

Experimental substantiation of the choice of caking additives according to the data of the study fluid non-volatile products of thermal filtration

L F Butuzova^{1,3}, V A Pechen¹, S Marinov², M Stefanova² and G N Butuzov¹

¹Donetsk National Technical University, 58 Artema str., Donetsk 83000, Ukraine

²Bulgarian Academy of Sciences, Institute of Organic Chemistry, 9 Acad. G. Bonchev str., Sofia 1113, Bulgaria

E-mail: ludmila.lfb@yandex.ua

Abstract. Extracts of fluid non-volatile products isolated from the plastic layer of caking and low-caking coals of different genetic types by reductivity were first studied in detail using EPR-spectroscopy and gas chromatography-mass spectrometry (GC-MS) methods to reveal the components responsible for caking. According to a study of extracts caking additive selection was carried out. Choice of conditions and experimental verification of the effect of the proposed anthracene additive on the plastic layer formation has been established. The rate of coal decomposition in different periods of pyrolysis has been calculated by the results of derivatography method.

1. Introduction

Mining of valuable coals suitable for coking has been decreasing in the world. The part of mining of low-caking, non-caking and sulphurous coals is being increases at impressive rates in Donets Coal Basin. One of the simplest ways of improving the caking ability of low-caking coals and their blends is the usage of the various organic additives.

In order to obtain high-quality metallurgical coke in the conditions of deficiency of well caking coals K and J Grade, it is necessary to solve the key question of the caking theory - the question of the nature of caking components of coals, which can be used as caking additives to increase the proportion of low-caking and sulfur coals in the blends. These coals prevail in the Donetsk basin, but are related to the category of energy coals [1,2].

In literature the mechanism of the interaction of additives with the coal organic mass (COM) is insufficiently studied; the process of a plastic layer formation for coals formed under reductive (RC) and less reductive conditions (LRC) is not described; there are no criteria for selecting organic additives taking into account the component composition of the blends [3-6].

To solve these problems, a scientifically grounded approach is needed. We found it necessary to search for caking components in coal extracts [7], considering the fact that this proposal was made by F. Fisher in the early 20-ies of XX century.

The purpose of this work is to reveal the compounds responsible for the caking processes by studying the extracts of fluid non-volatile products obtained by centrifugal thermal filtration of coals with different caking ability; choice of conditions and experimental verification of the effect of the proposed additive on the plastic layer formation.



2. Experimental

Coals of the Donets Coal Basin with different type by reductivity were chosen for this study [6]. It was coals of G-Grade and J-Grade according to Ukrainian classification (table 1).

Table 1. Proximate and ultimate analyses of parent coals.

Coal mine	Coal Grade, seam	Type	Proximate analysis, %			Elemental analysis, %			
			W ^a	A ^d	V ^{daf}	S _t ^d	C ^{daf}	H ^{daf}	(O+N) ^{daf}
Tsentralnaya	G, k ₇	LRC	2,2	5,2	36,0	1,22	85,1	5,11	8,71
Dimitrova	G, l ₁	RC	2,1	4,4	38,7	2,49	83,8	5,34	9,50
Zasyad'ko	J, l ₄	LRC	1,4	2,6	31,6	1,09	87,8	5,16	7,00
Zasyad'ko	J, k ₈	RC	0,8	2,7	31,7	2,81	87,3	5,23	7,20

As it is known about 73% of coals of Donets Coal Basin coal mines are composed of coals with high sulfur content (type of LRC). Coal of J-Grade is the basic irreplaceable component of coke blends. G-Grade coal represents components with reduced caking ability.

The proximate and ultimate analysis of samples were determined by using standard methods (GOST P 53357-2013 and GOST P53355-2009). These coals and their blends (J_{RC}+G_{LRC}=70:30 and J_{RC}+G_{LRC}=50:50) were pyrolyzed in a special centrifuge (Ukrainian National Standard 17621-89) under the conditions described previously [6]. This method allows to separate the plastic layer and determine the amount of the following products: the solid over-sieve residue (OR), fluid non-volatile products (FNP) and vapour-gas compounds (VG). The amount and composition of FNP largely determine the processes of caking and coking [6,8,9].

A Bruker ER 200D SRC radiospectrometer was used to determine the concentration of paramagnetic centers (N) of the coals and pyrolysis products [6].

Derivatogrammes were registered in a Q-1500D derivatograph of Paulic-Paulic-Erdei system at the rate 10°C/min in a closed platinum crucible under the layer of quartz sand up to 1000°C. The kinetic parameters, i.e. the rate of decomposition in different periods of pyrolysis were calculated by the results of the continuous measurement of the weight loss.

Extraction, column chromatography and gas chromatography-mass spectrometry (GC-MS) of the saturated and aromatic hydrocarbon fractions were used to the separation and identification of coal extracts [2,10,11]. The composition of the above fractions was calculated using peak areas from the gas chromatograms in relation to that of internal standards. The concentrations were normalised to the C^{daf} content in the sample [2].

3. Results and discussion

Gas chromatography-mass spectrometry analysis of aliphatic and aromatic fractions of the extracts revealed significant quantitative differences in the composition of components extracted from caking and low-caking coals (figure 1).

An absolute content of n-alkanes (43,5–45,5%) is in 10 times higher in G-grade samples in comparison with J-grade. The blends show n-alkanes ranging from 31% to 43%. The content of biphenyls in G-coals and blends does not exceed 1%, and in J-grade LRC and RC is 13,63% and 7,72%, respectively. Aromatic components are presented by compounds with a number of rings from 1 to 5, most of which are alkyl-substituted. The value for anthracenes and phenanthrenes content is about 4,6 times higher for the sample of J-grade LRC in comparison with RC coal of brand G.

Comparison of the yield of FNP, the PMC concentration in them and the GC-MS results for a pair of J and G-grade coals (table 2) allows us to conclude that caking ability is associated, first of all, with the presence of PAH, anthracenes, fluorenes, phenanthrenes and biphenyls. These compounds are presented mainly in the form of alkyl-substituted compounds containing 1-4 substituents. The proportion of alkyl-substituted aromatics is more than 91%. This fact, of course, affects the stability of radicals due to the spatial effects, and affects the size of the regions of unpaired electrons

delocalization in the polyconjugation system.

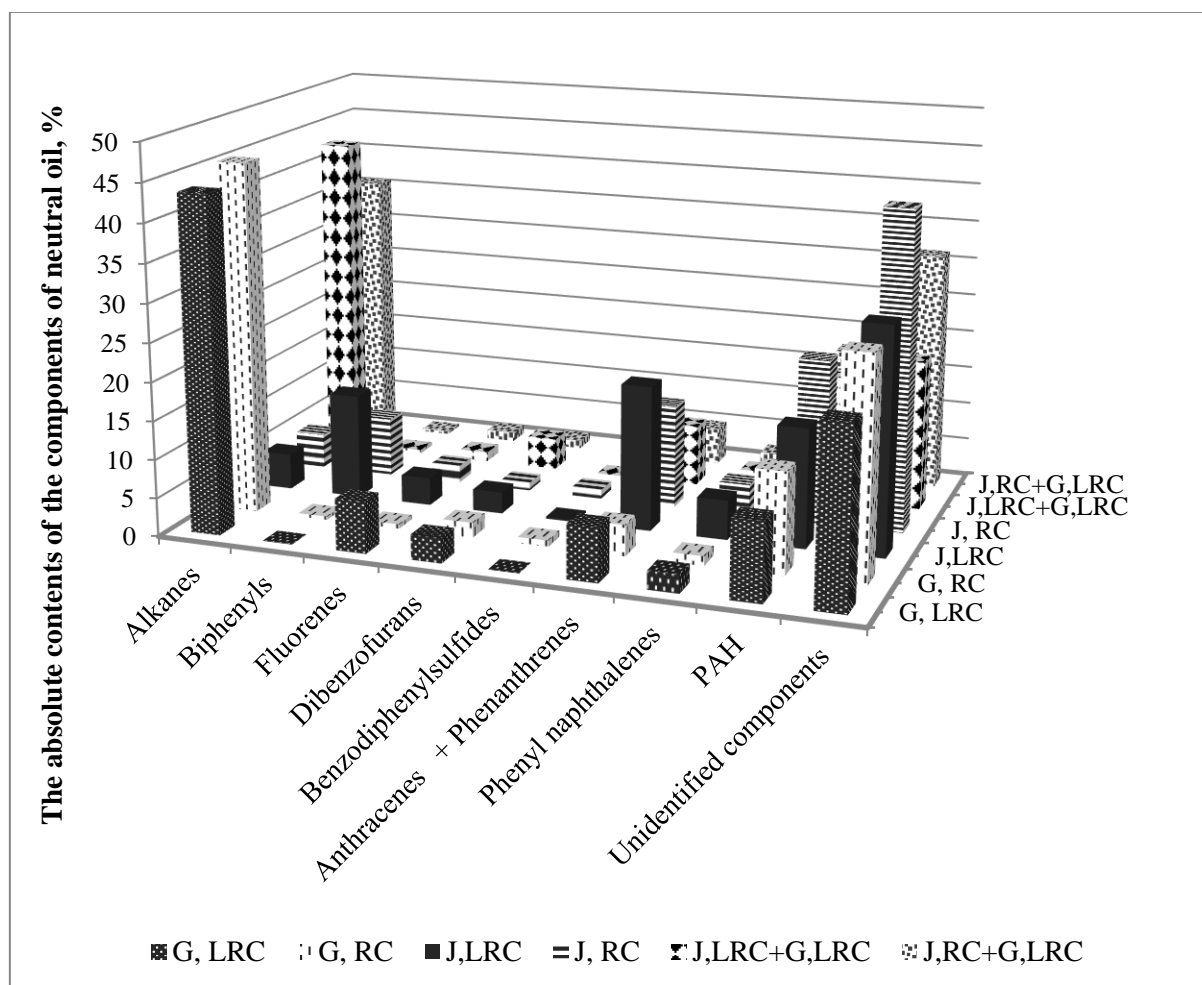


Figure 1. Comparative composition of basic compounds of neutral oils extracted from the FNP of the investigated coals and blends.

Table 2. Comparative characteristics of extracts from FNP of investigated coals.

Coal characteristics	G _{LRC}	G _{RC}	J _{LRC}	J _{RC}	J _{LRC} +G _{LRC} 50/50	J _{LRC} +G _{LRC} 70/30	J _{RC} +G _{LRC} 50/50	J _{RC} +G _{LRC} 70/30
N, spin g ⁻¹ x 10 ⁻¹⁷ in FNP	38,5	1,8	114,9	159,9	-	43,1	-	111,4
Yield of FNP	12,44	4,28	21,33	39,28	24,11	20,71	22,22	26,19
Content of components in neutral oil of FNP, %								
Alkylated PAHs	8,40	11,92	13,95	20,14	15,10	3,93	15,44	10,70
Total PAHs	10,23	13,12	15,57	21,47	16,57	6,03	17,40	14,33
Alkylated benzo-fluorene and fluorene (R=1÷3)	5,73	0,51	3,61	2,27	0,63	9,27	0,35	9,80
Total fluorenes	6,71	0,57	3,61	2,27	1,24	10,47	1,21	13,00
Alkylated anthracenes + phenanthrenes	6,76	3,72	16,70	12,62	7,51	5,65	4,51	4,90

(R=1÷4)

Total anthracenes + phenanthrenes	7,07	4,07	18,83	13,50	7,99	5,98	4,78	5,13
--------------------------------------	------	------	-------	-------	------	------	------	------

Extracts of the $J_{LRC} + G_{LRC}$ blend differ by 6% less yield of FNP, by half the content of alkylated PAHs with a lower PMC concentration, compared with the blend $J_{RC} + G_{LRC}$. At the same time, an increase in the content of fluorenes in the extracts of blends, especially in the $J_{RC} + G_{LRC}$ blend, is observed, which is 2-4 times higher as compared to the extracts of the initial coals.

Previously it is shown that caking capacity of coal is associated with the presence of high concentrations of PMC in FNP [6]. It can be argued that when forming a plastic layer in the mesophase, radicals of the following types are formed: diphenylmethyl, fluorenyl, phenyl naphthyl, phenoxyl and others, taking into account the presence of a connection between the yield of FNP and the concentration of PMC in them, as well as the results of GC-MS of neutral oils.

The number of fluorenyl and phenyl naphthyl type radicals, based on alkyl-substituted anthracenes, phenanthrenes in G_{RC} is much lower than to other coals. Comparison of the degree of substitution of these radicals shows that it is significantly below for G_{RC} in comparison with G_{LRC} for phenyl naphthalenes, anthracenes and phenanthrenes, i.e. it can be assumed that the G_{RC} radicals are less stable.

Accounting that content of anthracene is much higher in neutral oil of FNP of caking J-coals in comparison with low-caking G-coal, anthracene was selected as an additive for further research. The boiling point of anthracene (340°C) is close to the decomposition temperature of coal, so it is possible its interaction with the coals decomposition products. Besides, anthracene is characterized with by high reactivity of carbon atoms in 9 and 10 positions. It easily interacts with free radicals.

To study the influence of used additives on the yield of the of thermal filtration products a planned experiment was conducted. In the planned experiment, the effect of the amount of anthracene additive on coal J_{RC} at different heating rates of the samples has been studied. Processing of the obtained results in coded and natural form for the linear model has been performed using the program StatGraphics 5.0.

Designations of factors and parameters: X1 – the heating rate °C/min; X2 – anthracene additive content; Y1 – yield of solid residue (semi-coke), %; Y2 – yield of fluid non-volatile products, %; Y3 – yield of the vapor-gas phase, %.

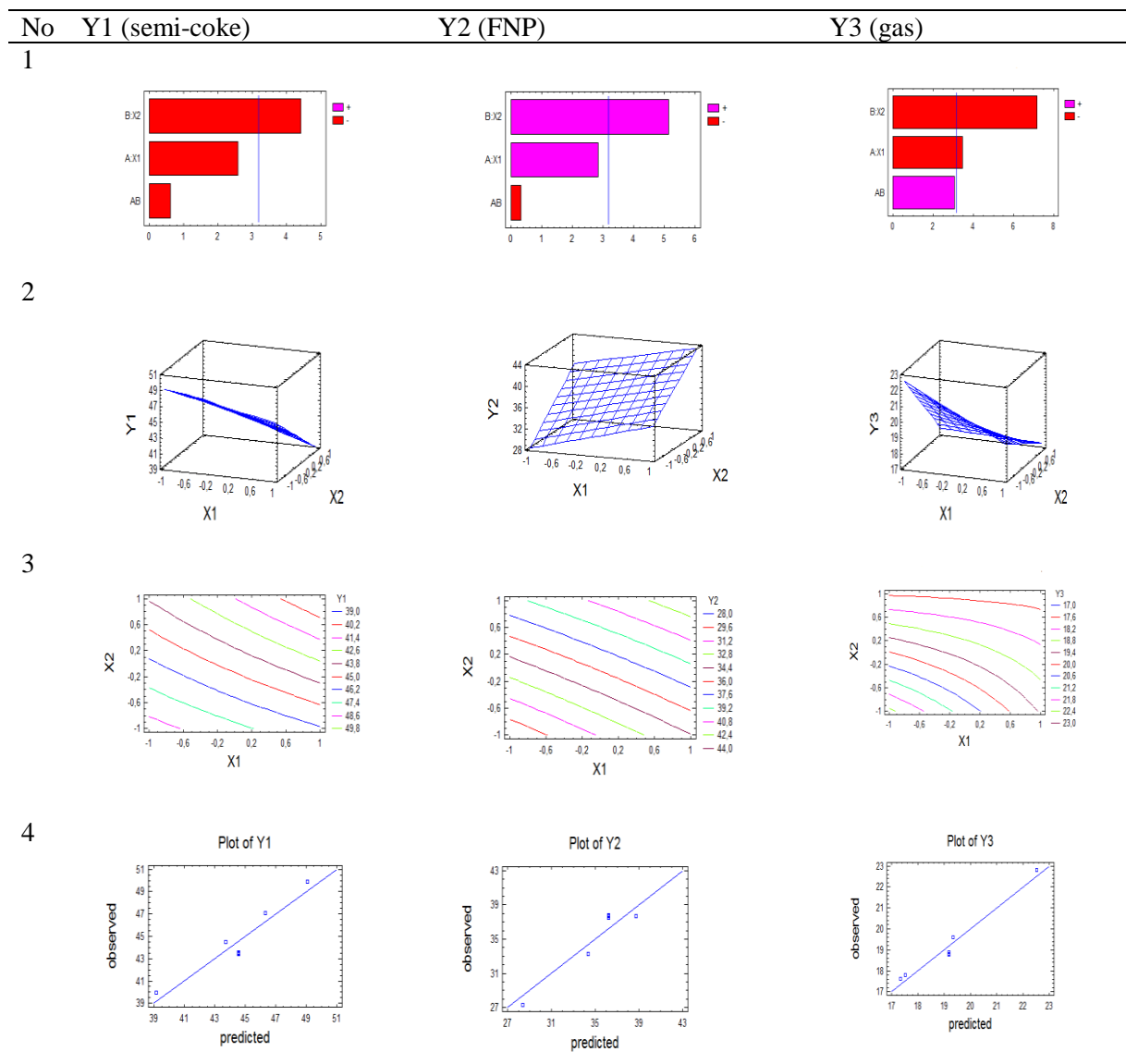
Table 3 shows the matrix of the complete factorial experiment in coded and natural form. Data analysis is given in tables 4 and 5.

As it is seen from table 3, chemical treatment of coal results in increase yield of FNP, responsible for the caking processes, as compared to similar parameters for the original coal (30,70% daf). In this case the yield of fluid non-volatile products depends on the percentage of the additive used [12]. The yield of FNP increases slightly when using 5% additive. The use of 10-15% additive leads to an increase in the yield of FNP by 7-12%.

Table 3. Matrix of the complete factorial experiment in coded and natural form.

Experience number	X1	X2	X1	X2	Y1	Y2 ^a	Y3
1	+1	+1	75	15	39,96	42,43	17,61
2	-1	+1	65	15	44,51	37,65	17,84
3	+1	-1	75	5	47,12	33,27	19,61
4	-1	-1	65	5	49,90	27,30	22,80
5	0	0	70	10	43,44	37,80	18,76
6	0	0	70	10	43,58	37,54	18,88
7	0	0	70	10	43,47	37,67	18,80

^a The yield of the products of thermal filtration for coal J_{RC} without additives is 30,70% daf.

Table 4. Graphical models of the experiment in coded form.**Table 5.** Regression equations obtained.

Response	Form	Regression equation	R ² , %
Y1	Cod.	$Y1 = 44,5686 - 1,8325 \cdot X1 - 3,1375 \cdot X2 - 0,4425 \cdot X1 \cdot X2$	89,9
	Nat.	$Y1 = 64,1086 - 0,1895 \cdot X1 + 0,6115 \cdot X2 - 0,0177 \cdot X1 \cdot X2$	
Y2	Cod.	$Y2 = 36,2371 + 2,6875 \cdot X1 + 4,8775 \cdot X2 - 0,2975 \cdot X1 \cdot X2$	92,0
	Nat.	$Y2 = -19,4729 + 0,6565 \cdot X1 + 1,8085 \cdot X2 - 0,0119 \cdot X1 \cdot X2$	
Y3	Cod.	$Y3 = 19,18 - 0,845 \cdot X1 - 1,75 \cdot X2 + 0,75 \cdot X1 \cdot X2$	96,0
	Nat.	$Y3 = 55,51 - 0,469 \cdot X1 - 2,45 \cdot X2 + 0,03 \cdot X1 \cdot X2$	

In table 4, the rows represent the following: 1-standardized Pareto-Map; 2 – estimated response surface; 3 – response reflection contours; 4 – adequacy of the equation.

Table 4 shows that the main and significant factor affecting the yield of semi-coke (Y1), fluid non-volatile products (Y2) and the vapor-gas phase (Y3) is the factor X2, which corresponds to the content of the additive in the sample. This is indicated with by the fact that the corresponding column (line 1)

crosses the vertical line. In addition, an important factor is X1.

According to table 4, it can be concluded that the effect of anthracene additive (X2) in all experiments is higher than the effect of heating rate (X1). The combined influence of factors X1 and X2 is significantly weaker than each factor separately.

In table 5 it is given the regression equations in coded and natural form.

The equations obtained allow to predict the response values at the given factors, to calculate the yield values of thermal filtration products in different experimental conditions.

Thus, all the above permits to make an conclusion on the effective action of anthracene as a caking additive. Wherein, the optimal value of fluid non-volatile products yield is achieved in the following experimental conditions: the heating rate - 75°C/min and the percentage of anthracene additive - 15%.

The result of Thermogravimetry method indicates that the coals decomposition process may be presented as a sum total of seven independent steps (linear parts on the curve TG). Table 6 shows the values of temperature intervals (T_i-T_f), corresponding mass loss (Δm , %) and maximum values of mass loss rates (W_{max}) for different steps of coals pyrolysis process.

Table 6. Maximum values of mass loss rates at individual stages of coals pyrolysis process, mg/min·g.

Coals, blends	Stages of pyrolysis ^a /(T_i-T_f), ^b for different steps, °C					
	I	III	IV	V	VI	VII
	100-140	350-415	415-480	480-595	595-867	867-930
J _{RC}	1,17	2,53	11,92	5,71	4,14	14,90
G _{LRC}	4,22	4,50	12,39	4,40	8,50	4,97
J _{RC} +G _{LRC} ,50:50	2,35	2,61	10,97	7,94	4,46	5,39
J _{RC} +G _{LRC} ,50:50 anthracene	3,52	1,95	9,93	7,17	4,40	5,58

^a II step is occurred without mass loss.

^b T_f - temperature of the final state; T_i - temperature of the initial state.

It can be seen from the table 6, that the most intensive decomposition of samples occurred at the IV step which is known to be related to formation of the main bulk of the semi-coking products. IV step corresponds to the interval of the main decomposition on the derivatogram. Thermal decomposition of blend is characterized with a comparative deceleration of the mass loss at the V, VII steps in comparison with J_{RC}.

When anthracene was added, an intensification of gas evolution processes at I stage and a significant deceleration of blend decomposition at III-V stages are observed, i.e. induces thermal decomposition of less thermostable structures, whereas promotes development of polyrecombination and polycondensation reactions. Anthracene is a carrier of aromatic condensed structures, which ensure the formation of an anisotropic liquid-crystalline phase.

In addition, it is known that anthracene oil is a good solvent for aromatics. Apparently, this also contributes to the positive effect of the additive on caking.

4. Conclusions

The positive effect of anthracene additive, which prevails in the extracts of caking coal, on the yield of fluid non-volatile products under the conditions of thermal filtration is scientifically substantiated and experimentally proved. The optimal amount of additive has been established, which is 15% of the additives at a heating rate of 75°C/min. These results confirm the previously stated assumption that anthracene, which is a carrier of aromatic condensed structures, provides the formation of an anisotropic liquid crystal phase.

It is shown that during transition to a plastic state, anthracene effectively affects those pyrolysis stages during which polycondensation reactions dominate leading to the formation of more cross-

linked high molecular compounds that promote the caking of coal particles. In addition, anthracene can play the role of an internal solvent, which also leads to an increase in the yield of FNP.

Thus, the use of the anthracene additive is of great interest due to its ability to influence the yield of thermofiltration products, and consequently on the caking of coals. This can be one of the ways to solve the problems arising in connection with the deterioration of the coking feedstock base and the growth in the requirements of metallurgists for the quality of coke.

References

- [1] The Donetsk Coal Chemistry Research Institute 1972 The Catalogue of the Donetsk and Lviv-Volyn basins black coals and anthracites quality (Nedra, Moscow) p 168
- [2] Bechtel A, Butuzova L and Turchanina O 2002 Thermochemical and geochemical characteristics of sulphur coals *Fuel Processing Technology* **77-78** 45-52
- [3] Fernandez A M, Barriocanal C, Diez M A and Alvarez R 2009 Influence of additives of various origins on thermoplastic properties of coal *Fuel* **88** 2365-72
- [4] Zubkova V and Czaplicka M 2012 Changes in the structure of plasticized coals caused by extraction with dichloromethane *Fuel* **96** 298-305
- [5] Butuzova L, Safin V, Marinov S, Yaneva N, Turchanina O and Butuzov G 2009 The pathways for thermal decomposition of coals with high content of sulphur and oxygen *GeoLines* **22** 15-9
- [6] Butuzova L, Makovskyi R, Budinova T and Marinov S P 2014 *Fuel Processing Technology* **125** 246
- [7] Zubkova V and Witkiewicz Z 2016 Chromatographic analysis of chemical compositions of coals and changes in them during technological processing *Critical Reviews in Environmental Science and Technology* **46** 701-55
- [8] Biryukov Y V 1980 Termicheskaya destruktziya spekayushchikhsya uglei (Moskow: Metallurgiya) p 120
- [9] Safin V, Butuzova L, Marinov S and Yaneva N 2009 Bituminous coals thermodestruction by the thermofiltration method *Geolines* **22** 58-61
- [10] Hamza K, Abdussalam A A, Ayiman A, Aejeeliyah Y, Salheen G 2017 Gas chromatography - mass spectrometry (gc-ms) in organic geochemical investigation of crude oils from kikinda and velebit fields in serbia *International Journal of Research - Granthaalayah* **5** 550-60
- [11] Butuzova L, Razvigova M, Krzton A and Minkova V 1998 The effect of water on the yield and structure of the products of brown coal pyrolysis and hydrogenation *Fuel* **77** 639-45
- [12] Kulakova V, Butuzova L, Andrade J M, Shevkoplyas V and Turchanina O 2016 Characterization of sulfur coal-derived liquids as a source of hydrocarbons to produce chemicals and synthetic fuels *Fuel* **184** 314-24