPD (11))

Tab. 3 Flotation tests with different dosage of collector for coal saamples LAZY

Tab. 3 Testy flotacyjne z różnymi dawkami kolektorów próbek węgla LAZY

Flotation collector	Fraction	Dosage					
		250(g/t)		375(g/t)		500(g/t)	
		Yield(%)	Ash(%)	Yield(%)	Ash(%)	Yield(%)	Ash(%)
P550	Concentrate	36.87	9.33	49.74	11.67	56.61	9.32
	Tailings	63.13	46.67	50.26	59.06	43.39	76.51
	Feed	100	32.9	100	35.48	100	38.47
KOPD (9)	Concentrate	54.81	8.85	76.92	18.15	73.36	16.88
	Tailings	45.19	55.75	23.08	88.89	26.64	86.55
	Feed	100	30.04	100	34.47	100	35.44
KOPD (11)	Concentrate	74.84	13.98	72.25	13.7	67.68	14.43
	Tailings	25.16	84.12	27.75	84.8	32.32	85.27
	Feed	100	31.62	100	33.43	100	37.32
Montanol 551 +Vypírací oil	Concentrate	55.37	9.53	67.84	17	71.33	19.65
	Tailings	44.63	53.96	32.16	85.42	28.66	83.06
	Feed	100	29.35	100	39	100	37.82

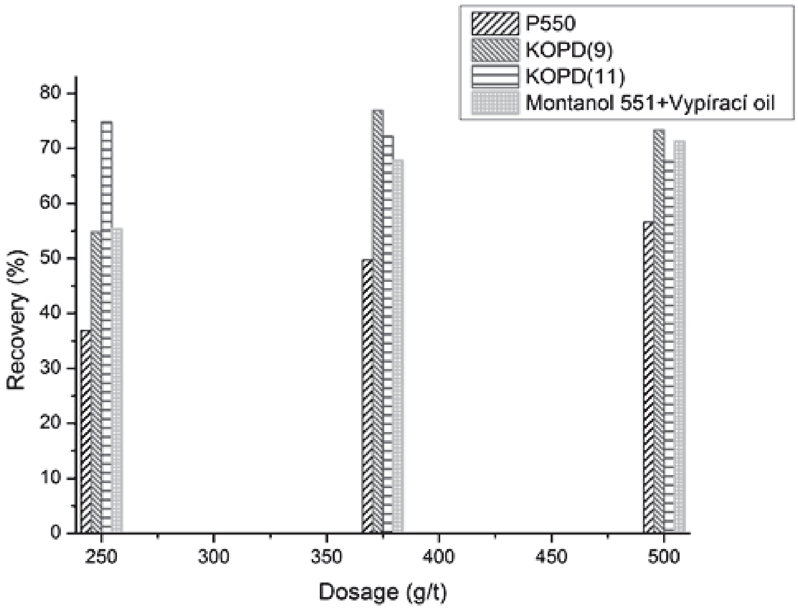

Fig. 3 Dependence of the recovery on the collector dosage

Rys. 3 Zależność uzysku od dawki kolektora

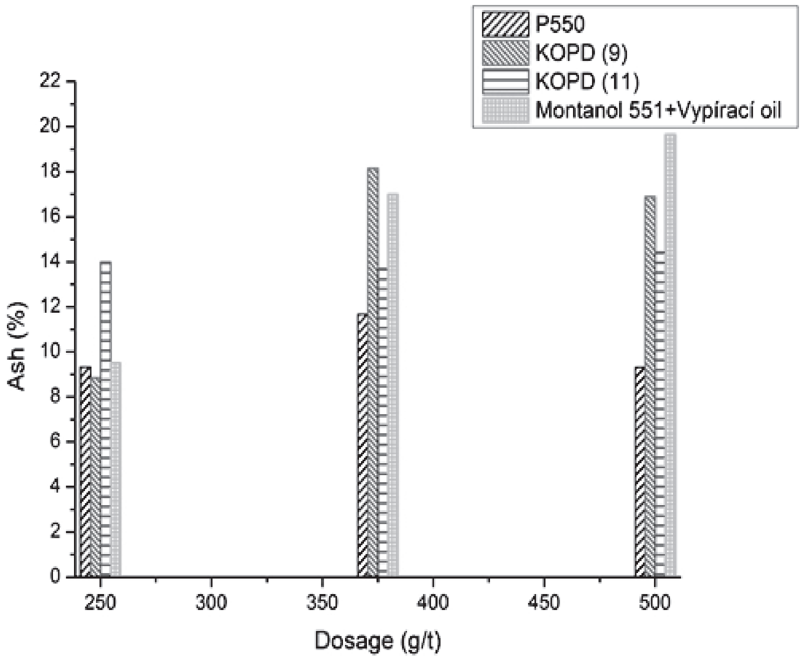

Fig. 4 Dependence of the ash on the collector dosage

Rys. 4 Zależność zawartości popiołu od dawki kolektora

recovery of 54.81% was obtained using pyrolysis oil KOPD (9).

On the other side the best ash concentration results were achieved using P550 when the spending of collector was two times bigger (500 g/t) than in the first experiment (250 g/t) when the the ash concentration was almost the same quality 9.33% (Table 3).

Using diferent kinds of waste for producing the pyrolysis oils and reduction the ash content in coal concentrate by flotation, causes the decreasing of pollution in natural environment.

Acknowledgement

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Oleje pirolityczne we flotacji węgla

Celem tego artykułu jest zbadanie nowych reagentów do flotacji, które były wytworzone w procesie pirolizy różnego typu odpadów. Potencjalne nowe reagenty do flotacji są organiczną fazą ciekłą z pirolizy opon, plastiku i materiałów drewnianych. Kolejnym celem do osiągnięcia jest flotacja węgla o zawartości popiołu poniżej 10%.

Uzyskane wyniki sugerują, że możliwe jest produkowanie kolektorów flotacyjnych z odpadów różnego typu, które mogą znaleźć zastosowanie we flotacji węgla kamiennego. Produkowanie i zastosowanie odpowiednich kolektorów, które mogłyby być interesujące pod względem ekologicznym jak i ekonomicznym, jest nieodłączną częścią procesu flotacji.

Słowa kluczowe: oleje pirolityczne, węgiel kamienny, nowe odczynniki flotacyjne