

## New Flotation Reagents on the Base of Tetrahydropyran for the Processing of High-Ash Coals

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### Article info

*Received:*  
12 March 2019

*Received in revised form:*  
25 May 2019

*Accepted:*  
4 July 2019

#### Keywords:

Coal,  
Synthesis,  
Flotation,  
3-amyltetrahydropyran-4-ol  
acetate,  
Concentrate

### Abstract

The given paper presents the study results of flotation beneficiation of high-ash coals with new flotation reagent on the base of acetate of 3-amyltetrahydro-pyran-4-ol which incorporates apolar and heteropolar groups. The use of a picric acid as a catalyst of hydroxymethylation reaction instead of sulfuric acid made it possible to halve the synthesis time and increase the yield of the target product. The structure of the obtained heterocyclic compound was identified by elemental analysis, infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR). Waste of high-ash coal production from the Saryadyr deposit (Kazakhstan) was selected as an object of flotation. It is found that the beneficiation process efficiency depends on the fineness of the coal material and increases with the transition from  $-0.8 + 0.4$  mm to  $-0.2 + 0.08$  mm. Comparison of the efficiency of coal flotation using pine oil as a traditional collector and 3-amyltetrahydropyran-4-ol acetate showed an increase in the degree of extraction of coal mass into a concentrate and a simultaneous decrease in its ash content when using a synthesized heterocyclic compound. It is concluded that 3-amyltetrahydropyran-4-ol acetate shows both a modifying effect and a foaming ability.

## 1. Introduction

Considering the fact that there are no new consumption markets in the coal sector or their growth will be extremely slow, the prospect of growth in coal demand is about 1% per year [1–3]. In this regard, issues of improving the quality and expanding the range of produced coal not only as fuel, but also as raw materials for the chemical industry become relevant. Considering the fact that the quantity of extracted high-quality coal is decreasing every year, the increase in production volumes can only be achieved on account of exploiting through the development of deposits of hardly concentratable high-ash coal [4–6].

Therefore, the problem of beneficiation of this kind of coal is presented as a main direction of development of the production potential of coal basins. At present, coal processing plants use gravity and flotation methods of beneficiation [7]. For the

use of flotation, taking into account the fact that coal refers to non-polar minerals with high natural hydrophobicity, it is necessary to select the appropriate reagents. However, selection of reagents is most often empirical and does not have sufficient theoretical justification. In this regard, in modern studies aimed at increasing the efficiency of coal flotation, special attention is paid to the use of modifying reagents having apolar and heteropolar groups in their composition [8].

Therefore, the aim of the study was to synthesize 3-amyl-tetrahydropyran-4-ol derivatives containing apolar and heteropolar fragments in their structure, and use them as flotation reagents for flotation of high-ash coals.

## 2. Experimental

Were used as components for the synthesis of 3-amyltetrahydropyran-4-ol acetate. Acetic acid, paraformaldehyde, picric acid, octene-1, sodium carbonate and sodium hydroxide. All the reagents had “Chemically pure” degree of purity.

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Experiments on flotation were carried out using the waste of high-ash coal mining represented by the coal fines of the Saryadyr deposit in the Akmo-la region (Kazakhstan).

To study the surface morphology of the samples electron microscopy was carried out on a scanning electron microscope Quanta 3D 200i Dual system. To identification the composition of coal have been used X-ray analysis, IR spectroscopy and gas chromatography.

### 2.1. The main procedure for obtaining 3-amyltetrahydropyran-4-ol acetate

A catalytic amount of picric acid, 0.5 mol of paraformaldehyde and acetic acid was placed in a round-bottom flask equipped with a reflux condenser, a mechanical stirrer and a dropping funnel. The content of the flask was heated until paraformaldehyde was completely dissolved, after that 0.25 mol of octene-1 was added dropwise. The reaction mass was endured at 110 °C for 1 h. After distilling off acetic acid, the mixture was neutralized with sodium carbonate.

After neutralization the residue of the substance was extracted with benzene and dried over calcined magnesium sulfate. The reaction product was isolated by distillation. The boiling temperature is 122–125 °C ( $n_D^{20} = 1.4420$ ). Found: %C 67.45 %H 9.81  $C_{12}H_{22}O_3$  Calculated: %C 67.29 %H 10.28. The yield of 3-amyltetrahydropyran-4-ol acetate was 85%.

The structure of the obtained heterocyclic compounds was identified by elemental analysis, IR and NMR spectroscopy.

### 2.2. Flotation methods

Flotation was carried out by foam flotation in a laboratory flotation machine FML 1 (237 FL, Russia) with a working chamber volume of 500 ml.

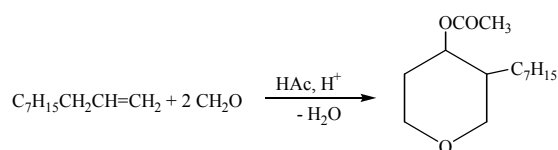
Dry coal of a certain fineness in the amount of loaded into a water-filled chamber of the flotation machine and intensively mixed for 5 min without air supply. Then the flotation reagent was fed for 3 min with stirring. The pulp level in the chamber was brought up with water to the set level and maintained at all stages until the end of flotation, preventing its overflow. Further, a dosed amount of air was supplied to the chamber for 15 sec at a rate of 0.4 l/min. The flotation products were dried and weighed, after that the efficiency of the process was calculated. The optimal flotation time was de-

termined by the results of individual experiments, based on the total amount of coal fraction in the concentrate and it found to be 12 min. The ash content of all flotation products was determined in accordance with the Interstate Standard "Solid Mineral Fuel: Ash Determination Methods" #11022-95 [9].

Pine oil was used as a reference flotation collector reagent.

## 3. Results and discussion

One of the main directions of the synthesis of 3-alkyltetrahydropyran-4-ol derivatives is the reaction of oxymethylation of alkenes-1 in acetic acid in the presence of strong acids.



It is known that sulfuric acid [10, 11], trifluoroacetic acid [12], hydrogen halides [13], aluminum and iron chlorides are used as oxymethylation catalysts. In this study, it was found that, when using picric acid, the yield of 3-amyltetrahydropyran-4-ol acetate was 78–85%, while, when using sulfuric acid, the yield of the product was 70%. In addition, due to the use of picric acid, it is possible to reduce the synthesis time of the heterocyclic compound from two hours to one hour.

The IR spectrum of 3-amyltetrahydropyran-4-ol acetate (Fig. 1) contains absorption bands: at 1739  $cm^{-1}$ , corresponding to the acetate group and at 2800–3000, 1465 and 1373  $cm^{-1}$ , corresponding to C-H bonds of methyl and methylene groups of the substituent and the ring, as well as the band at 1236  $cm^{-1}$  belonging to essential oxygen.

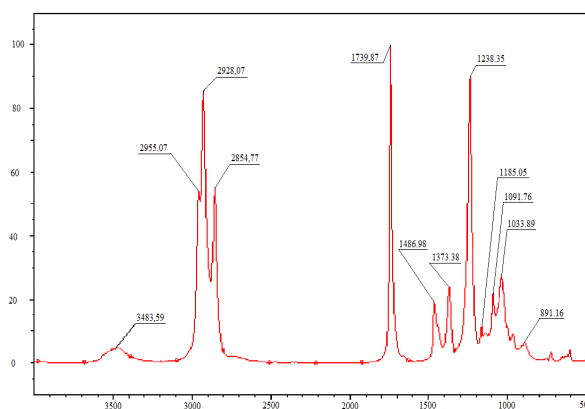


Fig. 1. The IR spectrum of 3-amyltetrahydropyran-4-ol acetate.

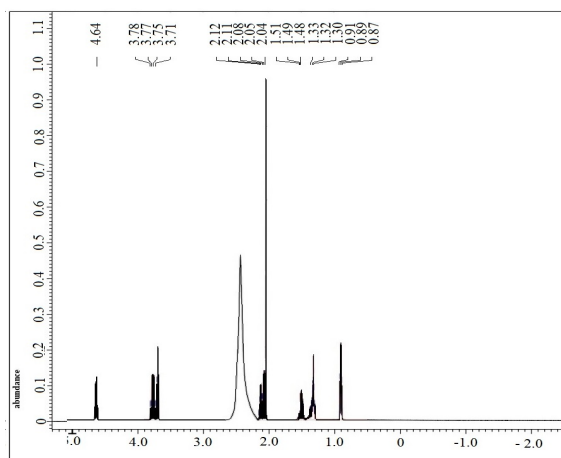


Fig. 2. The NMR spectrum of 3-amyltetrahydropyran-4-ol acetate.

In the  $^1\text{H}$  NMR spectrum of 3-amyltetrahydropyran-4-ol acetate (Fig. 2), multiple signals are observed in the regions of 3.77, 2.11, 4.64, 2.07 and 3.70 ppm corresponding to protons at  $\text{C}_2\text{-C}_6$  tetrahydropyran ring, singlet at 2.04 ppm correlated with the proton of the carboxyl group and multiplets at 1.48, 1.37, 1.31, 1.32, 0.89 ppm correlated with methyl and methylene protons of the alkyl substituent. The experimental results correlate well with the data described in [14, 15].

Samples of 3-amyltetrahydropyran-4-ol acetate were studied as a flotation reagent for the beneficiation of coal waste, with a particle size of less than 10 mm. A study of the material composition (Fig. 3) of coals indicates the presence of a complex of mineral impurities, the bulk of which is clay, quartz, carbonates and iron oxides. A study of the chemical composition of coal showed the presence of oxides of alkali, alkaline earth and amphoteric metals, as well as a wide range of rare and trace elements. The data on the main elements are given in Table 1.

The investigation results on the elemental composition showed that the content of carbon in the coal fines varies from 55 to 65% depending on the fractions.

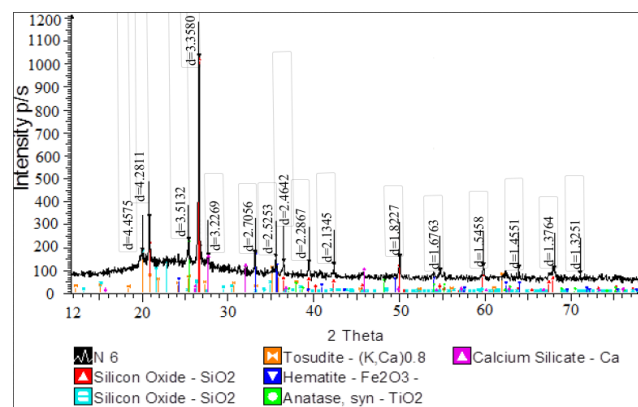


Fig. 3. X-ray phase analysis of the mineral part of coal.

Analysis of the IR spectra (Fig. 4) of the studied coals showed the presence of halide compounds ( $400\text{--}700\text{ cm}^{-1}$ ), alkanes and alkyl fragments ( $700\text{--}1300\text{ cm}^{-1}$ ), aromatic compounds ( $1300\text{--}1800\text{ cm}^{-1}$ ) of benzene, phenol, toluene, aromatic alcohols, as well as primary amines ( $1800\text{--}4000\text{ cm}^{-1}$ ). The data of IR spectroscopy are confirmed by the analysis of the gas phase obtained by heating coal in an inert atmosphere in the temperature range  $200\text{--}600\text{ }^\circ\text{C}$ , where more than 20 substances referring to the indicated group of compounds were identified. Thus, we can conclude that there is a significant amount of “active” oxygen in the form of hydroxyl and carbonyl groups on the surface of the studied coal material.

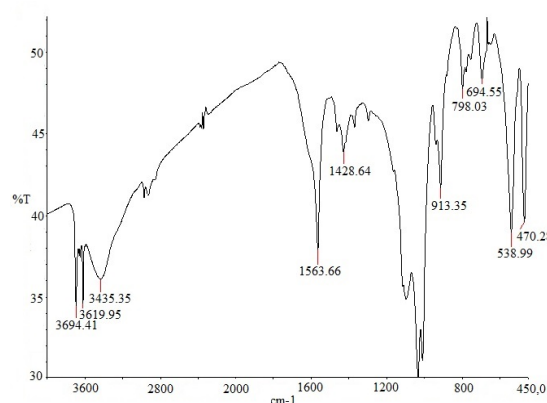


Fig. 4. IR spectrum of the organic part of coal.

**Table 1**

The elemental composition of the averaged sample of coal fines and sludge from the Saryadyr deposit

Coal sample	The elemental composition, wt.%										
	C	O	Na	Mg	Fe	Al	Si	K	S	Ti	Ca
1	55.98	25.54	0.12	0.15	1	5.42	10.04	0.42	0.17	0.25	2.43
2	64.98	20.59	0.11	0.14	1	4.73	6.86	0.37	0.66	0.78	3.85
3	66.83	21.43	0.13	0.16	1	2.96	0.65	0.38	0.28	0.98	3.29
Averaged sample	62.60	22.52	0.12	0.15	1	4.37	5.85	0.39	0.37	0.67	3.19

**Table 2**  
Effect of consumption of 3-amyltetrahydropyran-4-ol acetate on coal flotation

Reagent consumption, g/ton	Yield, %	Ash content, %	Ash extraction, %	Coal extraction, %	Efficiency, %
400	38.25	38.43	28.74	48.2	19.47
600	57.95	38.04	45.19	70.1	24.91
800	61.29	34.21	44.4	76.42	32.02
1200	44.69	37.7	34.59	54.29	19.07
1600	67.06	35.1	52.25	79.22	26.97
2000	48.55	36.36	36.36	60.06	23.71

The energy unsaturation of the surface of the studied coals, due to the presence of microcracks, large pores, oxygen-containing groups and mineral impurities, largely determines the nature of the interaction of coals with reagents during flotation (Fig. 5).

The experiments on flotation of coal fines at various consumption rates of 3-amyltetrahydropyran-4-ol acetate carried out on a fraction of  $-0.8 + 0.4$  mm showed low flotation efficiency (Table 2), this allowing us to draw a conclusion about the insufficient breaking coal grains during crushing.

At the same time, the experiments carried out on the fineness of coal material equal to  $-0.2 +$

$0.08$  mm (Table 3) during the main flotation and re-purifying operations made it possible to achieve coal extraction up to 88.28%. At the same time, experiments with the traditional collector as pine oil under the same conditions allowed to reduce the ash content only to 33%, while extracting coal about 65%.

The experimental results showed that 3-amyltetrahydropyran-4-ol acetate shows simultaneously modifying and foaming abilities, this ultimately meaning that heterocyclic derivatives of this class of compounds can be used as a collector in the flotation process.

**Table 3**

The influence of re-purifying operations on coal flotation at a consumption of 3-amyltetrahydropyran-4-ol acetate – 400 gram per ton

Flotation products	Ash content, %	Coal extraction, %
Main flotation		
Basic concentrate	25.82%	88.28%
Tails	70.53%	11.72%
Initial concentrate	37.01%	100.00%
Re-purifying operation 1		
Concentrate 1	22.48%	66.63%
Industrial product 1	34.49%	21.65%
Basic concentrate	25.82%	88.28%
Re-purifying operation 2		
Concentrate 2	20.55%	53.13%
Industrial product 2	29.25%	13.50%
Concentrate 1	22.48%	66.63%
Re-purifying operation 3		
Ready concentrate	18.60%	42.20%
Industrial product 3	27.28%	10.93%
Concentrate 2	20.55%	53.13%

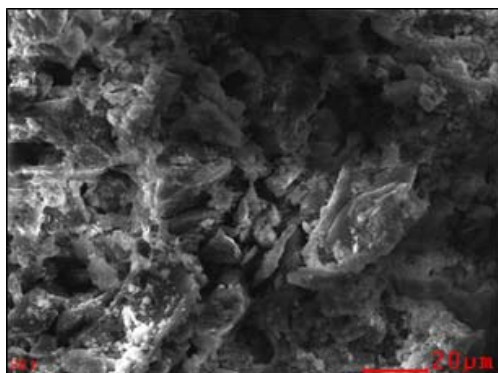
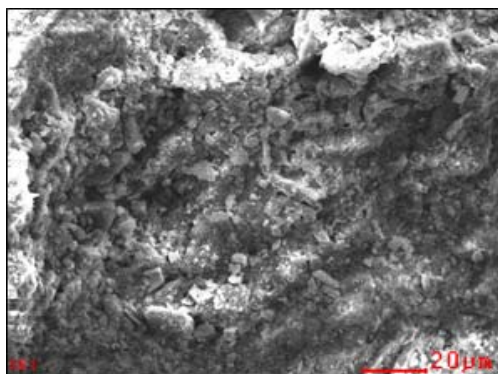


Fig. 5. Microphotographs of the surface of samples of an averaged sample of coal fines from the Saryadyr deposit.

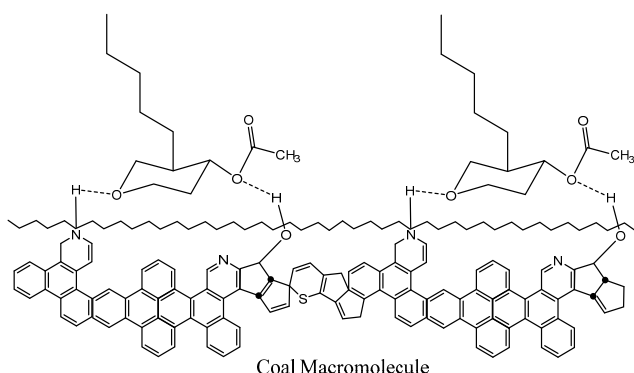


Fig. 6. Fixation of a flotation reagent molecule on the surface of coal.

The results can be explained from the standpoint of the following mechanism.

In the structure of 3-amyltetrahydropyran-4-ol acetate, the apolar (hydrocarbon substituent) and heteropolar (oxane ring) parts can be distinguished. The heteropolar part forms hydrogen bonds with the nitrogen and oxygen centers of the coal macromolecule [16], and is fixed on its surface (Fig. 6).

In this case, there is a chemical modification of the surface of coal and its hydrophobization. The hydrocarbon substituent of the apolar part of the flotation reagent, located on the opposite side from the coal surface, provides sufficient hydrophobization of the surface of the coal particle and enhances the attachment to them an air bubbles. This improves the quality of coal flotation.

#### 4. Conclusion

Thus, according to the results of the study, we can conclude on the development of a new universal reagent based on tetrahydropyran-4-ol derivatives for flotation of high-ash coals. As a result of the use of 3-amyltetrahydro-pyran-4-ol acetate, the carbon fraction in the concentrate was increased to 90%, this making it attractive for the use in the chemical and metallurgical industries.

#### Acknowledgments

The work was carried out as part of the project «Development of technology of flotation enrichment and processing of coal fines and slimes, with obtaining of commercial products of various functional purposes» (AP05135514) grant financing of the Ministry of Education and Science of the Republic of Kazakhstan.

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