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Original Research

Complex Fertilizers Produced from the Sunflower Husk Ash

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Abstract

Sunflower husk ash containing the primary and secondary plant nutrients – phosphorus (10.94% P_2O_5), potassium (25.84% K_2O), calcium (19.07% CaO), magnesium (18.58% MgO), and also some micronutrients (zinc, copper, cobalt, manganese, iron, and molybdenum) may be used for fertilization of variety plants. The sunflower husk has low plasticity, and the granulation process occurs better when binding materials (sugar factory lime, molasses, urea formaldehyde resin) are used. This study investigates determination of the optimal parameters of the granulation process as recycling and moisture content, ratio of ingredients and influence of additives by using laboratory equipment. The main product quality parameters as chemical composition, static crushing strength of granules, granulometric composition, and pH of 10% solution by standard method were examined. The results show that sunflower husk may be used for fertilizers of 0-6-13 grade production.

Keywords: sunflower husk ash, sugar factory lime, molasses, fertilizers, granulation, physicochemical properties, environment

Introduction

Vegetable waste – tree leaves, sawdust, straw, rapeseed stalks and others are increasingly being used as alternative fuels, reducing the consumption of fuel oil or natural gas and environmental contamination. The combustion product of this waste, ash, is a valuable material that can be used to fertilize different plants. Ash contains a significant content of primary and secondary plant nutrients – phosphorus, potassium, calcium, magnesium, and some micro elements (ME): zinc, copper, cobalt, manganese, and iron [1].

During the industrial processing of sunflowers, sunflower husks remain unused. Depending on growing conditions and fertilizer the husks application, the husk contain a variety of plant nutrients and micro elements. Therefore ash obtained from burning husks can be used to fertilize plants.

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Ash utilization becomes more efficient when a homogeneous mass is obtained and particle size is uniform. This is achieved by ash granulation.

The granulation method is selected by taking into account the particle agglomeration determining the plasticity of raw materials, as well as the physical-chemical properties of the granulated product (granulometric composition, crushing strength of granules, hygroscopicity), which determines product caking and powdering. In addition, economic indicators of the process are significant (energy consumption, waste generation) and the capacity of the installation. Non-traditional fertilizer granulating equipment is often selected for the granulation of low-plasticity material: tableting equipment, extruders, forming equipment.

Ash has no plasticity and its agglomeration is difficult. Ash granulation in drum granulators can be expected only with the addition of binding materials. It is known that polyamin alkylol [2] or ETEC-dolomite [3] are effective for ash granulation. There are some data on ash granulation in American [4] and Japanese [5] literature.

The waste product of sugar production (sugar factory lime – SFL) can be used for the improvement of plasticity for ash granulation. Its influence on fertilizer granulation parameters and product quality indicators was analyzed by us earlier [6], thus extending its utilization potential, enriching fertilizer with calcium, and solving a major environmental problem.

We believe that the plasticity of granulated powdery material can be affected by another sugar industry waste product, molasses (M), that results from the processing of sugar beets. It contains necessary plant nutrients and ME. M composition is dependent on climatic conditions of beet cultivation, fertilizer application, and technological processing conditions.

Agglomeration of granulated materials is also affected by urea formaldehyde resins (UFR) [7], so it can also be used for ash granulation.

The purpose of this study was to determine the opportunities for sunflower husk ash granulation in a drum granulator. In order to achieve this purpose, we needed to determine the ash granulation parameters by using various additives – SFL, M, UFR – and evaluating physical and chemical properties of the obtained product.

Materials and Methods

The following materials were used for the production of granular fertilizers: Moldovan sunflower ash, Marijampolė's (Lithuania) sugar factory waste (SFL and M) as well as urea formaldehyde resin (UFR). Water (W) was used for mixture moisturizing.

The chemical composition of SFL and some properties have been investigated and presented previously [6]. M composition varies within the range (%): dry particles content 76-82, non-sugar substances 32-34, reducing materials 0.5-2.5, raffinose 0.6-1.4, lactic acid 4-6, acetic acid 4-8, and conductometric ash 6-10. M also contains micro elements (Fe, Mn, Zn, Cu, Co, Mo) [8]. UFR is a whitish color liquid (grade KF-MEM) [9].

The nitrogen content in the samples was determined by the standard method [10], the phosphorus was determined on a photocolorimeter KFK-2 [11], magnesium and calcium content were determined by the complexometric titration method [12], potassium and sodium content was determined on a flame photometer PFP-7 [13].

The atomic absorption spectrometry method was applied for the determination of micro elements content [12] and the A Analyst 400 device from Perkins Elmer Company. In all cases acetylene (C_2H_2) was used to get the flame and, for the determination of the concentration of molybdenum, N_2O was applied. Chemically pure or analytically pure materials were used and the samples were prepared by decomposing dry material with unconcentrated (1:1) HCl acid and filtering the obtained solution and diluting it in water.

Ash X-ray radiation diffractive analysis [14] was carried out by X-ray difractometer DRON-6 (Cu K_α radiation, Ni filter, detector's step length – 0.02º, duration of intensity measurement in the step – 0.5 s, voltage U=30 kV, current I=20 mA).

Simultaneous thermogravimetric and differential scanning calorimetry (TG–DSC) [14, 15] was carried out by a NETZCH STA 409 PC Luxx thermal analyzer. Samples were heated to 500ºC, speed of raising the temperature was 10ºC/min, air atmosphere.

IR spectra [16] were obtained on a Perkin Elmer FT-IR spectrometer. The samples were produced by pressing the tablets from the ashes and the optically pure dried KBr. The tablet was prepared by mixing 1 mg of the test substance and 200 mg of potassium bromide.

Fertilizers were granulated in the laboratory drum-type granulator-dryer, at 3 degrees of tilt angle and a constant (26 rpm) rotation speed. The raw materials were supplied to the granulator preheated up to 70ºC, hot air was supplied for drying the granules into the drum-type granulator by air fan. For irrigation, 0.1% phosphoric acid solution or water was used, which was injected into the raw material mixture upstream of the drum-type granulator-dryer [17]. By using the sunflower husk ash (fraction <2 mm), samples were granulated in the laboratory technique (1-24 sample). The quantities of components used in granulation, and additives improving the characteristics of fertilizers are represented in Table 1.

The resulting granular product, depending on the used content of W, SFL, M, and UFR, was dried in an oven from 7 to 21 hours at 60-70ºC, then physical chemical properties were identified.

The static strength of granules was determined using an IPG-2 device. Its measurement range was 5-200 N, margin of error ±2.00% from the upper limit of measurement (when temperature is 20±5ºC). Calculations were made using a standard methodology [11].

Hygroscopic moisture of granulated fertilizer, pH, granulometric composition of ash, and bulk density were determined using the standard procedures [11].

The experimental granulation results are presented as an average of tree measurements. Student's criterion (t-test) was applied for determining statistical reliability of granulation results. To determine a statistical significance of physical-chemical properties use Fischer's criterion (F-test).

Results and Discussion

The chemical composition of sugar factory lime was analyzed [6] and the concentration of primary and secondary nutrients and ME were identified in dry substance. It was also identified that SFL contains approximately 30% of moisture. The moisture content is continuously decreasing if the material is stored at room temperature. Therefore, it is recommended to dry the SFL before storage (at a temperature of up to 100ºC) and measure the moisture content every time. Water solution of 10 SFL is alkaline, its pH is 8.68.

Chemical and instrumental analysis of Moldovan sunflower husk ash was carried out (Table 2) (Figs. 1-3).

Table 1. Quantities of components.

Sample	Quantities of components,%						
	Ash	SFL	M	UFR	W	Recycling	Sum
1	71.43	0.00	0.00	0.00	28.57	0.00	100
2	35.71	0.00	0.00	0.00	28.57	35.71	100
3	78.13	0.00	21.88	0.00	0.00	0.00	100
4	69.77	0.00	30.23	0.00	0.00	0.00	100
5	71.43	0.00	9.52	0.00	19.05	0.00	100
6	71.43	0.00	14.29	0.00	14.29	0.00	100
7	71.43	0.00	19.05	0.00	9.52	0.00	100
8	71.43	0.00	21.43	0.00	7.14	0.00	100
9	35.71	0.00	14.29	0.00	14.29	35.71	100
10	41.67	41.67	0.00	0.00	16.67	0.00	100
11	43.35	43.35	13.29	0.00	0.00	0.00	100
12	39.47	39.47	21.05	0.00	0.00	0.00	100
13	41.21	41.21	5.86	0.00	11.72	0.00	100
14	41.67	41.67	8.33	0.00	8.33	0.00	100
15	39.47	39.47	14.00	0.00	7.05	0.00	100
16	40.54	40.54	14.19	0.00	4.73	0.00	100
17	20.27	20.27	0.00	0.00	18.92	40.54	100
18	20.49	20.49	9.02	0.00	9.02	40.98	100
19	70.42	0.00	0.00	0.30	29.28	0.00	100
20	70.42	0.00	0.00	0.59	28.99	0.00	100
21	40.54	40.54	0.00	0.19	18.73	0.00	100
22	40.54	40.54	0.00	0.38	18.54	0.00	100
23	40.54	0.00	0.00	0.19	18.73	40.54	100
24	19.74	19.74	0.00	0.42	20.63	39.47	100

The data of chemical analysis indicates that ash contains significant content of some primary and secondary nutrients: K_2O 25.84%, CaO 19.07%, and MgO 18.58%, as well as Na_2O and N – only traces. Individual ME content varies across a broad range. The most abundant element found in ashes is iron (2,940.46 mg/kg), there is also a significant content of Mo (472.17 mg/kg), Mn (410.45 mg/kg), and Cu (405.61 mg/kg); less of Zn (167.23 mg/kg) and of Co (0.44 mg/kg).

The data of simultaneous differential scanning calorimetry and thermogravimetry (DSK-TG) analysis (Fig. 1) indicate that at 89.0ºC the DSK curve displays insignificant endothermic effect, and in the TG curve it corresponds to the mass loss, which is attributed to the adsorptive water removal in ashes. At 438.0ºC one can see that another insignificant endothermic effect, by its nature, may be the result of enantiotropic conversions.

Table 2. Quantity of primary and secondary nutrients and microelements in ash.

Main and secondary nutrients, %		Micro elements, mg/kg	
N	0.01	Fe	2940.46
P_2O_5	10.94	Cu	405.61
K_2O	25.84	Zn	167.23
CaO	19.07	Mn	410.45
MgO	18.58	Co	0.44
Na_2O	0.03	Mo	472.17

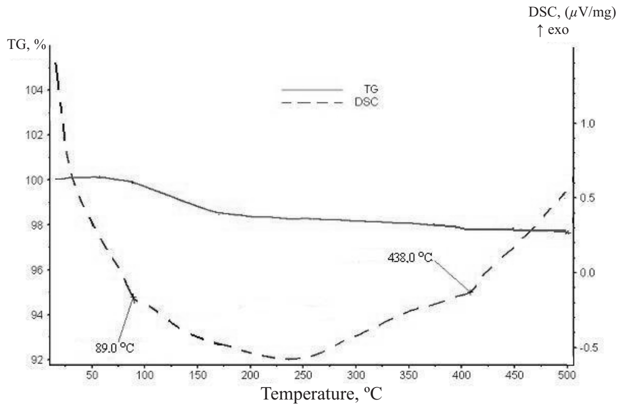

Fig. 1. DSK-TG analysis curves of Moldovan sunflower husk ash.

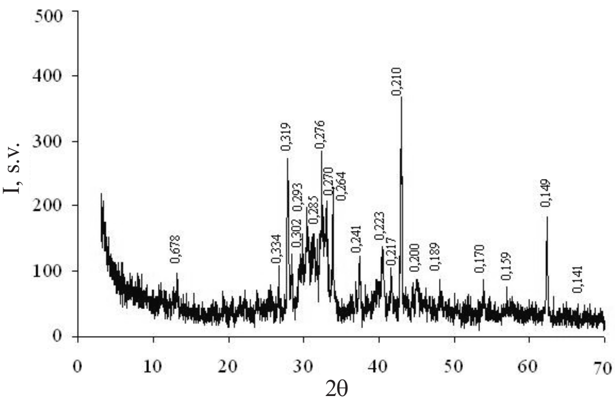

Fig. 2. X-ray diffractive curve of Moldovan sunflower husk ash.

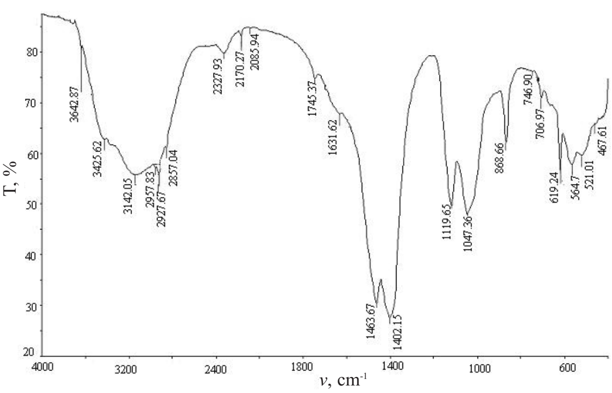

Fig. 3. Moldovan sunflower husk ash – IR spectrum.

Table 3. Physical properties of ash.

Granulometric composition, %					Bulk density, kg/m^3
<1 mm	1-2 mm	2-3 mm	3-5 mm	>5 mm	
38.84	31.49	7.71	12.08	9.88	708

X-ray diffractive analysis curve (Fig. 2) contains the peaks that correspond to calcium carbonate (0.302, 0.285, 0.210, 0.189 nm), potassium carbonate (0.319, 0.285, 0.223, 0.200, 0.170, 0.159, 0.149 nm), magnesium carbonate (0.241, 0.170, 0.149, 0.141 nm), potassium–calcium carbonate (0.264, 0217 nm), potassium-calcium phosphate (0.270, 0.159 nm), potassium-manganese oxide (0.678, 0,276, 0.241 nm), magnesium-phosphate (0.293 nm) and oxide (0.149 nm), and elemental carbon (0.334, 0.285, 0.159 nm) characteristic diffractive reflexions.

In the spectrum obtained during IR spectral analysis (Fig. 3), in the area of approximately about 3,600-3,400 cm^{-1}, one can distinguish a low-intensity vibration typical of O-H connection valentic vibration of water molecules. Oscillations in the frequency range of approximately 3,200-2,800 cm^{-1} can be attributed to the CH group, and non-intensive vibrations in the range of 2,500-1,600 cm^{-1} are typical of the CO connection. The spectrum has a very pronounced vibration of CO_3^{2-} functional group in the frequency range of approximately 1,400 and PO_4^{3-} approximately 1,100 cm^{-1}, and less pronounced in the absorption frequency range of 900-500 cm^{-1} characteristic to CaO and MgO.

The identified ash physical properties (granulometric composition and bulk density) and the obtained results are presented in Table 3. As we see from the data, the majority of ash consists of particles less than 2 mm in size. Sunflower ash bulk density equals 708 kg/m^3.

It was visually determined that ash content depends on various admixtures, for example unburned sunflower particles. These impurities explain some absorption bands in the spectrum characteristic of silicate substances. The view of separate fractions of Moldovan sunflower ash is different and is presented in Fig. 4.

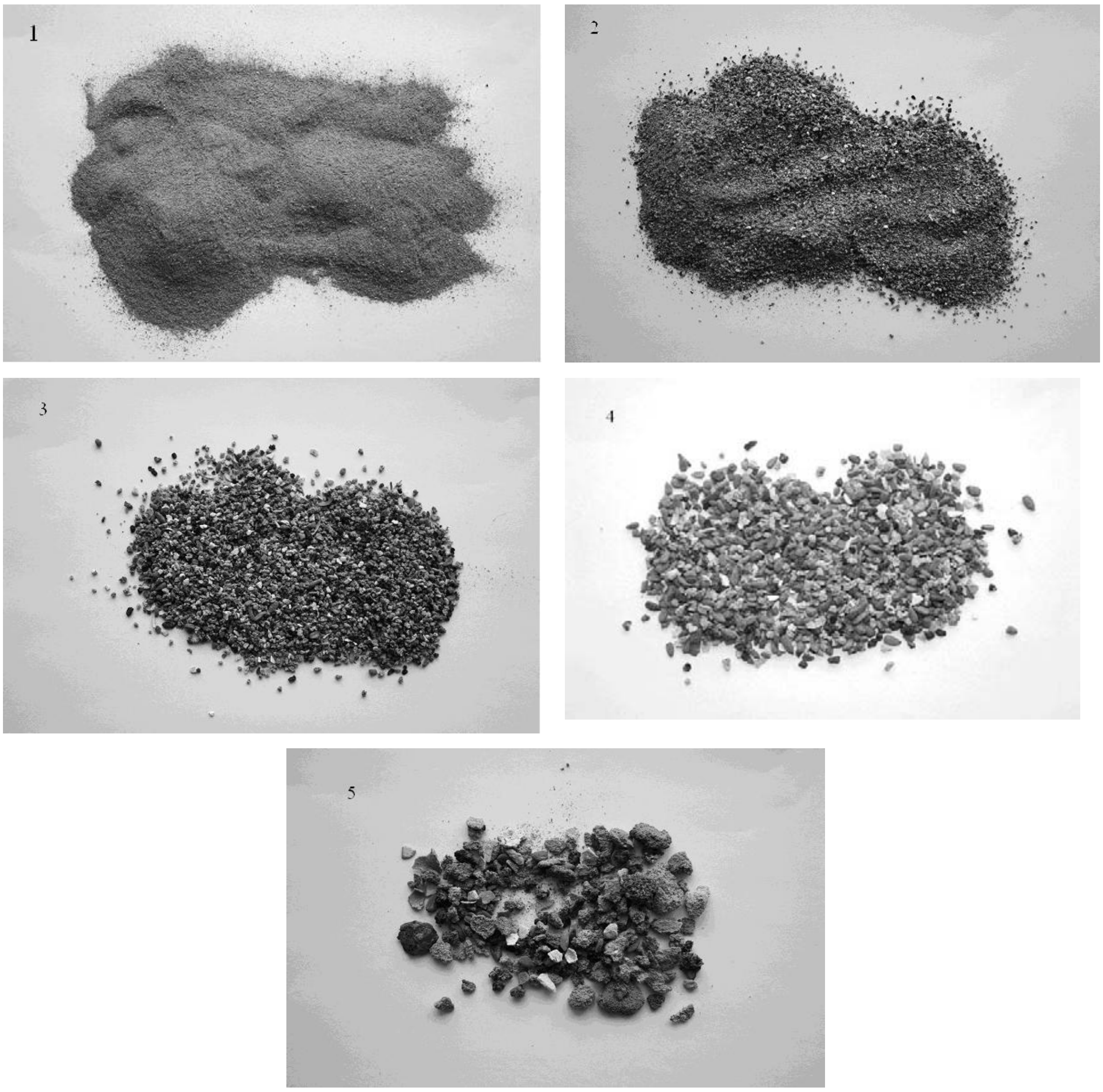

Fig. 4. Images of separate fractions of Moldovan sunflower husk ash: 1: – <1 mm; 2 – 1-2 mm; 3 – 2-3 mm; 4 – 3-5 mm; 5 – >5 mm ash fraction.

Table 4. Ash-granulating conditions and results.

Sample	Humidity of raw materials, %	Granulometric composition of product, %					Mass change after drying, %	pH (10%)	Crushing strength, N/gran,
		>5	3-5	2-3	1-2	<1			
1	28.57	9.77	25.85	17.73	30.70	15.94	8.207	12.76	12.4
2	28.57	10.65	15.81	18.42	37.00	18.12	11.195	12.39	16.9
3	4.38	27.45	22.30	17.53	19.55	13.17	1.655	12.22	18.1
4	6.05	74.54	19.19	4.58	1.07	0.62	4.089	12.04	19.6
5	20.95	15.44	25.17	40.01	14.85	4.53	9.184	12.32	21.1
6	17.14	18.69	15.95	30.46	30.25	4.66	6.496	12.28	15.2
7	13.33	20.10	15.62	33.82	15.23	15.23	7.430	12.44	12.1
8	11.43	29.71	26.72	33.42	7.66	2.49	5.127	12.28	14.6
9	17.14	65.02	30.29	1.80	1.42	1.47	11.841	12.07	16.9
10	28.20	47.31	17.63	15.06	16.05	3.96	16.609	12.03	10.4
11	14.65	19.77	24.15	20.59	22.83	12.65	7.642	11.42	16.4
12	15.13	84.61	8.06	3.47	2.22	1.64	10.002	11.59	15.4
13	24.29	59.66	26.23	9.06	2.80	2.25	16.123	11.75	21.1
14	21.53	35.43	18.20	16.55	23.58	6.25	11.922	11.69	14.6
15	20.78	73.59	16.58	4.28	2.98	2.57	14.022	12.1	19.3
16	18.79	51.33	23.70	12.73	7.47	4.77	11.299	11.98	15.6
17	24.53	16.90	14.23	28.41	34.68	5.78	13.782	11.92	10.1
18	16.49	49.36	32.93	15.26	1.83	0.63	13.643	11.87	19.5
19	29.28	8.05	10.51	15.49	41.42	24.53	5.966	12.67	8.3
20	28.99	7.12	14.58	22.87	39.33	16.10	11.836	12.49	14.7
21	29.95	37.56	19.88	17.11	18.79	6.65	14.565	12.08	9.4
22	29.76	29.98	26.52	26.86	13.93	2.71	18.301	11.89	15.9
23	18.73	10.46	14.28	22.77	43.63	8.86	10.618	12.66	11.3
24	26.09	8.59	13.63	49.47	25.54	2.76	15.458	12.16	11.7

The properties of granular product – granulometric composition, mass change after drying, pH of 10% solution and static crushing strength of 3-5 mm fraction granules – was identified and these results are presented in Table 4.

Sunflower ash was granulated by moistening with water (sample 1) and granulating ash with 50% of recycling (sample 2). For improvement of product properties, ash was mixed with molasses (samples 3 and 4) or samples were moistened with water solution of molasses at different concentrations (samples 5-8). Molasses content in the mixtures prepared for granulation varied from 9.5 to 30.23%. The best product characteristics, as marketable product (diameter of 2-5 mm) yield approximately 65% and the granule crushing strength equals 21.1 N/gran. are obtained with the minimum molasses additive (sample 5). A significant output of marketable fraction (approximately 60%) is obtained also at larger (21.43%) content of molasses (sample 8), but in this case the crushing strength of granules is reduced up to 14.6 N/gran., as well as the granules drying duration being significantly extended. The results show that the largest quantity of marketable fraction is obtained at the minimum and maximum ratio between the M and W (samples 5 and 8), therefore it is inappropriate to increase the content of molasses additive significantly if it is enough to moisten the mixture with water.

When granulating ash with 50% of recycling and using water solution of molasses for moistening of mixture (M:V=1:1) (sample 9), the output of marketable product is approximately 32%, and the static strength of granules equals 16.9 N/gran.

The sunflower ash mixture with SFL, when both components are taken in equal parts, was granulated by moistening with water (sample 10), and using molasses (samples 11 and 12) or its water solutions (samples 13-

Fig. 5. Granulated fertilizer of 0-6-13 grade.

16) as a binding additive. M content in other granulating mixtures varied from 5.8 up to 21.05%. Granule strength of granular product depends on the quantity of M added: the highest (21.1 N/gran.) is in sample 13, where M content is 5.86%. The quantity of marketable granule fractions depends not only on the quantity of the binding additive – M – but also on the general humidity of raw material mix. The best yield of marketable production (approximately about 45%) by granulating sunflower husk ash with M additive was obtained in sample 11, when the M content was 13.29%.

When the ash and SFL mixture containing 50% recycling and water was used for mixture moistening (sample 17), approximately about 43% of marketable fraction was received with granule strength of 10.1 N/gran. When the ash and SFL mixture with 50% was moistened with a water molasses solution (M:W=1:1), marketable fraction contain of approximately about 48%, and granules strength was equal 19.5 N/gran. (sample 18).

Sunflower husk ash (samples 19 and 20) and ash-SFL mixture (samples 21 and 22) were granulated by moistening them with water UFR solution. After ash granulation, at 0.30% of UFR (sample 19), very poor quality indicators are obtained: the output of marketable product is approximately 26%, crushing strength of granules is 8.3 N/gran. If the UFR amount is increased to 0.59% (sample 20), the quality parameters improve: yield of marketable product is approximately 7%, and the crushing strength of granules is 14.7 N/gran. When UFR is used as a binding component, the highest strength of granules (15.9 N/gran.) and the largest yield of marketable product (53%) are obtained in sample 22. In this case the ash-SFL mixture (with UFR content in the mixture) was 0.38% granulated.

When granulation of ash (sample 23) as well as ash-SFL and (sample 24) occurs with 50% of recycling and using water UFR solution for mixture moistening, quite similar quality parameters of granular product were obtained. When granulation of the SFL mixture occurs with 50% of recycling, the yield of marketable product increases up to 63.1%, and the average static crushing strength of granules equals 11.7 N/gran.

After the experimental study it was identified that the granular product can be obtained by granulating ash. Better granular product parameters were obtained by granulation of ash-SFL. The granulation process and the marketable parameters of the product are improved by using molasses or UFR additives. Returning recycling to the granulated mix changes the marketable parameters of a product insignificantly.

The results of granulating the sunflower husk ash and SFL mixture showed that fertilizer of 0-6-13 grade and suitable marketable parameters may by produce. The granular product photo is provided in Fig. 5. The composition of fertilizers is (%): 0.08 N; 5.94 P_2O_5, 12.97 K_2O, 24.27 CaO, 10.00 MgO, 0.03 Na_2O, 0.27 Fe, 0.02 Cu, 0.01 Zn, 0.04 Mn, and 0.06 Mo.

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