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Activated Carbons from Co-Mingled Liquid and Solid Organic Wastes

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Abstract

Data on a synergetic phenomena of the components of the co-mingled solid and liquid wastes occurs during their thermolysis were used for the development of the co-activation approach to wastes recycling. Co-activation was aimed at generation of porous solid valuable secondary products (activated carbons). The development of the design parameters for the activated carbons syntheses was done at valorization of the re-polymerization, re-association and the polycondensation reactions between the reference structural fragments of the components in the ternary composite systems "*Spent Petroleum Product Waste – Biomass – D-grade coa*l" and "*Coal Processing Sludge – Biomass – D-grade coal*". From elaborated comprehensive investigations the main factors, which influence the carbonized chars formation and the properties of the resulted activated carbons were evaluated. The porous solid secondary products of uniform particle size and pore size distribution were obtained during co-processing in the co-mingled systems. The surface area is ranged between 600-1100 m^2/g, the total pore volume is of 0.32-0.47 m^3/g and the yield is of 21-27%. Additionally, an efficiency of the catalytic co-processing of natural organic solid and liquid wastes with coal in a presence of the K/Na carbonates was studied aiming at novel adsorbents usage for wastewater purification from heavy metals.

Introduction

In any industrial activity, wastes are generated in the process streams. Industrial wastes are generally having undesirable physical and chemical characteristics, such as toxicity, ignitability, carcinogenicity that may have significant adverse effect on the environment, if not properly handled and safety disposed off.

The Waste Hierarchy [1] has taken many forms over the past decades, but the basic concept has remained aiming at waste minimization strategies (Fig. 1). Thus, the main objectives of the waste hierarchy are to extract the maximum practical benefits from products and to generate the minimum amount of waste.

The waste hierarchy refers to, as called, the 3Rs concept of Reduce, Reuse and Recycle, which classifies the waste management strategies according to their desirability.

Recycling is a key component of modern waste management and is the third component of the 3Rs concept. Recycling involves waste processing into new products, thus (i) prevent losses of potentially useful materials; (ii) reduce raw materials and energy consumption; (iii) reduce needs for conventional waste disposal and, like that, reduce air pollution (due to incineration) and water pollution (due to landfilling), and (iv) lower greenhouse gas emissions as compared to primary products production [1-5]. The majority of the thermal methods currently used for organic wastes recycling, such as pyrolysis, gasification or combustion, are resulted from a long-term evolution of the engineering and technological solutions and, thus, characterized by favorable energetic and environmental content [3-5]. However,

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the restrictions imposed on the processes of organic waste thermal processing, namely their low selectivity (in any mode of the thermal approaches both solid and gaseous and liquid products of complex composition are simultaneously generated), force the researchers to search and develop more economically and ecologically perspective methods and approaches to the waste recycling [3, 4].

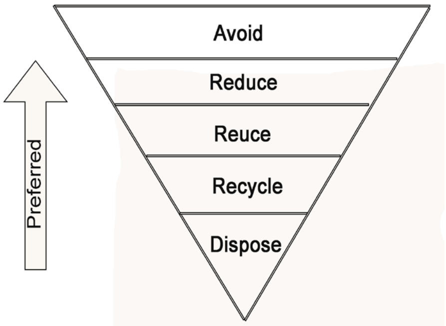

Fig. 1. The Waste Hierarchy Scheme.

In order to increase the efficiency of waste the *3Rs* concept, a new generation of advanced thermal approaches, so-called co-processing, is developed. In this case, the co-mingled wastes (blends of carbon-containing waste) are subjected to the thermal treatment. Co-processing aimed at synergism of the blends components during thermolysis favoring chemical and energy upgrading of the wastes by improved selectivity and quality of the secondary generated either liquid or gaseous or solid products.

Co-processing contributes to the industrial competitiveness, is a complementary technology to the recycling and should be considered as a treatment alternative within an integrated waste management concept.

Co-processing is recognized preferred option on the waste management hierarchy for the materials which cannot be re-used. In this case, the co-processing could be also considered as a recovery activity. Co-mingled wastes could be recovered into the secondary valuable materials, source of energy, or both (Table 1). Waste materials used for co-processing are referred as alternative fuels and raw materials [AFR]. Therefore, co-processing is considered as a proven sustainable development approach based on the principles of industrial ecology. In summary, the benefits of co-processing are the following: (i) reduced demands on natural resources (due to material recycling) and fossil fuels such as coal, petroleum and gas (due to energy recovery), thus reduced dependence on primary resource markets; (ii) reduced pollution and landfill space, thus contribution to reducing the environmental footprint.

In last decades, some energy intensive industries offer the co-processing as a sustainable waste management service. Based on the co-processing concept, several commercial waste recovery approaches were successfully developed and implemented for the selective production of the direct valuable end-products, such as (i) a coke (solid non-porous products) by the co-pyrolysis concept implementation [28]; (ii) a syngas via the co-mingled materials co-gasification [29, 30], and (iii) liquid fuels production applying the co-liquefaction concept [31]. An interest to this approach development and usage remains for the economic and environmental reasons.

Despite simplicity of the co-thermolysis concept, its practical application is associated with many technical issues, which require further attention and better knowledge of the governing thermolysis parameters and their effect on a yield/quality of the secondary generated products.

There are many studies on the valorization of the parent carbon-containing materials by co-processing with others waste (Table 1). Working with the co-processing concept authors reported either an absence of any synergistic effects between the components [2-5, 32, 33] or evidence for a synergistic behavior in co-gasification [29-31, 34] or co-liquefaction [28, 35] or superior properties of co-pyrolyzed composite materials [30, 36].

The synergistic effects were found by authors for co-thermolysis in the binary systems of the biomass, coal-processing and petroleum waste [37, 38]. Namely, re-structurization followed by re-association of the carbon matrix of the parent materials due to chemical interaction between the reference structural fragments of the components were observed. The results of the co-thermolysis showed the superior properties of co-pyrolyzed composite materials of environmentally acceptable grade [37, 38].

The synergistic behavior of the components was used in a present study for the development and manufacture of the high efficient activated carbons aimed at valorization of the parent carbon-containing co-mingled materials of the biomass, low grade coal and petroleum or coal-processing wastes. Additionally, the efficiency of catalytic co-processing of natural organic wastes with coal in a presence of the alkali metals carbonates was studied aimed at novel adsorbents usage for wastewater purification form heavy metals.

In a boarded perspective, the main goal of the work is further development of the co-processing concept; namely, development of the co-activation approach to the solid and liquid co-mingled wastes recovery into porous solid valuable secondary products.

Table 1
Valorization of the parent carbon-containing materials by co-processing with other waste

Co-mingled wastes [*AFR* materials]	Process	Secondary generated products	Synergetic effects	Ref.
rice stalk + waste seed oil	co-pyrolysis	produce olefins and aromatics	-	[6]
light petroleum residue+waste plastics	co-liquefaction	liquid fuels	yes	[7]
heavy oil+coal	co-liquefaction	synthetic crude oil	yes	[8]
natural gas+coal+biomass	co-gasification	hydrogen, mathane, or methanol fuel	-	[9]
polylactic acid + biomass	co-liquefaction	bio-oil	yes	[10]
pine cone + synthetic polymers	co-liquefaction	chemicals or fuels	yes	[11]
sawdust + waste tire	co-liquefaction	liquid oil	yes	[12]
willow + polyhydroxybutyrate	co-liquefaction	bio-oil	yes	[13]
Cryptomeria japonica + anthracite coal	co-pyrolysis	fuel	yes	[14]
pine wood + synthetic polymers	co-pyrolysis	liquid and gases	yes	[15]
legume straw + coal	co-pyrolysis	fuels	yes	[16]
plastic + pine wood sawdust	co-pyrolysis	fuels	yes	[17]
sludge + sawdust	co-pyrolysis	dispose of the excessive activated sludge	no	[18]
sludge + rice husk	co-pyrolysis	dispose of the excessive activated sludge	no	[18]
hazelnut shell + peat	co-pyrolysis	production of energy and fuels	yes	[19]
hazelnut shell + lignine	co-pyrolysis	production of energy and fuels	yes	[19]
hazelnut shell + bituminous coal	co-pyrolysis	production of energy and fuels	no	[19]
hazelnut shell + anthracite	co-pyrolysis	production of energy and fuels	no	[19]
coal + wheat straw	co-gasification	gaseous fuel	no	[20]
plastics + wood pine	co-gasification	fuel gases	yes	[21]
coal + pine + plastics	co-gasification	fuel gases	yes	[22]
lignine coal+ used tire + super-critical water	co-liquefaction	oil products	yes	[23]
kukersite oil pine + pine bark	co-liquefaction	synthetic petrolium	no	[24]
kukersite oil pine + peat	co-liquefaction	synthetic petrolium	yes	[24]
waste plastics + lignine	co-liquefaction	hydrocarbon synthesis	-	[25]
Japanese cedar + Mulia coal	co-gasification	hydrocarbon fuel	yes	[26]
corncob + cattle manure	co-pyrolysis	bio-oil	yes	[27]

Experimental

Materials

The low-grade coal and some solid and liquid organic wastes, such as biomass, coal processing and refinery wastes, were used in a present studies as the components of the co-mingled systems. All of the materials were from the Donbass region sources of Eastern Ukraine:

- *The D-grade coal* (or bituminous long-flame coal) was supplied by the Lidievka coalmine from the h_8^b, L_1–shelf.
- *The Sunflower husks* (or *Biomass*) were graciously provided by the Joint American-Ukrainian Enterprise KARGIL.
- *The Coal Processing Sludge (CPS)* (or coal processing waste) was kindly provided by *the Avdeevka Coke-Chemical Plant (AKKhZ)* from the sludge pond.
- *The Spent Petroleum Product Waste (SPPW)* (or refinery waste) were kindly provided by the Odessa port from the oil-handling reservoirs.

The parent materials were characterized by elemental and proximate analyses using Automatic *CHNS-O* elemental analyzer and Flash EATM 1112 equipment (Table 2). The liquid waste´s samples taken from the oil reservoirs of the Odessa port and the *AKKhZ* sludge pond were analyzed without preliminary sample preparation. The degree of aromaticity of the liquid wastes was determined by H^1 NMR-spectroscopy with a Bruker AS250 instrument of a working frequency of 300 MHz, using deuterated chloroform as solvent and tetramethylsilane as an internal standard. The following integration intervals were used: hydrogen attached to aromatic carbon (H_{ar}) of 9.0–6.0 ppm; hydrogen of methyl groups attached to aromatic rings ($H_{(\alpha\text{-}2)}$) of 4.5–3.5 ppm; hydrogen attached to α – carbon atoms (H_α) of 3.5–2.0 ppm; hydrogen attached to β – carbon atoms (H_β) of 2.0 1.0 ppm; and hydrogen attached to γ – carbon atoms (H_γ) of 1.0–0.5 ppm.

Based on the experimental data, the S*pent Petroleum Product Waste* having H_{ar} of 14 %; $H_{(\alpha\text{-}2)}$ of 1%; H_α of 56%; H_β of 23% and H_γ of 6% was considered as *aliphatic petroleum waste*. The main structural components of SPPW are long-linear (or weakly branched) hydrocarbons (up to 79%) with a small fraction (up to 14%) of aromatic carbons.

The Coal Processing Sludge (CPS) was considered as aromatic tar waste with the aromatic carbons content (H_{ar}) of 26% and $H_{(\alpha\text{-}2)}$ of 4%; H_α of 23%; H_β of 28% and H_γ of 19%.

Characteristics of the liquid wastes, including data on the direct distillation and fractionation of bitumen by sequential solvent extraction is given in Table 3.

Table 2

Elemental and proximate analyses of the parent carbon-containing materials

Samples, waste source	Elemental composition, %				Proximate analysis, %		
	C^{daf}	H^{daf}	N^{daf}	S^{daf}	A^d, %	W^a, %	V^{daf}, %
D-grade Coal	80.0	5.3	2.0	3.8	2.3	11.2	43.8
Sunflower husks	54.6	6.7	0.8	0.1	6.7	10.0	81.0
Spent Petroleum Product Waste	71.8	11.2	0.7	1.4	2.9	33.0	73.4
Coal Processing Sludge	79.2	8.9	0.9	1.6-2.3	4.3-11.8	18-22	54.6

Table 3

Analysis of liquid carbon-containing wastes (*Spent Petroleum Product Waste and Coal Processing Sludge*)

Sample	Spent petroleum product's waste	Coal Processing Sludge
Density at 25 ºC, g/cm^3	0.9	1.2
Water content (according to Dean–Stark), vol.%	33.0	18-22
Vapor flash temperature, ºC	73	110
Aqueous layer acidity, pH	7.5-7.8	6.5-7.3
Initial boiling/softening temperature (ring-and-ball method), ºC	63.0	84.0
Kinematic viscosity, m^2/s (cST) at 50 ºC	7.4	37.8
Ash content (concentration of suspended solids), wt.%	2.9	7.2
Direct distillation data		
Fraction 1, T, ºC; vol.% (composition)	63–99, 46.0 (33.0% water and 13.0% light hydrocarbons)	100–120, 31.4 (7.7% water, 10.8% naphthalene, and 13.9% light hydrocarbons)
Fraction 2, T, ºC; vol.% (composition)	100–250, 8.1 (heavy hydrocarbons)	120–170, 50.2–40.7 (16.2% water and 24.5–34.0% oil)
Distillation residue, vol.% (composition)	42.6 (33.0% liquid fraction, d = 0.879 g/cm^3, and 9.6 % tars)	17.8–26.4 (tars and asphaltenes)
Losses, vol.%	3.3	0.5
Sequential solvent extraction (bitumen fractionation), wt.%		
Fraction 1 (heptanes soluble), *Malthenes*	72.4	41.8
Fraction 2 (toluene soluble), *Asphaltenes*	26.0	36.5
Fraction 3 (toluene insoluble), *Heavy tar products*	1.6	21.7

To evaluate the effect of alkali metal additives on co-thermolysis phenomena, the double eutectics salt of alkali metals carbonates (29% Na_2CO_3/71% K_2CO_3) with a melting point at 350 ºC was used [39].

Investigation techniques. Thermolysis of the carbon-containing materials was investigated by thermogravimetric analysis (TG/DTG) using Q1500D Paulik–Paulik–Erdei analyzer under low heating rate of 5 0/min over a temperature range between 20 ºC and 950 ºC.

About (0.3 ± 0.03) g of the sample placed in a ceramic crucible with a cap (15 mm in height and 5 mm in diameter) was heated under reacting atmosphere of outgoing gases, in order to keep the possible interaction of secondary generated products during the devolatilization stage. Thermogravimetric parameters such as the temperature of the initial weight loss ($T_{initial}$) and the temperature of the final weight loss (T_{final}) were determined from the TG curves. The temperatures (T_{max}) of a maximum rate of weight loss were determined from the DTG curves. The weight loss at certain temperature, (mg/g) or (%), and the total weight loss at 950 ºC were determined from the TG curve. The average and maximum rates of the weight loss (mg g^{-1} s^{-1}) were determined from the DTG curve following the standard procedures [40]. In this work, the weight loss corresponds to a yield of volatile products. The weight loss rate is the rate of volatile products formation upon heating.

The thermogravimetric analysis has been carried out for two ternary systems "*Spent Petroleum Product Waste – Biomass – D-grade coal*" and "*Coal Processing Sludge – Biomass D-grade coal*" and their mixtures with the K/Na catalytic additives. Thermogravimetric analyses of the individual components (the sunflower husks, the coal processing sludge, the spent petroleum product wastes and the D-grade coal) and their mixtures with the K/Na eutectics could be found elswere [37, 38, 41].

Activated carbon synthesis. The activated carbons were prepared from the co-mingled natural organic liquid and solid wastes. There were three stages of the co-processing: blending, carbonization and activation.

Blending stage: A fixed components ratio (1:1:2) was used for the blending process: namely, 25% of the Biomass, 25% of the *D-grade coal* and 50 % of either the *aromatic tar* (the CPS) or the *aliphatic petroleum stock* (the SPPW).

In order to obtain a homogeneous mixture, the solid components were pre-treated as followed:

D-grade coal: Samples of particle sizes of 0.25–1.00 mm with no visible bituminous rock inclusions with decreasing ash content were studied. Before analyses, the samples were dried at (105 ± 5) ºC.

Biomass: Samples were pre-pulverized and dried at (105 ± 5) ºC to the moisture content of 6.1 wt.%. Then, the husks powder was sieved to remove a fraction with particle sizes smaller than 0.45 mm (which is about 7.0 wt.%). This decreased the ash content by 35.0%.

Then, solid components were carefully mixed with liquid ones (the SPPW or the CPS). In order to avoid coke formation during the activation process, the binary eutectics of the K/Na carbonates (~10 % to the blend weight) was used.

To improve the catalyst dispersion (to obtain a uniform distribution) in the pores and on the surfaces of waste materials, the incipient wetness method for eutectic salts impregnation was used. The finely dispersed powder of the K/Na eutectics salt was added directly to the liquid component (either SPPW or CPS). The catalyst loading was of 3.3 wt.% per a carbon-containing component, thus a total of 9.9 wt.% per the ternary system. The pre-dried, powdered solid components (the sunflower husks milled into fine powder of diameter less than 1 mm and the D-grade coal grounded and sieved to the particle sizes of 0.45–0.63 mm) were then loaded (in a proportion of 1:1:2) to the liquid component mixed with the K/Na eutectics. About 100 g of the mixture of the components was placed in a cylindrical stainless steel reactor (220 mm height, 100 mm diameter) and carefully stirred (~120 rpm) to favor blending. The blend was extruded via fillers to particles size of 2×3 mm, oven-dried at (105 ± 5) ºC for 24 h and stored in desiccator.

Neither weight loss nor interaction between the components were observed during the blending process (Fig. 2).

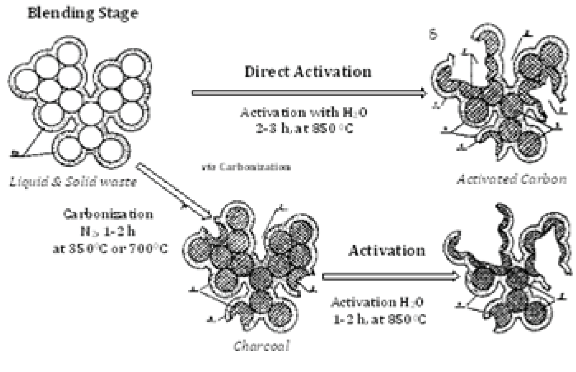

Fig. 2. Scheme of the co-processing in the studied ternary systems.

Carbonization/Activation stages: the development of the design parameters for the activated carbons syntheses was based on the results obtained early [37, 38, 41] during treatability studies of the thermolysis of the individual components of the chosen co-mingled systems and co-thermolysis processes in their binary systems. From the accomplished DTG/TG analyses, the temperature ranges of the synergetic effects and the reference structural fragments of the component responsible for them were evaluated. The data obtained are used for the development of the carbonization/activation processes of the co-mingled liquid and solid organic wastes. Emphasis is made on the polycondensation and re-polymerization reactions, which mainly proceed above 350 ºC (where the K/Na eutectics acts as a melt) between the reference structural fragments via secondary gas solid phase interactions of the blend components, and are influenced by the K/Na eutectics.

For the activated carbons syntheses either direct high-temperature activation with steam at 850 ºC or the activation via carbonization process were used, as presented in Fig. 2.

The soaking time of the both processes was varied from 1 to 3 h. The carbonization was carried out at both low (350 ºC) and high temperatures (700 ºC) in order to use the observed synergetic phenomena effectively during co-activation step.

Activated carbon characterization

The structural parameters of the resulting carbon were evaluated using nitrogen gas adsorption at 77 K. The experiments were carried out using Micromeritics ASAP instrument. Prior to the adsorption test the samples were out gassed at 240 ºC for 24 h under a pressure of 10^{-3} Pa. The apparent surface areas were determined from the adsorption isotherms using the BET equation. The Dubinin-Raduskhevich and B.J.H. methods were applied respectively to determine the micro- and mesopores volume.

Temperature-Programmed Desorption (TPD) was used for characterization of the functional groups of the activated carbons. The experiments were carried out using Micromeritics TPD/TPR 2900 instrument. TPD profiles were obtained with a custom built set-up, consisting of a U-shaped tubular micro-reactor, placed inside an electrical furnace. The mass flow rate of the helium carrier gas and the heating rate of the furnace were controlled with appropriate units. The amounts of CO and CO_2 desorbed from the carbon samples were monitored with a SPECTRAMASS Data quad quadrupole mass spectrometer. The assignment of the TPD peaks to the specifics surface groups was based on the data published in the literature [42]. Thus, a CO_2 peak results from decomposition of the carboxylic acid groups at low temperatures (below 400 ºC), or lactones at high temperatures (650 ºC); carboxylic anhydrous decompose as CO and CO_2 at the same temperature (around 650 ºC). Ether (700 ºC), phenol (600-700 ºC) and carbonyls/quinones (700-980 ºC) decompose as CO.

By this method the carboxylic, lactone, phenolic and quinone groups have been identified on the carbon surface.

The pH at the point of zero charge (pH_{PZC}) for the carbon was measured using the pH drift method [43].

Homogeneity/heterogeneity of the texture of the resulted activated carbons was studied by Scanning Electron Microscopy (SEM) with Philips XL30 ESEM-FEG equipment; and the topography of the surface was also studied by high resolution Auger Depth Profiling with PHI SAM–660 equipment.

Results and Discussions

Thermolysis in the Ternary systems of the Co-Mingled Liquid and Solid Wastes

In order to gain some insight into the reactions which may occur between the components of the co-mingled wastes, thermal decomposition of the individual components (the sunflower husks, the coal processing sludge, the spent petroleum product wastes and the D-grade coal) and their binary mixture (including ones with the K/Na eutectics additives) was studied by thermogravimetric analyses. Results of these studies could be found elswere [37, 38, 41]. In order to evaluate possible synergetic effects (i.e. component´s interaction during co-thermolysis of the co-mingled wastes), emphasis was done at a correlation of the experimental data with theoretical ones (i.e. calculations based on the components thermodestruction in additive manner).

Thermal decomposition of the blend resulted in simultaneous proceeding of numerous cracking reactions generating the volatile products, and polycondensation reactions favoring formation of the char carbons. The TG/DTG data reveal that the components of the binary blends interact during co-thermolysis, changing the temperature ranges of components thermodestruction, maximum rate of their weight loss, and the yield of the volatile products and char.

The main goal of the present work was further valorization of the parent carbon-containing materials via development of the co-activation approach to the solid and liquid co-mingled wastes recycling. The synergistic phenomena evaluated during co-thermolysis in the ternary systems of "*Spent Petroleum Product Waste – Biomass – D-grade coal*" and of "*Coal Processing Sludge– Biomass – D-grade coal*" were used to obtain valuable co-pyrolyzed solid composites. The efficiency of catalytic co-activation of the co-mingled wastes with the K/Na eutectics were used to develop a porous structure in the resulted activated carbons.

Thermolysis in the Ternary System "Spent Petroleum Product Waste – Biomass – D-grade coal"

Based on teoretical prediction for the co-thermolysis in an additive form for the "*SPPW – Biomass – D-grade coal*" system, seven peaks of thermodestruction of the reference structural fragments should be observed:

1. Water release (peak with T_{max} at 105-120 ºC);
2. Polar group of the *D-grade* coal decomposition (peak with T_{max} at ~130 ºC);
3. Decomposition of the hemicelluloses fraction of the biomass with the light/heavy hydrocarbons of the SPPW (peak with T_{max} at ~ 280 ºC);
4. Decomposition of the cellulose fraction of the biomass with the saturated hydrocarbons of the SPPW (peak with T_{max} at ~305 340 ºC);
5. Joint decomposition of three reference structural fragments: the lignin of the *biomass*, the malthenes of the SPPW and the first pseudo-macro fragment of the *D-grade coal* (OMC1), (peak with T_{max} at ~400 ºC);
6. Second pseudo-macro fragment (OMC2) of the *D-grade coal* thermodestruction, (peak with T_{max} at 429 ºC);
7. Third pseudo-macro fragment (OMC3) of the *D-grade coal* thermodestruction, (peak with T_{max} at 527 ºC).

In experiment, after thermogramm deconvolution, (Table 4, Fig. 3a) there are five peaks of thermodestruction of the reference structural fragments of the components in the ternary system of "*SPPW–Biomass D-grade coal*":

1. Water release, (peak with T_{max} at ~100 ºC);
2. Polar group decomposition of the *D-grade coal*, (peak with T_{max} at ~130 ºC);
3. Decomposition of the hemicelluloses fraction of the biomass with the light/heavy hydrocarbons of the SPPW, (peak with T_{max} at 250 ºC);
4. Decomposition of the fragment cellulose fraction of the biomass with the saturated hydrocarbons of the SPPW, (peak with T_{max} at 300 ºC);
5. Joint decomposition of the following reference structural fragments: the lignin of the biomass, the tars of malthenes fractions of the SPPW and all of three structural pseudo-macro-fragments of coal D (peak with T_{max} at 395 ºC). The total weight loss is 15.7% with respect to 8.6% of the theoretically predicted one.

Thus, the synergetic phenomena (interaction between the parent components) in their ternary system are evident. They are the following:

Thermolysis of *D-grade coal* proceeds in one stage at lower temperature (for ~30-100 ºC) contrary to three high temperature peaks observed for the coal decomposition in the binary systems or individually [37, 38, 41].

The total weight loss for the last thermal event of joint decomposition of the lignin structural fragment of the biomass, the tar of the *SPPW* with the organic mass of coal, is of 15.7% with respect to 8.6% of the theoretically predicted one.

The total weight loss for thermodestruction of the hemicelluloses and cellulose fragments of the biomass with the light, heavy and saturated hydrocarbons of *SPPW* is changed. For two thermal events (peaks with T_{max} at 250 ºC and T_{max} at 300 ºC) the weight loss decreases by 3.2-3.8%.).

The water release became of ~2 times lower; however this finding requires additional research.

After all thermal events in the system, the global weight loss of 43.6% is contrary to 50.6% of the theoretically predicted one. This fact suggests that there is a cumulative negative synergetic effect (decrease in the solid product yield) due to numerous cracking reactions proceeding in the system and resulting in volatiles generation.

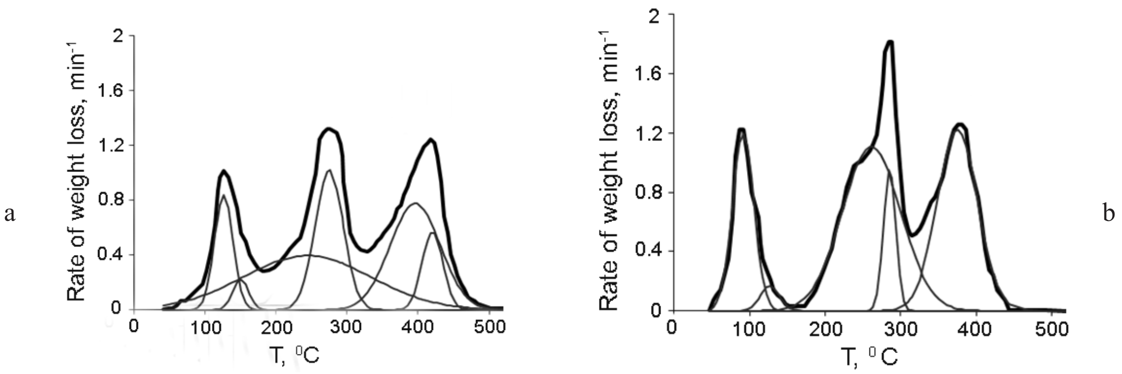

Fig. 3. Thermolysis in the system "*SPPW – Biomass – D-grade coal*":
a – "without" and b – "with" the K/Na eutectics additives.

Table 4

Thermolysis in the system "*SPPW – Biomass – D-grade coal*". Influence of the K/Na eutectics

System "*SPPW – Biomass – D-grade coal*"								
Temperature of the maximum of main peaks of decomposition for the individual components, (T_{max}, ºC)								Global WL, %
T_{max} SPPW	123	-	283	337	412	-	-	
T_{max} Biomass	130	-	276	306	389	-	-	
T_{max} D-grade coal	101	132	-	-	400	429	527	
Weight Loss ($WL_{Theor.}$) of the original components thermolysis, %								
WL_{Theor} SPPW	10.2	-	0.8	1.9	4.2	-	-	17.0
WL_{Theor} Biomass	2.8	-	12.4	3.2	3.1	-	-	21.6
WL_{Theor} D-grade coal	1.1	0.8	-	-	1.1	1.7	0.2	5.0
WL_{Theor} "SPPW + Biomass + Coal D"	14.1	0.8	13.2	5.1	8.4	1.7	0.2	43.6
Temperature of the maximum of weight loss (T_{max}) and the weight loss ($WL_{Exper.}$) in the system "*SPPW – Biomass– D-grade coal*"								
T_{max}, ºC	91	132	250	300	395	-	-	
WL_{Exper}, %	8.6	1.1	21.3	3.8	15.7	-	-	50.6
WL_{Exper}./WL_{Theor}	0.6	1.3	1.6	0.8	1.9	-	-	1.2
System "*SPPW– Biomass – D-grade coal*" + a K/Na eutectics								
Temperature of the maximum of main peaks of decomposition for the individual components, (T_{max} ºC)								
T_{max} "SPPW + eutectic"	105	-	-	320	385	415	415	-
T_{max} "Biomass + eutectic"	138	-	227	276	359	424	424	-
T_{max} "D-grade coal + euthectic"	125	-	219	-	400	408	408	470
Weight Loss ($WL_{Theor.\ K/Na}$) of the original components thermolysis, %								
$WL_{Theor\ K/Na}$ "SPPW + eutectic"	13.9	-	-	3.6	4.6	4.4	-	26.6
$WL_{Theor\ K/Na}$ "Biomass + eutectic"	1.5	-	3.1	8.4	4.3	0.5	-	17.8
$WL_{Theor\ K/Na}$ "D-grade coal + euthectic"	1.6	-	0.3	-	0.5	2.9	1.26	6.5
$WL_{Theor\ K/Na}$ "SPPW + Biomass + Coal + K/Na"	17.0	-	3.5	12.9	9.4	7.8	1.26	50.9
Temperature of the maximum of weight loss (T_{max}) and the weight loss ($WL_{Exper\ K/Na}$) in the system with a K/Na eutectics								
T_{max}, ºC	127	145	250	276	399	422	-	55.5
WL_{Exper} K/Na, %	4.6	1.1	17.9	9.3	14.5	8.2	-	
WL_{Exper} K/Na/WL_{Theor} K/Na	0.3	-	5.2	0.8	1.5	1.1	-	1.1
WL_{Exper}. K/Na/WL_{Exper}.	0.5	0.9	0.8	2.4	0.9	-	-	1.1
WL_{Theor}. K/Na/WL_{Theor}	1.2	-	0.3	2.4	1.1	4.5	5.3	1.2

For the system "*SPPW – Biomass – D-grade coal*" in a presence of the K/Na eutectics, after the experimental profile deconvolution, six peaks are assigned to the reference structural fragments thermodestruction. Namely:

1. Water release, (peaks with T_{max} at 127 ºC);
2. Polar groups of the *D-grade coal* decomposition, (peaks with T_{max} at 145 ºC);
3. Decomposition of the hemicelluloses fraction of the biomass with the light/heavy hydrocarbons of the *SPPW*, (peaks with T_{max} at 250 ºC);
4. Decomposition of the cellulose of the biomass and the saturated hydrocarbons of the malthenes fractions of the SPPW, (peaks with T_{max} at 276 ºC);
5. Co-thermolysis of the aromatic hydrocarbons of the malthenes fractions of the SPPW, the lignin fractions of the biomass and OMC1 of the D-grade coal, (peak with T_{max} at 399 ºC).
6. Co-thermolysis of the tars of the *SPPW* malthenes and asphaltenes with the lignin of the biomass and the OMC2 and OMC3 of D-grade coal, (peak with T_{max} at 422 ºC).

Therefore, in a presence of the K/Na eutectics the character of the components decomposition in the system "*SPPW – Biomass – D-grade coal*" is essentially changed (Table 4, a Fig. 3b): Thermolysis of the hemicelluloses fraction of the biomass begins at lower temperature (by 100 ºC) and proceeds more deeply over the entire temperature range. The total weight loss is of 17.9% with respect to 3.5% for an additive thermodestruction of the hemicelluloses. The temperature of the maximum rate of weight loss (T_{max}) corresponds to its typical position at 250 ºC.

Some redistribution of the intensity and the degree of thermodestruction of the reference structural fragments of the components are observed. The weight loss for the third thermal event (peak with T_{max} at 250 ºC) decreases by ~4 %, and increases by ~5 %, for the forth thermal event (peak with T_{max} at 276 ºC).

The free and bounded water, most probably, influence the components interaction, however this questions requires additional research. The weight loss due to the water release is of 4-5% against of 17.0% calculated.

High-temperature decomposition of the lignin fraction of the biomass, the organic mass of the *D-grade coal* and the tars of the *SPPW* proceeds in an agreement with the theoretical expectations (Table 4).

The global weight loss for the systems in the presence of the K/Na eutectics is of 55.5% in contrast to 50.9% calculated, and to 50.6% for the system without the K/Na additive. These data suggest that there is a cumulative negative synergetic effect (decrease in the solid product yield) in the system "*SPPW – Biomass – D-grade coal*" in the presence of the K/Na carbonates.

Thermolysis in the ternary system "Coal Processing Sludge – Biomass – D-grade coal"

According to the theoretical expectations, seven peaks should be observed in the ternary system "*Coal Processing sludge– Biomass – D-grade coal*" due to thermodestruction of the reference structural fragments. Namely:

1. Bounded water release, (peak with T_{max} at ~105-120 ºC);
2. Thermodestruction of the polar group of the D-grade coal and of the Coal Processing sludge fraction of the naphthalene derivatives; (peak with T_{max} at ~130-140 ºC);
3. Decomposition of the hemicelluloses fraction of the biomass with the organic mass of the Coal Processing sludge; (peak with T_{max} ~280 ºC);
4. Decomposition of the cellulose fragment of the biomass with the tars of the Coal Processing sludge; (peak with T_{max} at ~305-350);
5. Joint decomposition of the lignin of the biomass and the first pseudo-macro fragment of the *D-grade coal* (OMC1); (peak with T_{max} at ~400 ºC;
6. OMC2 of the D-grade coal degradation, (peak with T_{max} at 429 ºC);
7. OMC3 of the D-grade coal degradation, (peak with T_{max} at 527 ºC).

However in a practice, five basic peaks of the reference structural fragments thermodestruction (Table 5, a Fig. 4 a) are observed:

1. Bounded water release, (peak with T_{max} at ~120 ºC);
2. Decomposition of the hemicelluloses fraction of the biomass with the organic mass of the Coal Processing sludge, (peak with T_{max} 250 ºC);
3. Decomposition of the cellulose fragment of the biomass with the tars of the Coal Processing sludge, (peak with T_{max} at 300);
4. Joint decomposition of the lignin of the biomass and the first pseudo-macro fragment of the D-grade coal (OMC1), (peak with T_{max} at 395 ºC);
5. OMC3 of the D-grade coal thermolysis, (peak with T_{max} at 542 ºC).

The synergetic effect in the ternary system "*Coal Processing Sludge – Biomass – D-grade coal*" is evident in two temperature ranges:

At low temperature, there is no destruction of the coal polar groups and the naphthalene fraction of the Coal Processing Sludge, as should be expected.

At a high-temperature (single peak with T_{max} at 395 ºC), there is an overlap of the decomposition of the coal organic mass (the OMC1 and OMC2 structural fragments) with either the lignin of the biomass or the Coal Processing Sludge tar destruction. The total weight loss increases up to 8.1% in comparison with 6.1% calculated.

There are no synergetic effects in the temperature range between ~200-350 ºC.

Water influences the co-thermolysis of the components. The weight loss due to free water release decreases more than two times; and the bounded water retains and does not release, in opposite to the theoretical expectation.

The total weight loss of 34.8% is lower than the calculated value of 41.3%. These facts suggest that there is the positive cumulative synergetic effect (increase in the solid product yield) in the composite system "*Coal Processing Sludge – Biomass –D-grade coal*".

The additive of the K/Na eutectics reversed the tendency in the studied system (Table 5, Fig. 4 b).

At a low temperature (peak with T_{max} at 128 ºC), there is pronounced thermodestruction of the coal polar groups and the Coal Processing sludge naphthalene fraction. The total weight loss is of 8.3%.

At a high-temperature thermolysis of all of the three pseudo-macro fragments of the coal organic mass (the OMC1, OMC2 and OMC3) overlaps with the thermodestruction of the lignin fraction of the biomass (single peak with T_{max} at 405 ºC). The total weight loss is two times lower than the theoretically expected one for the given reference structural fragments.

Table 5

Thermolysis in the ternary system "*Coal Processing sludge – Biomass– D-grade coal*". Influence of the K/Na eutectics.

System "*Coal Processing sludge – Biomass – D-grade coal*"								
Temperature of the maximum of main peaks of decomposition for the individual components, (T_{max}, ºC)								Global WL, %
T_{max} Coal Processing sludge	120	144	282	361	-	-	-	
T_{max} Biomass	130	-	276	306	389	-	-	
T_{max} D-grade coal	101	132	-	-	400	429	527	
Weight Loss ($WL_{Theor.}$) of the original components thermolysis, %								
WL_{Theor} Coal Processing sludge	4.9	2.2	7.5	0.2	-	-	-	14.5
WL_{Theor} Biomass	2.8	-	12.4	3.2	3.1	-	-	40.5
WL_{Theor} D-grade coal	1.1	0.8	-	-	1.1	1.7	0.2	8.9
WL_{Theor} "*Coal Processing sludge + Biomass + Coal D*"	8.8	3.8	19.9	3.4	4.2	1.7	0.2	41.3
Temperature of the maximum of weight loss (T_{max}) and the weight loss ($WL_{Exper.}$) in the system "*Coal Processing sludge – Biomass – D-grade coal*"								
T_{max}, ºC	123	-	250	300	395	-	542	
WL_{Exper}, %	4.7	-	18.0	2.5	8.1	-	1.5	34.8
$WL_{Exper.}/WL_{Theor}$	0.5	-	0.9	0.7	1.9	-	6.0	0.8
System "*System Coal Processing sludge – Biomass – D-grade coal*" + a *K/Na* eutectics								
Temperature of the maximum of main peaks of decomposition for the individual components, (T_{max} ºC)								
T_{max} "*Coal Processing sludge + eutectic*"	110	188	-	263	-	-	-	
T_{max} "Biomass + eutectic"	138	-.	227	276	359	424	-	
T_{max} "D-grade coal + euthectic"	125	-	219	-	400	408	470	
Weight Loss ($WL_{Theor.\ K/Na}$) of the original components thermolysis, %								
WL_{Theor} K/Na "*Coal Processing sludge +* eutectic"	6.8	0.1	7.0	-	-	-.	-	13.9
WL_{Theor} K/Na "Biomass + eutectic"	1.5	-	3.1	8.4	4.03	0.5	-	17.8
WL_{Theor} K/Na "D-grade coal + euthectic"	1.6	-	0.3	-	0.5	2.9	1.3	6.5
WL_{Theor} K/Na "*Coal Processing sludge + Biomass + Coal +K/Na*"	9.8	0.1	10.5	8.4	4.8	3.4	1.3	38.3
Temperature of the maximum of weight loss (T_{max}) and the weight loss (WL_{Exper} *K/Na*) in the system with a *K/Na* eutectics								
T_{max}, ºC	113	128	250	321	405	-	-	
$WL_{Exper\ K/Na}$, %	11.1	8.3	10.8	6.6	5.2	-	-	41.3
$WL_{Exper\ K/Na}./WL_{Theor\ K/Na}$	1.1	103.5	1.0	0.8	1.1	-	-	1.4

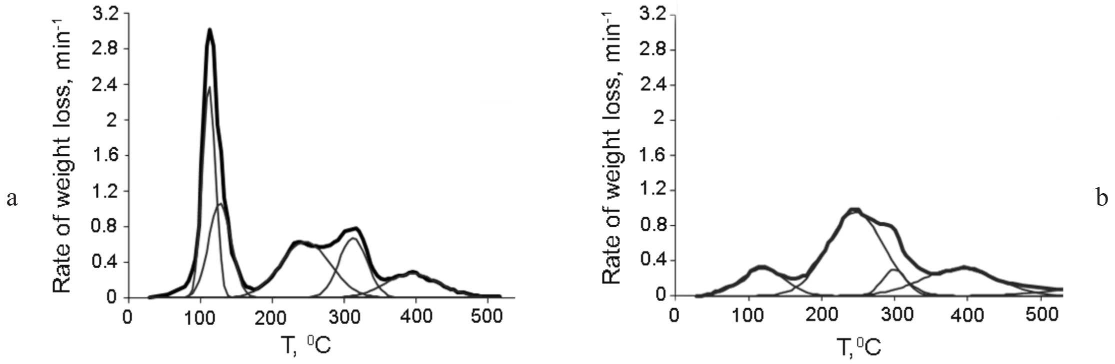

Fig. 4. Thermolysis in the ternary system "*Coal Processing Sludge – Biomass – D-grade coal*" a – "without" and b – "with" the K/Na eutectics.

In the temperature range between ~200-350 ºC, the components of the ternary system behave in an additive manner. There are two single peaks (with T_{max} at 250 ºC and 321 ºC), due to the joint destruction of the organic mass and the Coal Processing Sludge tar with the hemicelluloses and the cellulose fragments of the biomass.

The global weight loss (of 41.9%) remains basically unchanged with respect to 38.3% of theoretically predicted for the system "*Coal Processing Sludge – Biomass – D-grade coal*" in the presence of K/Na eutectics.

Activated Carbons from the Co-Mingled Wastes

From the accomplished DTG/TG analysis the temperature ranges of the synergetic effects and the reference structural fragments responsible for them are evaluated. The data obtained are used for the development of the carbonization/activation processes of the co-mingled liquid and solid organic wastes. Emphasis is done to the polycondensation and re-polymerization reactions *via* secondary vapor – solid phase interaction.

The development of the design parameters for activated carbons syntheses in their ternary systems is based on the results obtained during treatability studies of the activated carbon production from single components and their co-mingled binary and ternary systems. Using the waste co-processing procedure, three different approaches are used in order to optimize the conditions for the activated carbon production, namely:

- Approach 1.
  High temperature activation via low temperature carbonization (at 350 ºC). (Two steps activation).
- Approach 2.
  High temperature activation via high temperature carbonization (at 800 ºC). (Two steps activation).
- Approach 3.
  High temperature activation without carbonization (Direct activation).

Comprehensive investigations of the influence of the co-processing parameters (nature and composition of the blends, the temperature and soak time of the carbonization/activation processes, and the additive of K/Na eutectics) on the properties (the yield and the apparent surface area) of the activated carbon obtained are accomplished.

Data are summarized in Tables 6 and 7 for the individual components, their binary and ternary systems processing using the above mentioned approaches to the co-activation.

From the analysis of the experimental data (Tables 6 and 7, Figs. 5a, b, c) one could conclude that, the developed approaches to the waste co-processing, affect the properties of the activated carbons in different ways. The parameters [SYH] (Surface area, Yield and Homogeneity) are chosen for qualification (in terms of High/the Highest or Low/the Lowest) of an overall efficiency of the certain approach (summery is also given in Table 8), namely:

- Approach 1.
  High temperature activation *via* low temperature carbonization resulted in the activated carbons with the lowest surface area and the highest yield with respect to that of the approaches 2 and 3 (Fig. 5a). [$S_{tL}Y_{tH}H_{tH}$] according to Table 8. (Two steps activation).
- Approach 2.
  High temperature activation via high temperature carbonization resulted in higher surface area and lower yield with respect to that of the approach 1 (Fig. 5b). [$S_{H}Y_{tL}H_{H}$] according to Table 8. (Two step activation).
- Approach 3.
  High temperature activation without carbonization resulted in the same surface area and higher yield with respect to that of the approach 2; and higher surface area and the same yield with respect to that of the approach 1 (Fig. 5c). [$S_{tH}Y_{H}H_{tL}$] according to Table 8. (Direct activation).

The application of the developed approaches to the waste co-processing in their binary or ternary systems resulted in activated carbons of high surface area and the yield with respect to that obtained by conventional activation of the individual parent carbon-containing materials (Tables 6 and 7).

The yield of the activated carbons from the recovered co-mingled waste, vary between 20 to 40 %. The surface area for novel activated carbons (350-1100 m^2/g) is in the range of the surface area of the commercial-grade activated carbons.

Furthermore, the successful waste recovery into the environmentally friendly activated carbons from the ternary systems with high liquid waste content (up to 50 wt.%) offers a technological alternative to the disposal of the harmful petroleum waste, along with valorization of the biomass and low grade coal.

The questions of homogeneity/heterogeneity of the secondary generated solid products in the co-mingled systems are extremely important for the efficiency of waste co-processing into activated carbons.

The surface roughness and the solid products homogeneity were studied by Scanning Electron Microscopy using Philips XL30 ESEM-FEG equipment (Figs. 6 a-c). The surface topography changes at change of the conditions of the co-activation process in a following manner.

Table 6
Properties of the adsorbents from individual components and their binary and ternary composition systems

Carbonization process			Activation process			
T, ºC	Time, h	Burn off, %	T, ºC	Time, h	Yield, %	S_{BET}, m^2/g
D-grade Coal						
350	3	30	850	2	41	380
800	1	42	850	3	25	450
without carbonization			850	3	30	647
Coal Processing sludge – D-grade Coal						
350	3	36	850	2	22	220
800	1	48	850	3	28	360
without carbonization			850	3	46	410
Spent Petroleum Product Waste D-grade Coal						
350	3	47	850	2	34	290
800	1	41	850	3	29	540
without carbonization			850	3	21	580
Sunflower husks						
350	3	65	850	2	18	126
800	1	68	850	3	16	150
without carbonization			850	3	15	180
Coal Processing sludge – Sunflower husks						
350	3	59	850	2	26	230
800	1	67	850	3	18	400
without carbonization			850	3	20	430
Spent Petroleum Product Waste – Sunflower husks						
350	3	40	850	2	34	290
800	1	55	850	3	25	540
without carbonization			850	3	27	530
Sunflower husks – D-grade Coal						
350	3	55	850	2	31	380
800	1	58	850	3	29	450
without carbonization			850	3	28	410
Coal Processing sludge – Sunflower husks – D-grade Coal						
350	3	42	850	2	29	390
800	1	54	850	3	28	606
without carbonization			850	3	26	620
Spent Petroleum Product Waste – Sunflower husks – D-grade Coal						
350	3	42	850	2	24	790
800	1	56	850	3	19	840
without carbonization			850	3	21	920

Table 7
Properties of the adsorbents from individual components and their binary and ternary composition systems

Carbonization process			Activation process			
T, ºC	Time, h	Burn off, %	T, ºC	Time, h	Yield, %	S_{BET}, m^2/g
D-grade Coal + K/Na						
350	3	34	850	2	45	410
800	1	58	850	3	24	520
without carbonization			850	3	25	720
Coal Processing sludge – D-grade Coal + K/Na						
350	3	47	850	2	28	240
800	1	45	850	3	26	370
without carbonization			850	3	27	380
Spent Petroleum Product Waste – D-grade Coal + K/Na						
350	3	57	850	2	32	310
800	1	36	850	3	27	470
without carbonization			850	3	19	590
Sunflower husks + K/Na						
350	3	62	850	2	21	160
800	1	74	850	3	15	180
without carbonization			850	3	11	220
Coal Processing sludge – Sunflower husks + K/Na						
350	3	58	850	2	34	230
800	1	52	850	3	23	400
without carbonization			850	3	20	430
Spent Petroleum Product – Waste Sunflower husks + K/Na						
350	3	42	850	2	31	320
800	1	45	850	3	28	580
without carbonization			850	3	26	590
Sunflower husks – D-grade Coal + K/Na						
350	3	56	850	2	29	405
800	1	58	850	3	26	460
without carbonization			850	3	24	580
Coal Processing sludge – Sunflower husks – D-grade Coal + K/Na						
350	3	40	850	2	31	410
800	1	46	850	3	29	690
without carbonization			850	2	28	640
Spent Petroleum Product Waste – Sunflower husks – D-grade Coal + K/Na						
350	3	35	850	2	28	980
800	1	37	850	3	18	990
without carbonization			850	2	22	1042

Table 8

Summary of the influence of the co-processing conditions on the properties of the activated carbons

Approach	Surface area	Yield	Homogeneity
Two steps activation *via* carbonization at 350 ºC	the Lowest	the Highest	the Highest
Two step activation *via* carbonization at 800 ºC	High	the Lowest	High
Direct activation	the Highest	High	the Lowest

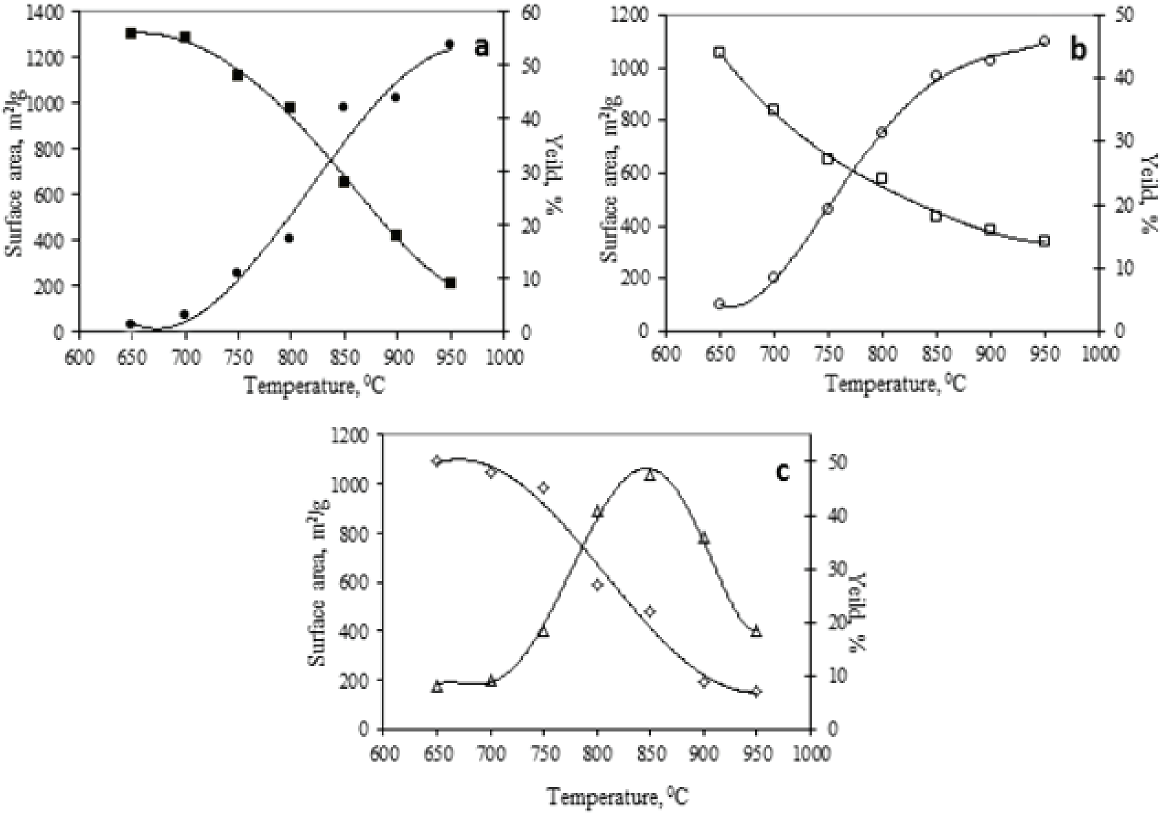

Fig. 5. Influence of the co-processing conditions on the properties of the resulted activated carbon[1] (example are given for the activated carbon from the ternary systems "*SPPW – Biomas – D-grade*" in the presence of *K/Na* eutectics):
a – Efficiency of the Approach 1: activation via low temperature carbonization at 350 ºC (■ yield and ● surface area);
b – Efficiency of the Approach 2: Activation via high temperature carbonization at 800 ºC (□ yield and ○ surface area);
c – Efficiency of the Approach 3: Direct high temperature activation at 850 ºC (◊ yield and Δ surface area).

[1] Example are given for the activated carbon from the ternary systems "*SPPW – Biomass – D-grade*" in the presence of K/Na eutectics.

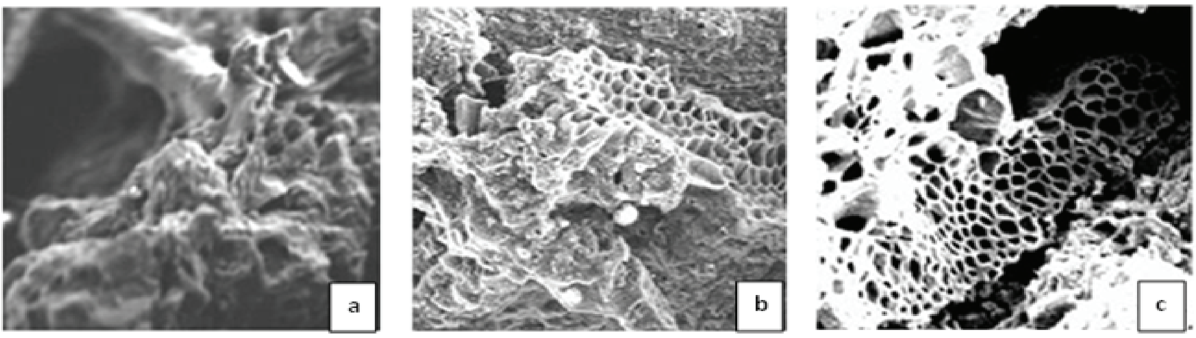

Fig. 6. Scanning Electron Microscopy data for the ternary system with SPPW:
a – activation *via* carbonization at 350 ºC; b – direct activation at 850 ºC; c – direct activation at 850 ºC.

Two steps activation, i.e. high temperature activation via carbonization (whatever the temperature) completely eliminates the parent components heterogeneity. The porous solid secondary products of uniform particle size and pore size distribution are obtained during co-processing in the co-mingled systems (Fig. 6a).

The co-mingled systems subjected to the direct activation resulted in heterogeneous activated carbons. Solid products contain both the co-pyrolyzed products (charcoal) and the fragments of the activated parent components. Despite of high surface area of the resulted activated carbons, there are the fragments of either the activated sunflower husks with wide pores of few microns or poor activated parts of the D-grade coal (Fig. 6 b, c).

The topography and the elemental analysis of the activated carbon surface were also studied using high resolution Auger Depth Profiling with PHI SAM–660 equipment. Auger Depth Profiling provided quantitative compositional information as a function of depth below the surface (near-surface characteristics).

The novel porous materials consisted mainly of carbon (up to 86%) and oxygen (up to 6.5%), depending on chosen approach to the co-processing (Table 9). The presence of oxygen, apart from its initial content in the blend's components, could be explained by its absorption from surrounding environment during co-activation process. The minor presence of other elements, like Si, Ba, Fe, etc., is due to mineral content of the parent components. The near-surface distribution of these elements is non-uniform.

Table 9

Auger depth profiling data

	Heterogeneous activated carbon	Homogeneous activated carbon
Atomic Concentration	Direct Activation S_{BET} 1038 m^2/g	Activation *via* Carbonization S_{BET} 979 m^2/g
C1	62.5	86.0
O1	6.5	5.8
N1	3.5	3.5
S1	2.0	3.3
Cl1	0.5	1.1

It has to be noted, that measurements of the depth concentration profiles by Auger technique did not reveal the presence of any other elements except for carbon.

Data analysis

From elaborated comprehensive investigations the main factors, which influence the formation of carbonized chars and the properties of the resulted activated carbons, are summarized in Table 10.

For the two steps activation process (activation via low (at 350 ºC) or high (800 ºC) temperature carbonization).

The surface area of the resulted activated carbons increases with time of the carbonized char activation along with decrease in their yield (Fig. 5a, b). This tendency is observed in the binary and ternary systems whatever the presence of the *K/Na* eutectics.

However, in the presence of the *K/Na* eutectics, the increase of the apparent surface area with time is higher with respect to that for the systems without the *K/Na* additive. While, the decrease of the solid products yield is less pronounced and remains high enough with time in contrary to that in the systems without the *K/Na* additive (c.f. data on yield and surface area in Fig. 7).

For the direct activation (high temperature activation at 850 ºC).

The surface area of the resulted activated carbons decreases with time of co- activation process along with decrease in the solid product yield (Fig. 5c).

The additive of the *K/Na* carbonates to the co-mingled systems resulted in increase of the apparent surface area and the yield of the activated carbons, whatever the approach to the co-processing (direct or two steps activation). This tendency is pronounced in the binary and ternary systems with liquid petroleum waste component: either aromatic tar stock (the Coal Processing Sludge) or aliphatic petroleum stock (the SPPW) (c.f. data on yield and surface area in Tables 6 and 7, and Fig. 7).

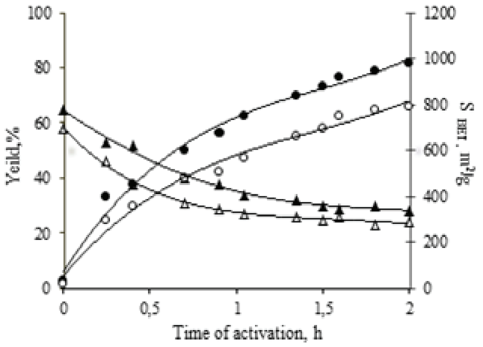

Fig. 7. General tendency of the *K/Na* eutectics influence on the properties of the resulted activated carbon[2]: Δ yield and ○ surface area in the system with *K/Na* eutectics; ▲ yield and ● surface area in the system without *K/Na* eutectics.

According to the laboratory regulation the following optimal conditions for the syntheses were chosen (Table 10): either direct high temperature activation with steam (850 ºC for 2 h); or two-step activation via low temperature carbonisation (at 350 ºC for 2 h under inert atmosphere) followed by high temperature activation with steam (at 850 ºC for 2 h). The optimal blends composition is of 25% the sunflower husks, 25% the D-grade coal and 50 % the petroleum wastes either aliphatic petroleum stock (the SPPW) or aromatic tar stock (the Coal Processing sludge) and of ~10 wt.% of binary eutectic the *K/Na* carbonates.

Under optimal conditions the activated carbons with developed surface area and well–balanced pore size distribution are obtained (Table 11).

Table 10
Optimal conditions for the co-mingled carbon-containing materials co-processing in the ternary systems

Direct activation	
Activation agent	Steam
Flow rate*	300 ml/min
Heating rate	5 ºC
Temperature of activation	825-850 ºC
Soaking time at 825-850 ºC	2-3 h
Activation *via* Carbonization	
Temperature of carbonization	350 ºC
Carbonization atmosphere	Inert (nitrogen)
Flow rate	200 ml/min
Heating rate	5 ºC
Soaking time at 350 ºC	2-3 h
Activation agent	Steam
Flow rate	300 ml/min
Heating rate	5 ºC
Temperature of activation	825-850 ºC
Soaking time at 825-850 ºC	1-2 h
Optimal Blends Composition	
Blends Components Ratio	2:1:1 *SPPW* (or *Coal Processing sludge*) (50 wt.%) *Biomass* (25 wt.%) *D-grade coal* (25 wt.%)
Additives	Binary eutectics K_2CO_3/Na_2CO_3 (10 wt.%) of blend weight
Method of a *K/Na* eutectics preparation	Fusion of finely ground binary mixture of sodium (29%) and potassium (71%) carbonates
Method of a *K/Na* eutectics impregnation	Incipient wetness method

* Vapor flow rate was optimized by procedure described elsewhere [44]

[2] Example are given for the activated carbon from the ternary systems "*SPPW – Biomass – D-grade*".
Co-process: high temperature activation via low temperature carbonazation at 350 ºC.

The direct activation seems to be more efficient for the surface and porous structure development, especially for the systems with the aromatic tar component (Table 11). However, the activation *via* low temperature carbonization allows to obtain much more homogeneous structure of the activated carbons (Table 9).

The properties (textural characteristics) of novel carbon materials are comparable with those of the commercial activated GAC Norit carbon (c.f. data in Table 11). While, the surface functionality (surface functional groups) is comparable with that of post-oxidized by 1M HNO3 GAC Norit commercial carbon (c.f. data in Table 12).

Table 11

Textural parameters BET surface area (S_{BET}), total pore volume(V_{total}), micropoervolume (V_{micro}), ratio between the mesoporous and microporous volumes (V_{meso}/V_{micro}), pH at point of zero charge (pH_{PZC}) of the activated carbons from the co-mingled waste. Influence of the blends composition and conditions of the activation process

Activated carbon on based on:	S_{BET}, m^2/g	V_{total}, cm^3/g,	V_{micro}, cm^3/g	V_{meso}/V_{micro}	pH_{PZC}
Direct activation					
Coal / Biomass / Aliphatic Petroleum Stock (1:1:2)	1038	0.47	0.39	0.20	3.42
Coal / Biomass / Aromatic Tar Stock (1:1:2)	638	0.32	0.23	0.39	5.85
Activation *via* carbonisation					
Coal / Biomass / Aliphatic Petroleum Stock (1:1:2)	979	0.46	0.38	0.21	3.27
Coal / Biomass / Aromatic Tar Stock (1:1:2)	411	0.11	0.15	1.4	5.65
Parent GAC Norit	770	0.40	0.39	0.02	6.92
Oxidized GAC Norit	837	0.56	0.49	0.14	4.41

Table 12

Surface oxygen groups of the activated carbons from the co-mingled waste

Sample	Carboxylic $\mu_{mol/g}$		Lactones $\mu_{mol/g}$	Phenols μ_{molg}	Quinones $\mu_{mol/g}$
	Hydrous	Anhydrous			
Coal / Biomass / Aromatic Tar Stock 1:1:2	0.05	0.13	1.01	2.18	0.19
Coal / Biomass / Aliphatic Petroleum Stock 1:1:2	0.29	-	0.75	0.58	0.48
Parent GAC Norit	-	-	0.21	0.50	0.19
Oxidized GAC Norit	1.15	0.14	0.76	2.52	1.82

Prototype Activated Carbon from the Co-Mingled Waste

Under optimal condition established from laboratory-scale experiments, the Prototype Activated Carbon from recovered co-mingled waste was produced in a framework of the NATO “Science for Peace Programme”, project SfP 977984 by the End- User/Partner Joint Stock Company “Electrod”, Ukraine.

The optimal synthesis conditions tested at pilot scale were two-step co-processing via carbonisation at 350 ºC for 2 h under inert atmosphere followed by high temperature activation at 850 ºC for 2 h with steam.

Novel powder and granular activated carbons from co-mingled biomass, petroleum waste stocks, coal processing sludge and low-grade coal are produced at pilot-scale. Their Trademarks are *ISQDON*, *ACW-Ar* and *ACW-Al*). The surface area is ranged from 600 to 1100 m^2/g, the total pore volume from 0.32 to 0.47 m^3/g, and the yield from 21 to 27%.

Conclusions

The *co-activation* approach to the solid and liquid co-mingled waste recycling aimed at porous solid valuable secondary products generation is developed. This approach allows obtaining cheap and high-quality activated carbons and valorization of the parent carbon-containing materials via their co-processing with others waste.

The conditions of co-activation in the ternary composite systems "*Spent Petroleum Product Waste – Biomass – D-grade D*" and "C*oal Processing sludge – Biomass – D-grade coal*" are optimized. According to the laboratory regulation the optimal conditions are the following: either direct high temperature activation with steam (850 ºC for 2 h); or two-step activation via low temperature carbonisation (at 350 ºC for 3 h under inert atmosphere) followed by high temperature activation with steam (at 850 ºC for 2 h); the optimal blends composition of 25% the sunflower husks, 25% the D-grade coal and 50% the petroleum wastes either aliphatic petroleum stock (the *SPPW*) or aromatic tar stock (the *Coal Processing Sludge*) and ~10 wt.% of binary eutectics the *K/Na* carbonates.

The *K/Na* carbonates are responsible for the cross-linked reactions, which prevent the coke formation and develop the porous structure of the resulted activated carbons. From the other hand, the *K/Na* additives catalyze the steam gasification process. The gas phase molecules are dissociated by the *K/Na* catalytic clusters and, as a consequence, the oxygen density at surface increases. The *K/Na* clusters are also active in catalyzing oxygen transfer reactions between gaseous molecules, e.g. the Water-Gas-Shift, the Boudouard reaction and methanation [44].

The results of the co-activation showed the superior properties of co-pyrolyzed composite materials of environmentally acceptable grade. The properties of novel carbon materials are comparable with commercial activated carbons.

However, the co-mingled systems subjected to the direct activation, despite of high surface area of the resulted activated carbons, produce heterogeneous solids. The process using, two steps activation, i.e. high temperature activation via carbonization, is more efficient to produce the homogeneous carbon structures. The porous solid secondary products of uniform particle size and pore size distribution are obtained during co-processing in the co-mingled systems.

Under optimal condition established at laboratory-scale, the Prototypes Activated Carbon (trademarks are ISQDON, ACW Ar and ACW Al) are produced at pilot-scale from co-mingled biomass, petroleum waste stocks, and low-grade coal. The surface area is ranged between 600-1100 m^2/g, the total pore volume is of 0.32-0.47 m^3/g and the yield is of 21 to 27%.

Within this context, the natural organic waste recovery into porous solid environmentally friendly products offers a technological alternative to their disposal.

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