KAUNAS UNIVERSITY OF TECHNOLOGY

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THEORETICAL AND TECHNOLOGICAL ASPECTS OF BIOMASS ASH GRANULATION

Summary of Doctoral Dissertation
Technological Sciences, Chemical Engineering (05T)

2015, Kaunas

Doctoral dissertation was prepared by extern in 2006–2014. Dissertation contains data obtained during industrial tests implemented in manufacturing companies, which are the property of CSC "ARVI" & Co.

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The official defence of the dissertation will be held at 1 p.m. on 15 October, 2015 at the public meeting of Dissertation defence board of Chemical engineering science field in the Dissetacion Defence Hall at Kaunas University of Technology.

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Summary of doctoral dissertation was sent on 15 September, 2015.
The doctoral dissertation is available on the internet http://ktu.edu and at the library of Kaunas University of Technology (K. Donelaičio St. 20, LT-44239 Kaunas, Lithuania).

KAUNO TECHNOLOGIJOS UNIVERSITETAS

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BIOMASĖS PELENŲ GRANULIAVIMO TEORINIAI IR TECHNOLOGINIAI ASPEKTAI

Daktaro disertacijos santrauka
Technologijos mokslai, chemijos inžinerija (05T)

2015, Kaunas

Disertacija rengta 2006-2014 metais ir ruošiama ginti eksternu. Disertacijoje naudojami UAB „Arvi“ ir ko gamybinėse įmonėse atliktų laboratorinių ir gamybinių pramoninių bandymų duomenys.

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Disertacija bus ginama viešame Chemijos inžinerijos mokslo krypties disertacijos gynimo tarybos posėdyje, kuris įvyks 2015 m. spalio 15 d. 13 val. Kauno technologijos universiteto disertacijų gynimo salėje.

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Disertacijos santrauka išsiųsta 2015 m. rugsėjo 15 d.
Su disertacija galima susipažinti internetinėje svetainėje http://ktu.edu ir Kauno technologijos universiteto bibliotekoje (K. Donelaičio g. 20, LT-44239 Kaunas).

1. INTRODUCTION

Relevance of the work. Traditional energy sources in Lithuania and throughout Europe are partly dependent on a single supplier therefore it causes serious economic and political problems. Raw materials of traditional energetics – natural gas and coal significantly affect the ecological balance of the world, pollute the environment and increase global warming.

In recent years alternative sources of energy – solar, wind, hydropower as well as biofuels become more important. Specifically Lithuania has been increasing the usage of solar power and biofuels. Biofuel reserves in Lithuania are quite large – insufficiently organized low-value timber waste, sawdust as well as waste of many plants – straw, which could be burned. According to the 2012–2013 data of Lithuanian Department of Statistics and the ratio of grain and straw, 4 million tons of straw were produced in Lithuania, mainly out of winter wheat, barley, winter and spring rape. Spring and winter rape straw constitutes 20 to 30 percent of all crops, which corresponds to 1.2 million tons. By burning these straw about 60 thousand tons of ashes can be obtained. There is a widespread discussion about the possibilities of using biofuels in heat production, but currently the use of straw and ash is not considered rational. Both wood and straw ashes are valuable products for agrochemistry, because they contain various key nutrients: 5–20 % of calcium, 1–3 % of phosphorus, 10–25 % of potassium and some other microelements.

Aforementioned ashes are characterized by alkaline features so they can be used not only as a fertilizer, but also as a neutralizing liming material for acidic soils.

The usage of biomass ash is not effective without special treatment. Since the particle size of ash varies, the spreading of such material into the soil might be difficult, because it could be distributed unevenly. In this case, the agrochemical effects of ash on plants and soil is not optimal.

The most suitable way to improve the physicomechanical properties of the ash is to employ granulation – when agglomeration is controlled and it leads to production of particles with almost the same diameter. Such granular product can be spread into the soil evenly and thus fertilizing plants uniformly.

Since the plasticity of biomass ash is negligible, granulation binders are required, such as clay, kieselguhr, various organic additives.

Some works show that the plasticity of mineral fertilizers could be increased by waste of sugar production from sugar beet – sugar factory lime. This material also can be used as a liming material, because it contains about 40 % of CaO as well as small quantities of some micronutrients beneficial for plants.

There are no data about ash granulation with sugar factory lime. There are also no data about the effect of molasses or urea-formaldehyde resin on ash plasticity. Therefore, these studies are important because their results allow creating compound fertilizers containing phosphorus, potassium and calcium. This product could be used both as fertilizer and liming material.

Aim of the work was to develop theoretical and technological assumptions and to create production technology of compound fertilizers from biomass ashes and other waste materials. Following tasks had to be accomplished in order to achieve the aim of this work:

1. To determine the chemical and physical properties of biomass – rape straw, sunflower husk ashes as well as sugar factory lime and to evaluate their suitability for fertilizer production.
2. To research and evaluate physical and chemical (strengh of granules, granulometric composition, moisture content, pH) properties of granulated biomass with additives and to determine technological parameters of their granulation.
3. To analyze the obtained experimental results by using software and to revise the determined technological parameters of biomass ash granulation, to create principal technological scheme for biomass ash granulation.
4. To produce compound NPK fertilizers by using biomass ash and sugar factory lime as well as to present technological assumptions for the production of compound fertilizers based on their physical and chemical properties.
5. Considering the obtained results, to develop the technology for NPK fertilizer production from biomass ash and sugar factory lime and to implement it in the industry.

Scientific novelty of the dissertation.

1. It was determined that the additives of sugar factory lime, molasses and/or urea-formaldehyde resin activates the granulation process and improves some physical and mechanical characteristics of the product (granulometric composition and strength of granules) or the amount of marketable yield.
2. By using software, the mathematical model of biomass ash granulation process was develop, which complexically describes the dependency of product parameters (granulometric composition, static strength of granules, moisture content) on the experimental conditions (composition of raw materials and moisture content, the amount of recycle).

Practical significance of the dissertation.

1. Optimal technological parameters of biomass ash granulation with sugar factory lime were determined and possible formulas of compound (PK) fertilizers with microelements were presented.
2. The principal technological scheme was created for production of compound (PK) fertilizers using biomass ash and sugar factory lime.
3. Created under laboratory conditions, the production of compound NPK fertilizers was tested under industrial conditions as well; the obtained product was qualitative and was introduced to the fertilizer market.

Approval and publication of research results. The research results are published in 4 articles, two of them are published in cited journals corresponding to the list of Thompson Reuters Web of Knowledge database; three conferences, two of them international and two patents were registered together with co-authors.

Structure and contents of the dissertation. The dissertation consists of an introduction, literature survey, experimental part, results and their discussion, conclusions, list of 176 references and publications, appendixes. The main material is presented in 96 pages, including 35 tables and 36 figures.

Statements presented for defense:

1. Sugar factory lime and molasses have positive effect on the granulation process of biomass ash and improves physical and mechanical properties of product: granulometric composition, strength of granules and increases the amount of marketable yield.
2. By using the mathematical model, the dependence of the product characteristics on the granulation process parameters can be complexically estimated, and determined regularities allow selecting optimal granulation conditions and controlling technological process qualitatively.
3. Under industrial conditions biomass ash can be used for the production of mineral compound fertilizers, the properties of which are consistent with the quality solid fertilizers.

2. EXPERIMENTAL

Materials used in this work were chemically and analytically pure reagents and substances: $Ca(NO_3)_2 \cdot 4H_2O$; $Mg(NO_3)_2 \cdot 6H_2O$; Na_2SO_4; $FeSO_4 \cdot 7H_2O$; $Cu(NO_3)_2 \cdot 3H_2O$; $Zn(NO_3)_2 \cdot 6H_2O$; $Mn(NO)_2 \cdot 4H_2O$; $CoSO_4 \cdot 7H_2O$; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.

The following materials were used for the production of granular fertilizers: Marijampole's sugar factory lime and molasses, urea-formaldehyde resin, Moldavian and Ukrainian sunflower husk ash, rape straw ash produced in laboratory and industry and products of fertilizer industry:

The nitrogen content in samples was determined by the standard method, the phosphorus was determined on a photocolorimeter KFK-2, magnesium and calcium content were determined by the complexonometric titration method, potassium and sodium content was determined on a flame photometer PFP-7.

The atomic absorption spectrometry method was applied for the determination of microelements content and the AAnalyst 400 device from Perkin Elmer Company. In all cases acetylene (C_2H_2) was used to get the flame and for the determination of molybdenum concentration N_2O instead of air was used. Chemically pure or analytically pure materials were used and samples were prepared by decomposing dry material with non-concentrated (1:1) HCl acid, filtering the obtained solution and diluting it in water.

Ash X-ray radiation diffraction analysis was carried out by X-ray diffractometer DRON-6 (Cu K_α radiation, Ni filter, detector's step length – 0.02°, 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) was carried out by NETZCH STA 409 PC Luxx thermal analyzer. Samples were heated to 500 °C, rate of temperature increase was 10 °C/min, air atmosphere.

IR spectra were obtained on a Perkin Elmer FT-IR spectrometer. 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 test substance and 200 mg of potassium bromide.

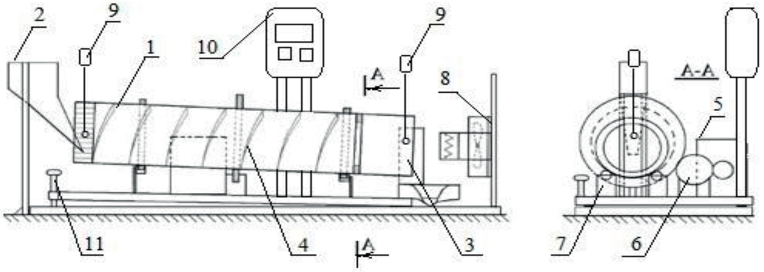

Fig. 2.1. Laboratory rotary drum-type granulator
1 – drum; 2 – supply of raw materials; 3 – product dropout; 4 – drum paddle; 5 – electric motor; 6 – cogwheel; 7 – bearing roll; 8 – supply of hot air; 9 – thermocouple; 10 – control unit; 11 – lock of drum inclination angle

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 70 °C, 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. By using the sunflower husk ash (fraction < 2 mm), samples were granulated in the laboratory technique (sample 1–24).

The resulting granular product, depending on the used contant of W, SFL, M and UFR was dried in an oven from 7 to 21 hours at 60–70 °C and 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±5 °C). Calculations were made using a standard methodology.

SGN (average particle size parameter) is calculated from the results of granulometric composition.

$$\mathrm{SGN} = d_{50} \cdot 100. \tag{1}$$

Average particle size of the fraction d_{50} is the size, which is bigger than 50 % of the product mass and is smaller than 50 % of mass. It (d_{50}) is calculated

$$d_{50} = Z_n + \frac{(50 - C_n)}{(C_{n+1} - C_n)}\left(Z_{n+1} - Z_n\right), \text{ mm} \tag{2}$$

here: Z_n – nominal sieve mesh size in mm, which cumulative approaches, but does not exceed 50 % of the weight; Z_{n+1} – the nominal sieve mesh size in mm, which cumulative approaches and exceeds 50 % by weight; C_n – cumulative weight in % on sieve n; C_{n+1} – cumulative weight in % on sieve n+1.

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

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

Analysis of data using standard spreadsheets (Microsoft Excel) is suitable only for the primary statistical analysis. Therefore, specialized software MATLAB was used in this work. It provides opportunities for better calculations both in comfort and function also permits complex analysis of experimental data for granulation process. While using MATLAB it is possible to determine the optimal conditions for the granulation process, depending on the initial composition of raw materials, experimental conditions and requirements for the final product.

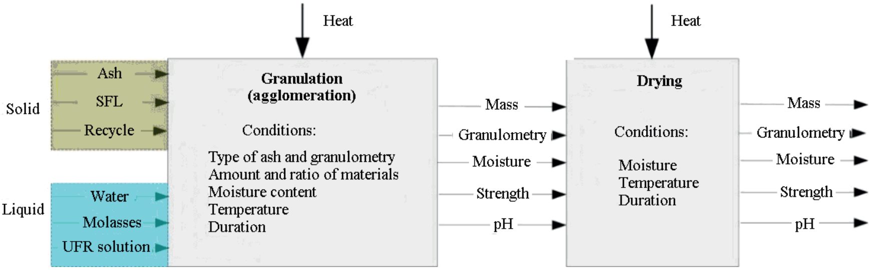

Fig. 2.2. Scheme of ash granulation

The scheme of experimental results analysis is presented in Fig. 2.3.

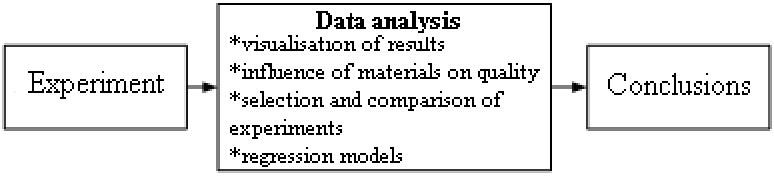

Fig. 2.3. Stages of statistical analysis

3. RESULTS AND DISCUSSION

3.1 Chemical composition and properties of biomass ash

The newest trends in modern industrial research and production are the recycling of agricultural waste (biowaste), the search of alternative energy resources as well as the rational use of raw materials (by-products and waste products). As an alternative to traditional chemical fertilizers ashes of plants can be used, which are originating from agricultural by-products (biofuels) – rape straw or sunflower husk. Different types of ashes – rape straw and sunflower husk, obtained under various burning conditions were experimentally investigated: rape straw burned in a laboratory at 400–500 ºC (RSL), rape straw burned under industrial conditions (RSI), sunflower husk from Ukraine (USH) and sunflower husk from Moldova (MSH).

Table 3.1. The chemical composition of various ashes

Main and secondary nutrients. %					Microelements. mg/kg				
	RSL	RSI	USH	MSH		RSL	RSI	USH	MSH
N	0.01	0.01	0.01	0.01	Fe	1201.87	7369.35	1773.72	2940.46
P_2O_5	6.23	2.36	5.34	10.94	Cu	7.03	193.89	403.65	405.61
K_2O	20.72	8.04	30.68	25.84	Zn	125.06	140.76	463.02	167.23
CaO	23.24	20.34	12.29	19.07	Mn	475.88	998.24	209.49	410.45
MgO	2.12	10.65	14.74	18.58	Co	90.40	15.35	—	0.44
Na_2O	0.19	0.30	0.04	0.03	Mo	806.80	564.34	508.03	472.17

The chemical analysis shows (Table 3.1) that all types of ashes contain some of the main and secondary nutrients: K_2O (from 8.04 to 30.68 %), CaO (from 12.29 to 23.24 %) and MgO (10.65 to 18.58%). Small amount of MgO (2.12 %) was found only in ashes burned in the laboratory. There are also small amounts of P_2O_5 and only trace amounts of N. Contents of microelements vary over a wide range: largest amounts of Fe were detected in RSI, of Mo in RSL, Mn – in RSI. The content of Zn and Cu is a bit lower with the exception of RSL ash – only 7.03 mg/kg. The amounts of cobalt were found to range from 0.44 to 90.40 mg/kg while Ukrainian sunflower husk ash didn't contain cobalt at all. The suitability of ash for the fertilizer production can be determined by the amounts of heavy metals, which in different types of ashes vary very little and are: 1.35–1.80 mg/kg of Cd, less than 0.005 mg/kg of Hg and less than 2.5 mg/kg of Pb.

In order to complement and confirm results of chemical analysis, thermal, thermogravimetric, X-ray diffraction analysis and Fourier transform infrared spectroscopy of ashes were performed.

As presented in Fig. 3.1, DSC-TG patterns of RSL and RSI ashes (curves 1 and 2) are very similar: at 460 °C weight loss (TG) as well as large exothermic peaks (DSC) is observed. Also a small endothermic effect can be seen in DSC curve of RSL ash at 150 °C, which can be explained by decomposition of unburnt components. TG curves of USH and MSH ashes (Fig 3.1 3 and 4) are also similar and do not indicate any significant changes while DSC curves at 90–150 °C contain a few small endothermic effects.

Diffractograms of various ashes (Fig. 3.2) are very similar and contain peaks, which correspond to the interplanar spacings of potassium, calcium and magnesium carbonates, phosphorus, magnesium and calcium oxide, calcium phosphate, sodium and potassium sulfates, and elemental carbon.

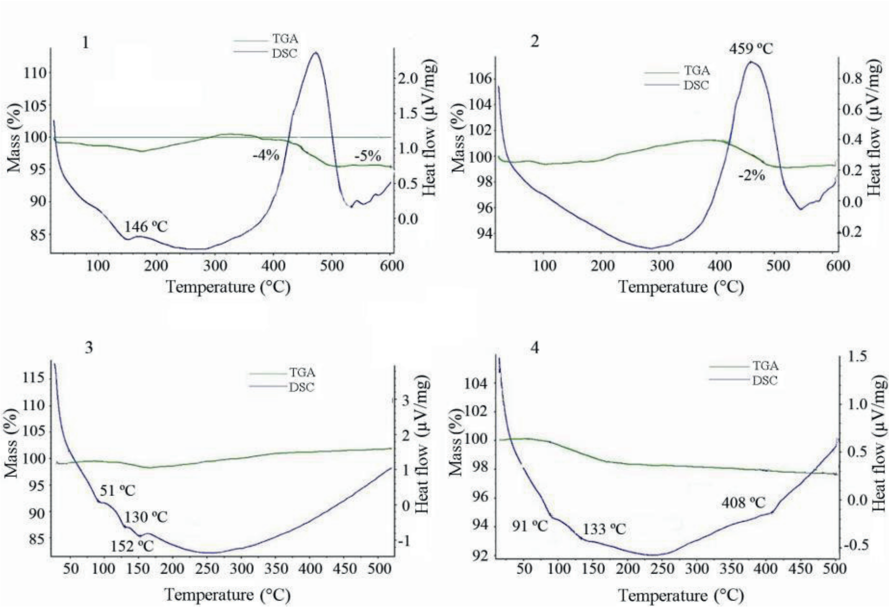

Fig. 3.1. DSC-TG analysis curves of ashes: 1 – rape straw burned under laboratory conditions (RSL); 2 – rape straw burned under industrial conditions (RSI); 3 – Ukranian sunflower husk (USH); 4 – Moldovan sunflower husk (MSH)

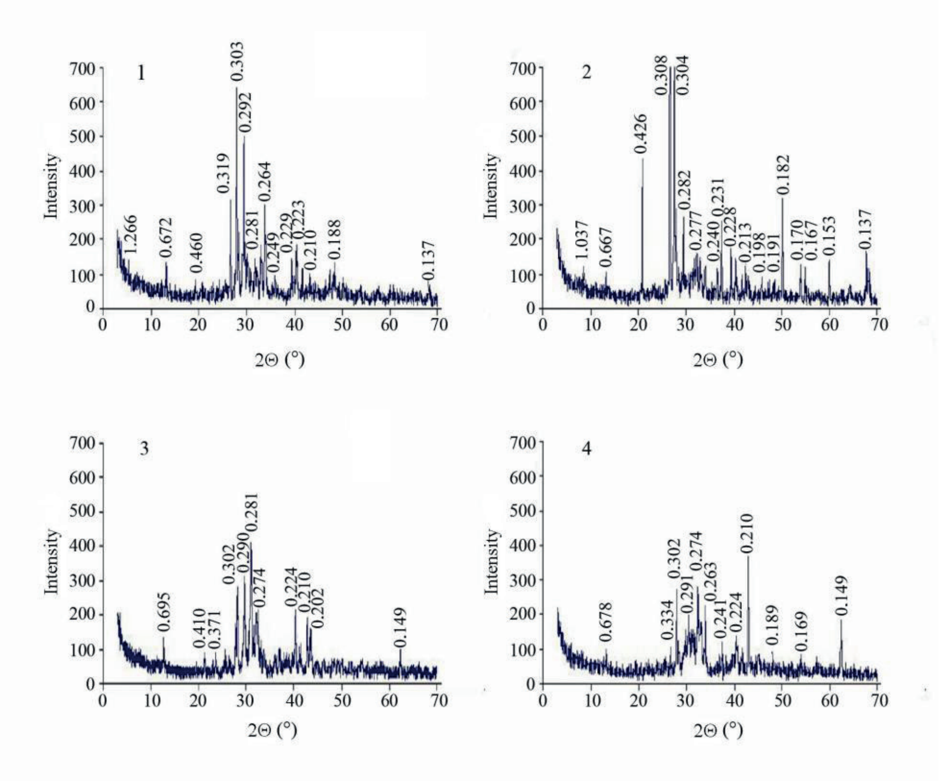

Fig. 3.2. X-ray diffractive curve of ashes: 1 – rape straw burned under laboratory conditions (RSL); 2 – rape straw burned under industrial conditions (RSI); 3 – Ukranian sunflower husk (USH); 4 – Moldovan sunflower husk (MSH)

IR spectra (Fig. 3.3) at 3400–2900 cm^{-1} show a broad absorption band attributable to H_2O molecules and at 2500–1600 cm^{-1} vibrations typical to CO bonds are observed. Very intense vibrations of CO_3^{2-} functional groups in the wavenumber range of 1400–800 cm^{-1} were also identified beside not-so-intense of SO_4^{2-} at 800–700 cm^{-1} and PO_4^{3-} at 600–500 cm^{-1}.

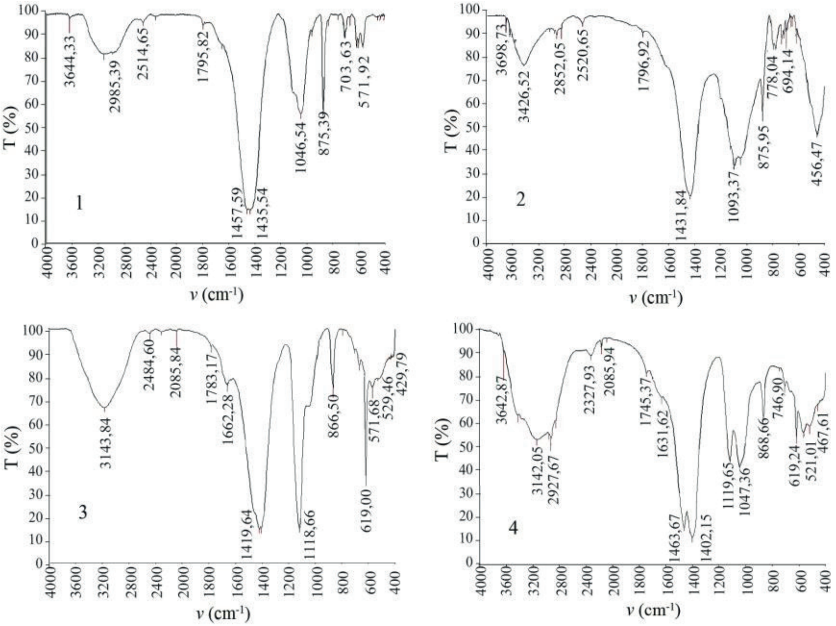

Fig. 3.3. IR spectra of ashes: 1 – rape straw burned under laboratory conditions (RSL); 2 – rape straw burned under industrial conditions (RSI); 3 – Ukranian sunflower husk (USH); 4 – Moldovan sunflower husk (MSH)

3.2 Granulation of biomass ash

In order to determine some optimal parameters of granulation process (composition of raw material, particle size, moisture content) of various organic materials (biomass ash and sugar factory lime) suitable for production of high-quality fertilizers, various mixtures of raw materials were granulated in laboratory conditions.

Granules (product), obtained from rotary drum-type granulator, were dried for about 7 hours in the heating oven at 60–70 °C. All the samples were cooled, fractioned, granulomeric compositions and SGN were determined, static strengths of granules of 3–5 mm fractions and 10 % solution pH values were measured. These results of the first 13 granulated samples are presented in Table 3.2.

Table 3.2. Granulation conditions of various ash and sugar factory lime mixtures

Sample Nr.	Content, %					Moisture content, %
	ash	SFL	water	recycle	sum	
1	0.00	100.00	0.00	0.00	100	27.67
2	0.00	81.97	18.03	0.00	100	18.03
3	100.00 (USH)	0.00	0.00	0.00	100	15.65
4	96.15 (USH)	0.00	3.85	0.00	100	3.85
5	74.07 (USH)	0.00	25.93	0.00	100	25.93
6	71.43 (MSL)	0.00	28.57	0.00	100	28.57
7	35.7 (MSL)	0.00	28.57	35.71	100	28.57
8	75.00 (RSL)	0.00	25.00	0.00	100	25.00
9	60.00 (RSL)	0.00	40.00	0.00	100	40.00
10	31.25(RSL)	0.00	37.50	31.25	100	37.50
11	33.33(RSL)	0.00	33.33	33.33	100	33.33
12	0.00 (RSL)	0.00	28.58	71.43	100	28.57
13	0.00(RSL)	0.00	37.50	62.50	100	37.50

The first sample – sugar factory lime was supplied as waste from sugar mills and it can be characterized by high content of moisture – 27.67 %, the second sample was dried sugar factory lime which was then moistened with 1 % phosphoric acid water solution to obtain the suitable consistency for granulation.

Granulometric composition of both samples was quite similar, but the strength of granules differed. The granules which were obtained by directly granulating moist waste sugar factory lime are two times stronger – 3.8 N/gran. (sample 1). However overall, granulation of sugar factory lime without any additives results in low static strength of granules, poor granulometric composition and subsequent drying causes the granules to fall to dust and become smaller. 10 % solution of the first sample of granular sugar factory lime has a pH of 8.61, while the second sample – 8.44.

In order to evaluate the possibilities of sunflower husk ash granulation experimental runs was carried out using Ukrainian (samples 3–5) and Moldovan (samples 6 and 7) sunflower husk ashes, which varies in moisture content. Sample 3 (USH ash) had 15.65 % of moisture and was granulated without any additional irrigation. Aditionally, the same material was dried up and granulated using the acidified water as irrigation solution. Higher yield of marketable fraction (46.65 %) was obtained when ashes were granulated without additional irrigation, while the highest strength of granules – 19.9 N/gran. was obtained when 3.85 % in acidified water was used for irrigation. The increasing of moisture content up to 25.93 % showed no positive effects. MSH ash granulation was performed at the constant amount of moisture – 28.57 % (samples 6 and 7). The main difference between the two is that the latter was granulated by adding 50 % of the recycle to the mixture of raw materials. Addition of recycle did not increase the yield of marketable fraction but increased the strength of granules a little bit. The analysis of pH values of 10 % solution of granular ashes showed that MSH ash is more alkaline than USH ash.

In similar laboratory conditions, burnt rape straw ash (samples 8–13) was granulated using different amounts of acidified water and the recycle in the mixture of raw materials. The lowest content of marketable fraction (4.99 %) and the highest content of recycle (90.16 %) were obtained during granulation of ash with high content of moisture (37.50 %). The best granulometric composition and the highest strength of granules (6.0 N/gran.) were achieved in the sample 9, which was granulated using a very large amount (40 %) of acidified water.

It can be concluded, that both sugar factory lime and ash, regardless of moisture content, origin of ash, addition of recycle, are difficult to granulate – the yield of marketable fraction and strength of granules does not meet the standard fertilizer quality requirements. At the same time, it confirms the argument, that ash does not have enough plasticity and its agglomeration is difficult. Therefore it needs improvements, specifically – agglomeration activators.

Studies have shown, that the granulation of biomass ash with sugar factory lime at ratio of 1:1 results in the granulated product which has better parameters than separate granulated components: the yield of marketable fraction varies from 16.52 % (sample 14) to 42.64 % (sample 18). The analysis of various biomass ashes influence on particle size shows, that when similar amount of acidified water (samples 14, 16 and 17) is used, granulation of sugar factory lime with sunflower husk ash (USH and MSH) results in product with better granulometric composition as comared to rape straw ash. Also granules made out of USH and MSH can be characterized by three times higher static strength (10.1–10.8 N/gran.) than RSL (3.2–3.8 N/gran.).

In order to improve the agglomeration of ashes, other additives for granulation – molasses (M) and urea-formaldehyde resin (UFR) were studied as well. Various mixtures were granulated and each of them consisted of every type of ashes, sugar factory lime, a certain amount of recycle, molasses solutions in water (MWS) produced in different proportions – M:W = 3:1; 2:1; 1:1; 1:2 and/or formaldehyde resin (1–5 %) solution in water. The composition of these mixtures (samples 19–32), prepared used rape straw ash obtained under laboratory conditions, is presented in Table 3.3.

Granular products were dried in an heating oven at 60–70 °C, for 7 to 56 hours, depending on the moisture content and especially on the amount of molasses or formaldehyde resin additive used, and then fractioned. Products were characterized by calculated SGN, static strength of granules and pH of 10 % solution. Analysis results are presented in Table 3.4.

Table 3.3. Composition of granulated mixtures

Sample Nr.	Content, %							Moisture content, %
	ash (RSL)	SFL	M	UFR	water	recycle	sum	
19	58.82	0.00	13.76	0.00	27.41	0.00	100	30.16
20	58.82	0.00	20.59	0.00	20.59	0.00	100	24.71
21	50.00	0.00	25.00	0.00	25.00	0.00	100	30.00
22	58.82	0.00	27.41	0.00	13.76	0.00	100	19.25
23	58.82	0.00	30.88	0.00	10.29	0.00	100	16.47
24	35.74	35.74	9.51	0.00	19.01	0,00	100	30,80
25	35.71	35.71	14.29	0.00	14.29	0.00	100	27.03
26	35.74	35.74	19.01	0.00	9.51	0.00	100	23.20
27	35.71	35.71	21.43	0.00	7.14	0.00	100	21.31
28	35.71	35.71	28.57	0.00	0.00	0.00	100	15.60
29	35.71	0.00	14.29	0.00	14.29	35.71	100	17.14
30	19.23	19.23	11.54	0.00	11.54	38.46	100	19.17
31	54.35	0.00	0.00	0.46	45.20	0.00	100	45.20
32	36.23	36.23	0.00	0.28	27.26	0.00	100	37.29

The results show, that the addition of MWS to the mixture of raw materials improves granulometric composition of the product and increases the strength of produced granules. Granulation of ashes without the additive of sugar factory lime (samples 19–23) results with the maximum strength of 64.5 N/gran. which is attributed to the sample 23 – RSL constitutes 30.88 % and moisture content is 16.47 %. The highest yield of marketable fraction was obtained when granulating sample 22 – rape straw ash with molasses (27.41 %). Under these conditions the granulation resulted in production of 45.15 % of granules having a diameter between 2 to 5 mm (SGN = 604). Similar SGN value (716) was obtained in the sample 23.

Granulation of the ash with 50 % of recycle (sample 29) yielded granules with adequate strength - 24.4 N/granule, but the marketable fraction decreased down to 22 % of the total amount of the product (SGN was 659). It can be stated, that the best RSL product can be obtained when granulation proceeds with the addition of large quantities of molasses (MWS with M:W = 3:1) and no recycle is applied. However, it takes 35 hours to dry such sample, so from the technological and economical standpoint it is not acceptable.

After the granulation of ash with the binding material – urea-formaldehyde resin (sample 31) it was determined, that obtained product was of worse quality as compared to the one with molasses – the yield of marketable fraction was about 25 % and the strength of granules – 8.4 N/gran.

The same concentration molasses solutions in water were used to granulate mixtures of ash and sugar factory lime (samples 24–28), also for comparison sample 29 was granulated with the addition of recycle. High strength of granules (30.4 N/gran.) can be attributed to the sample 32 which contained 28.5 % of pure molasses. But obtained product consists predominantly of large granules – bigger than 5 mm in diameter granules constitutes about 81 %, while the marketable fraction only 17 %. In addition, the obtained product is very moist and sticky, so it required the drying time of 56 hours. Larger amounts of marketable fraction were obtained when initial mixture is irrigated with MWS. It was found, that sample 24 had the best yield of marketable fraction – 54.5 % and it was produced when irrigating raw materials with MWS (M:W = 1:2). Although granules with the highest strength (33.9 N/gran.) were obtained when the irrigation with MWS of M:W = 2:1 was applied (sample 26).

Table 3.4. Prameters of product granulated with RSL

Sample Nr.	Granulometric composition, %					SGN	Mass decrease drying, %	pH (10 % solution)	Strength, N/gran.
	>5	3–5	2–3	1–2	<1				
19	22.84	14.44	16.43	23.62	22.67	223	15.765	11.33	20.4
20	61.35	21.90	11.54	4.52	0.69	1044	8.815	10.89	38.5
21	25.46	14.45	15.60	24.22	20.27	235	17.282	10.48	6.6
22	25.52	25.01	20.14	22.61	6.72	604	7.259	10.86	19.6
23	39.39	25.27	19.44	13.01	2.88	716	11.317	10.89	64.5
24	24.77	27.08	27.50	17.54	3.12	614	24.231	10.74	8.4
25	16.55	15.29	17.98	30.49	19.69	199	15.051	10.25	8.0
26	44.89	26.18	20.25	7.84	0.84	761	15.672	10.46	33.9
27	48.43	25.26	19.21	6.28	0.82	788	14.934	10.84	28.0
28	81.05	12.86	4.36	1.46	0.26	1087	14.163	10.64	30.4
29	42.90	10.04	12.02	25.42	9.62	659	0.455	11.19	24.4
30	25.81	16.31	16.14	36.70	5.03	251	11.914	10.88	20.5
31	13.22	11.75	13.53	30.57	30.92	162	22.305	10.71	8.4
32	18.56	19.10	19.18	30.92	12.24	236	28.512	10.61	11.4

Granulation of ash and sugar factory lime with addition of recycle (sample 30) and MWS (M:W = 1:1) resulted in the product of poorer granulometric composition – amount of marketable fraction is 32.45 % and the strength of granules – 20.5 N/gran. If urea-formaldehyde resin is used as the binding material instead of molasses during rape straw ash granulation with sugar factory lime (sample 32), the marketable fraction of product reaches 38 %, while the strength of granules – 11.4 N/gran. In this case, parameters of product are worse than when using MWS. The obtined granular product is alkaline (pH ranges from 10.3 to 11.2) and therefore can be used as a liming material.

Different composition mixtures of rape straw ash prepared under industrial conditions (RSI) with the addition of sugar factory lime and binding additives (MWS and UFR) as well as with or without 50 % recycle (samples 33–48) were also granulated. Composition of these mixtures is presented in Table 3.5.

Table 3.5. Composition of granulated mixtures

Sample Nr.	Content, %							Moisture content, %
	ash (RSP)	SFL	M	UFR	water	recycle	sum	
33	70.67	0.00	14.66	0.00	14.66	0.00	100	17.60
34	43.48	43.48	6.52	0.00	6.52	0.00	100	19.86
35	76.92	0.00	0.00	0.23	22.85	0.00	100	22.85
36	62.11	0.00	0.00	0.62	37.27	0.00	100	37.27
37	65.22	0.00	0.00	0.70	34.09	0.00	100	34.09
38	64.38	0.00	0.00	1.29	34.33	0.00	100	34.33
39	57.80	0.00	0.00	1.73	40.46	0.00	100	40.46
40	41.67	41.67	0.00	0.17	16.50	0.00	100	28.03
41	41.32	41.32	0.00	0.35	17.01	0.00	100	28.44
42	39.68	39.68	0.00	0.79	19.84	0.00	100	30.82
43	39.37	39.37	0.00	1.57	19.69	0.00	100	30.58
44	40.43	40.43	0.00	1.62	17.52	0.00	100	28.71
45	34.48	0.00	0.00	0.62	30.41	34.48	100	30.41
46	20.00	20.00	0.00	0.40	19.60	40.00	100	25.13

Experimentally obtained granular product was dried for 7 to 14 hours at 60–70 °C, depending on the content of molasses or formaldehyde resin and then analyzed. Parameters of granular product are presented in the Table 3.6. Comparison of results obtained during granulation of RSL and RSI ashes with or without addition of sugar factory lime mixture and using MWS (M:W = 1:1) shows, that in the latter case granulation requires lower content of moisture and results in a slightly stronger granules while the yield if marketable fraction stays the same (samples 19, 20, 33 and 34). It can be stated, that since there are no substantial differences in granulation parameters, the burning conditions of rape straw ash is not relevant.

After this experimental phase UFR solution influence on the granulation of RSI was investigated in more detail, because so far it has not yielded satisfactory results.

RSI ash (samples 35–39) was granulated with different amounts of UFR (0.23–1.73 %) binder and it was determined, that the use of certain concentration (1–2 %) UFR solutions, which corresponds to the content of 0.62 and 1.29 % in the mixture of raw materials, results in 46 % yield of marketable fraction (samples 36 and 38), while other amounts of UFR decrease this value. Accordingly, the highest SGN was also obtained in samples 36 and 38, which can be linked to the most suitable moisture content for the granulation.

When the content of UFR binder in raw materials is 0.23 %, marketable fraction of 22 % can be obtained (sample 35) and if UFR content reaches 1.73 %, the yield also increases to 40 % (sample 39). The strength of these granules also almost directly depends on the amount of UFR binder, because minimal strength (8.7 N/gran.) can be attributed sample 35 and highest (15.2 N/gran.) – to sample 39 (while UFR content increases from 0.23 % to 1.73 % respectively).

Table 3.6. Parameters of RSI granulation with UFR

Sample Nr.	Granulometric composition, %					SGN	Mass decrease drying, %	pH (10 % solution)	Strength, N/gran.
	>5	3–5	2–3	1–2	<1				
33	9.02	10.17	18.40	55.61	6.80	178	5.087	10.71	10.4
34	26.62	18.71	24.99	24.76	4.92	281	14.139	11.12	10.9
35	3.53	5.17	16.53	30.53	44.24	119	10.304	11.87	8.7
36	13.74	20.86	25.07	28.35	11.98	239	10.276	12.96	10.7
37	4.19	9.89	17.77	37.70	30.44	152	9.956	12.99	9.0
38	10.10	23.34	23.20	25.26	18.10	229	15.375	12.77	13.1
39	5.02	12.06	27.97	30.86	24.09	184	15.764	12.87	15.2
40	2.66	7.06	15.51	44.12	30.66	144	11.304	11.27	7.2
41	21.21	32.56	26.23	11.95	8.05	623	16.222	12.12	6.0
42	30.00	41.87	17.27	6.10	4.76	704	10.892	11.76	10.0
43	59.62	21.12	4.86	5.65	8.75	1039	14.341	12.36	16.1
44	27.71	30.93	19.44	10.42	11.49	656	17.632	11.84	12.3
45	1.05	4.74	20.10	45.32	28.78	147	13.917	12.28	12.3
46	2.41	6.99	17.35	36.41	36.84	136	17.006	11.77	11.9

When the content of UFR binder in raw materials is 0.23 %, marketable fraction of 22 % can be obtained (sample 35) and if UFR content reaches 1.73 %, the yield also increases to 40 % (sample 39). The strength of these granules also almost directly depends on the amount of UFR binder, because minimal strength (8.7 N/gran.) can be attributed sample 35 and highest (15.2 N/gran.) – to sample 39 (while UFR content increases from 0.23 % to 1.73 % respectively).

RSI ash mixed with sugar factory lime (samples 40–44) in equal parts was granulated with various amounts of UFR – changing from 0.17 % to 1.62 %. Direct dependence between the static strength of granules and the content formaldehyde resin was observed. The highest-strength granules (16.1 N/gran.) are obtained when the content of UFR in the mixture is 1.57 % (sample 43). Also while using the UFR aqueous solutions as a binder, the yield of marketable fraction varies between 22.57 % (sample 40, UFR 0.35 %) and 59.14 % (sample 41, UFR 0.35 %). Calculated SGN has a very high value in all cases, particularly sample 43 stands out when 59.62 % of the obtained granules has a diameter larger than 5 mm.

While granulating ash (sample 45) and mixture of ash and sugar factory lime (sample 46) with 50 % of recycle and UFR aqueous solutions as irrigation agent, lower quality product was received with lower content of marketable fraction. Similarly, the application of recycle somewhat lessens the strength of granules as compared the the product where no recycle was used.

Further experiments were conducted by granulating sunflower husk ash from Moldova (MSH). Under laboratory conditions, MSH ash was granulated alone and with sugar factory lime, with or without recycle as well as by adding some additives, which improves fertilizers' quality (molasses or UFR). Samples 47–66 were granulated by using MSH (Table 3.7).

Table 3.7. Composition of granulated mixtures

Sample Nr.	Content, %							Moisture content, %
	ash (MSH)	SFL	M	UFR	water	recycle	sum	
47	71.43	0.00	9.52	0.00	19.05	0.00	100	20.95
48	71.43	0.00	14.29	0.00	14.29	0.00	100	17.14
49	71.43	0.00	19.05	0.00	9.52	0.00	100	13.33
50	71.43	0.00	21.43	0.00	7.14	0.00	100	11.43
51	78.13	0.00	21.88	0.00	0.00	0.00	100	4.38
52	69.77	0.00	30.23	0.00	0.00	0.00	100	6.05
53	41.21	41.21	5.86	0.00	11.72	0.00	100	24.29
54	41.67	41.67	8.33	0.00	8.33	0.00	100	21.53
55	39.47	39.47	14.00	0.00	7.05	0.00	100	20.78
56	40.54	40.54	14.19	0.00	4.73	0.00	100	18.79
57	43.35	43.35	13.29	0.00	0.00	0.00	100	14.65
58	39.47	39.47	21.05	0.00	0.00	0.00	100	15.13
59	35.71	0.00	14.29	0.00	14.29	35.71	100	17.14
60	20.49	20.49	9.02	0.00	9.02	40.98	100	16.49
61	70.42	0.00	0.00	0.30	29.28	0.00	100	29.28
62	70.42	0.00	0.00	0.59	28.99	0.00	100	28.99
63	40.54	40.54	0.00	0.19	18.73	0.00	100	29.95
64	40.54	40.54	0.00	0.38	18.54	0.00	100	29.76
65	40.54	0.00	0.00	0.19	18.73	40.54	100	18.73
66	19.74	19.74	0.00	0.42	20.63	39.47	100	26.09

The resulting granular product was dried for 7 to 14 hours at 60–70 °C, depending on the content of molasses or formaldehyde resin. Quality parameters of granular product are presented in Table 3.8. Sunflower husk ash (MSH) was granulated by irrigating it with molasses aqueous solutions of various concentrations (samples 47–50) or mixing it with pure molasses (samples 51–52). The content of molasses in the granulation mixture varied from 9.5 % to 30 %. The maximum static strength of 2–5 mm granules was received in samples 47 and 52 which correspond to the molasses content of 9.5 % and 30.23 % respectively. The yield of marketable fraction depends on the total moisture content of molasses and raw materials. The largest amount of product (65.18 %) was obtained when granulating sunflower ash with MWS (ratio M:W = 1:2) and it contains 9.5 % of molasses (sample 47). Such product consists predominantly of 2–3 mm granules, because the estimated SGN of these samples ranges between 250 and 275, while only in one case (sample 50) increases to 648. Ash granulation with only molasses, produces high-strength granules (18.1 to 19.6 N/gran.), but SGN values are also much higher – between 300 and 1076 and they needed 24 hours to dry. 10 % solutions of granular products are very similar in all cases – varies from 12.04 to 12.44 and are strongly alkaline.

Table 3.8. Parameters of granulated MSH

Sample Nr.	Granulometric composition, %					SGN	Mass decrease drying, %	pH (10 % solution)	Strength N/gran.
	>5	3-5	2-3	1-2	<1				
47	15.44	25.17	40.01	14.85	4.53	277	9.184	12.32	21.1
48	18.69	15.95	30.46	30.25	4.66	250	6.496	12.28	15.2
49	20.10	15.62	33.82	15.23	15.23	258	7.430	12.44	12.1
50	29.71	26.72	33.42	7.66	2.49	648	5.127	12.28	14.6
51	27.45	22.30	17.53	19.55	13.17	300	1.655	12.22	18.1
52	74.54	19.19	4.58	1.07	0.62	1076	4.089	12.04	19.6
53	59.66	26.23	9.06	2.80	2.25	1039	16.123	11.75	21.1
54	35.43	18.20	16.55	23.58	6.25	640	11.922	11.69	14.6
55	73.59	16.58	4.28	2.98	2.57	1074	14.022	12.10	19.3
56	51.33	23.70	12.73	7.47	4.77	1006	11.299	11.98	15.6
57	19.77	24.15	20.59	22.83	12.65	271	7.642	11.42	16.4
58	84.61	8.06	3.47	2.22	1.64	1093	10.002	11.59	15.4
59	65.02	30.29	1.80	1.42	1.47	1055	11.841	12.07	16.9
60	49.36	32.93	15.26	1.83	0.63	796	13.643	11.87	19.5
61	8.05	10.51	15.49	41.42	24.53	161	5.966	12.67	8.3
62	7.12	14.58	22.87	39.33	16.10	186	11.836	12.49	14.7
63	37.56	19.88	17.11	18.79	6.65	675	14.565	12.08	9.4
64	29.98	26.52	26.86	13.93	2.71	649	18.301	11.89	15.9
65	10.46	14.28	22.77	43.63	8.86	194	10.618	12.66	11.3
66	8.59	13.63	49.47	25.54	2.76	244	15.458	12.16	11.7

Sunflower ash mixed with sugar factory lime in two equal parts was granulated with irrigation agent MWS (samples 53–56) and using pure molasses (samples 57 and 58). The content of molasses in the mixture prepared for granulation ranged between 5.86 and 21.05 %. As the data in Table 3.8 show, the static strength of product granules varies between 14.6 N/gran. and 21.1 N/gran., when content MWS is 8.33 % (ratio M:W = 1:1) and 5.86 % (ratio M:W = 1:2) respectively. Thus, the produced granules are stronger when certain optimal amount of molasses is used. Analysis of granulometric composition of these samples shows, that samples contains large amount of large fraction (> 5 mm) granules and it is confirmed by the calculated values of the SGN, which are very high (over 1000) in many cases. The highest yield of marketable fraction - 34.75 % and SGN value of 640 are obtained when granulating sunflower husk ash with 8.33 % of MWS (samples 54) although these results are also insufficient.

Granulation of ash and sugar factory lime mixture with only molasses of 13.21 % content, resulted in the majority of granules being of 1 – 3 mm diameter with SGN = 271. The increase of molasses content to 21.05 % also increased the size of granules – 84.61% of them being larger than 5 mm and the calculated SGN is very high – 1093. After 24 hours of drying, the strength of marketable fraction granules in both cases is sufficient and is very similar – 16 N/gran. 10 %

solutions of granulated ash and sugar factory lime with MWS are highly alkaline, but pH values are slightly lower – between 11.42 and 12.10 than of granulated ash.

Samples 59 and 60 consists of granulated ash and mixture of ash and sugar factory lime with 50 % of recycle and irrigation agent MWS (ratio of M:W = 1:1). Granulated product of ash and sugar factory lime mixture is somewhat better product than granulated ash alone because the yield of marketable fraction is about 48 % and the static strength of these granules is 19.5 N/gran. However, 50 % of recycle has not made any significant improvement to the characteristics of granular product, as calculated SGN values are 796–1000 and the static strength of granules varies between 16.9 and 19.5 N/gran. These parameters are not very different from the results obtained during granulation without recycle.

Sunflower ash and ash-sugar factory lime mixture were granulated by adding different amounts of UFR (from 0.19 to 0.59 %) aqueous solutions (samples 61–64). The granulated products of ash and mixture of ash and sugar factory lime with a smaller amount of UFR (0.3 % and 0.19 %) is characterized by lower static strength of granules (8.3 N/gran. and 9.4 N/gran.) and lower content of marketable fraction (26.00 % and 36.99 %) as compared to the same raw materials granulated with higher amounts of UFR (0.59 % and 0.38 %): 14.7 N/gran. and 15.9 N/gran.; 37.45 % and 53.38 % respectively. In general, the best results were achieved with the sample 62 when content of UFR is 0.59 %, and content of water – 28.99 %.

Granulation of similar mixtures of materials, but this time with application of recycle (50%) and irrigation with 2 % aqueous solution UFR (samples 65 and 66), in both cases yielded quite similar granulometric composition of the product, estimated SGN values being 194 and 244. Static strength of obtained granules was also similar with the higher value attributable to the product granulated with recycle – 11.3 N/gran. and 11.7 N/gran. This means that the use of recycle and irrigation of raw materials with UFR solution improves the quality of granulated product.

Some tests were performed with ashes from Ukraine. Granulation results with molasses solution in water (M:W = 1:1) and 5 % aqueous solution of UFR has shown, that better product is obtained while using M as a binder: granules are stronger – 16.3 N/gran., but larger granules prevail (SGN = 1062). In both cases the obtained products are alkaline – pH is 11.

The evaluation of laboratory test results suggests that the mixture of ash and sugar factory lime granulates better than separate components. Granulation of sunflower husk ash while irrigating with MWS or UFR solutions produced better results than the granulation rape straw ashes under similar conditions. Furthermore, with optimal amount of MWS as a binder, granulation of biomass runs better and higher strength granules are obtained as compared to granulation when UFR as a binder is used. However, the use of molasses makes system become more sensitive to the concentration and amount of the binder, making it more difficult to control. The use of recycle does not increase the yield of marketable fraction or granule's strength. Regardless of the type of raw materials and a binder used, 10 % solution of granular product is strongly alkaline, so the product has the properties of liming material.

3.3 Biomass ash with additives granulation technology

With the use of binders, such as aqueous solutions of molasses or urea-formaldehyde resin, ecological, granular and user-friendly biomass ash can be obtained. This product can be produced using a simple, batch operation and small-scale (50 tons/month) technology, which principal scheme is presented in Fig. 3.4.

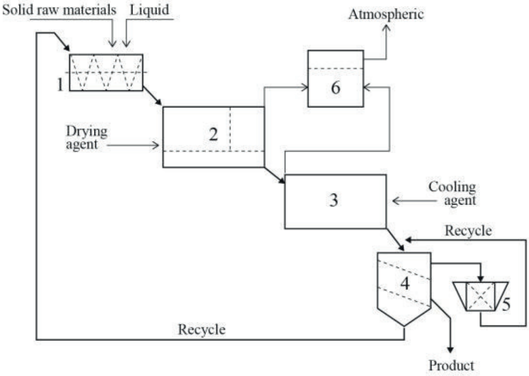

Fig. 3.4. Technological scheme for production of granulated biomass ash: 1 – mixer; 2 – rotary drum granulator; 3 – cooler; 4 – sieving machine; 5 – shredder

Biomass ash is packaged in bags (500 or 1000 kg) which can be transported to the company by auto transport or railway wagons. After the unloading, the fork-lift trucks transport bags to the warehouse of raw materials. In some cases, biomass ash may be transported in bulk, so provision should be made for making storage space for bulk materials.

During granulation process, biomass ashes would be poured into the metering hopper for solid raw materials and then constantly transported to the high intensity (eg., "Pug Mill") paddle mixer (1). The small fraction of biomass ash fraction (recycle) is supplied to the paddle mixer as well as other solid or liquid additional components. There the mass of components is constantly heated with steam, irrigated with water and transported to the rotary drum-type granulator (2). The granulator-dryer can be supplied with steam and water, so that during rotation of the drum particle agglomeration would proceed and granules of appropriate size would form.

Granular product is then transported to the cooler (3), where the granules cools down to 40 °C due to the opposite flow of supplied air. After cooling, granules (larger than 5 mm in diameter) are separated on the double-meshed sieve (4) and directed to the shredder (5). The sieved granular product is transported to the bins of product warehouse and then is carried by mobile bucket loader to packaging or bulk product loading facilities. The smallest fraction from underneath the lower mesh of the sieve (4) is again directed to the mixer (1).

Granulated biomass ash is packed in bags of 50 to 500 kg and can be stored in the company's territory. In order to improve the granular product with better physical properties, to reduce the hygroscopicity or to improve strength, technological process can be provided with nodes for spraying the curing agent (wax or paraffin).

The technological process is carried out without any by-products, is simple and easy to operate. All the equipment can be selected according to the planned amount of produced granular biomass ash. The technological process can operate continuously or produce suitable batches.

Granulation results of ashes and mixture of ashes and sugar factory lime with additives show that under certain conditions biomass ash can be granulated and the obtained product satisfies the usual criteria of fertilizer requirements. Due to a sufficiently alkaline pH values, the granulated product is suitable for the use as a fertilizer and as a liming agent. However, the granulation of biomass ash consumes large amounts of moisture and therefore considerably increases the drying time and thus energy consumption. Moreover, since biomass ashes and sugar factory lime does not contain nitrogen, PK fertilizer-liming material is obtained.

3.4 Biomass ash for the production of NPK fertilizers

Biomass ash and binder can be used to produce fertilizers containing potassium, phosphorus, calcium and some microelements, but it does not contain nitrogen and it has limited PK formula. The market for such type fertilizers is not explored in detail; therefore the demand may be limited moreover the supply of high-quality ash is not sufficient to establish large-scale production of such products. It is therefore beneficial to assess the possibilities to granulate ash together with standard fertilizer raw materials in various ratios. Under laboratory conditions while using industrial raw materials, 8-20-25+CaO+S NPK compound fertilizers were granulated with the addition of 11 % of modified raw biomass ashes (USH) and sugar factory lime. Selected composition for granulation is very similar to the popular 8-20-30 NPK fertilizer which is characterized by good physical characteristics.

The influence of biomass ash and sugar factory lime additives on the properties of the granular product – the amount of marketable fraction, SGN, granule's strength and pH was investigated. Also various ratios of raw materials and recycles as well as their influence on the granulation process parameters of the product (8-20-25+Ca+S NPK fertilizers) was determined. As the raw materials KCl, ammonium sulfate, ammonium and diammonium phosphate, sugar factory lime and biomass ash were used to produce 8-20-25+Ca+S fertilizer. Granulation process was maintained under the same conditions as while granulating ash. After the granulation, product was fractioned and analyzed. The physicochemical parameters of obtained product are presented in Table 3.9.

Table 3.9. Physicochemical parameters of 8-20-25+Ca+S fertilizer

Sample Nr.	Raw materials		Granulometric composition, %					SGN	Mass decrease drying, %	pH (10 % solution)	Strength, N/gran.
	Recycle, %	Moisture, %	>5	3–5	2–3	1–2	<1				
1	–	8.11	7.20	10.16	11.41	33.35	37.88	136	2.64	6.80	9.06
2	–	7.24	3.72	7.28	8.21	27.18	53.61	43	4.82	6.80	9.84
3	20	8.49	3.84	7.13	8.95	36.25	43.82	117	4.30	6.60	12.56
4	20	10.17	14.86	13.69	21.71	46.81	2.96	201	3.95	6.58	10.30
5	20	10.98	18.58	21.88	19.01	39.28	1.25	250	3.74	6.60	10.06
6	40	8.85	3.88	7.67	9.27	46.75	32.42	138	3.27	6.64	11.03
7	40	9.69	5.15	26.67	47.01	20.23	0.93	261	4.66	6.57	11.19
8	40	10.51	9.42	28.30	41.34	20.73	0.20	270	4.62	6.63	11.98
9	60	7.51	0.19	1.51	11.17	69.93	17.20	147	2.41	6.61	11.11
10	60	9.21	0.28	3.53	47.62	46.89	1.68	203	4.71	6.59	12.42
11	60	10.04	1.27	9.98	54.43	33.86	0.46	229	4.62	6.62	10.43
12	80	7.89	0.29	2.32	13.51	60.56	23.32	144	3.06	6.60	9.18
13	80	8.73	0.11	1.80	43.73	51.73	2.64	192	3.12	6.54	11.38
14	80	9.56	0.15	1.53	50.94	45.34	2.04	205	3.52	6.50	11.31

Samples 1 and 2 were granulated using only the initial mixture of components while other samples were granulated with the addition of 20, 40, 60 and 80 % of recycle.

As results in the Table 3.9 show, that the best product was obtained during granulation of samples 7 and 8 which corresponds to 40 % of recycle, and moisture content between 9,69 and 10,51 %. Under these conditions, the yield of marketable fraction constitutes from 69.64 to 73.68 %, and the static strength of granules is 11.19 N/gran. – 11.98 N/gran. The pH of 10 % solution of fertilizer is ~ 6.6.

It is evident, that physicochemical properties of produced fertilizers changes depending on the recycle content and if no recycle is applied – the worst product is obtained with minimal marketable fraction of only 21.56 %. Increasing the amount of recycle up to 40 %, the amount of marketable fraction also increases. Further increasing of recycle just worsens the quality of the product. The yield of marketable fraction depends also on the moisture content of initial mixture. At the same amount of recycle used higher moisture content of initial mixture results in larger amount of marketable fraction.

In summary it can be stated, that the use of biomass leads to the production of high-quality granulated 8-20-25+CaO+S NPK fertilizer. Marketable fraction of the granulated product depends on the moisture content in the mixture of raw materials and maximum yield (up to 69.64%) is obtained when the moisture content is 10–11 %. In almost all cases SGN value is not less than 300 and only one time is 43 (when moisture content is 7.24 %). The static strength of granules and pH of 10 % solution varies only slightly: from 9.06 to 12.56 N/gran. and from 6.5 to 6.8 respectively. It was also determined, that contrary to biomass ash or ash and sugar factory lime granulation, the granulation of 8-20-25+CaO+S NPK fertilizer benefits from the addition of recycle and in this case 40 % of recycle improves quality the best.

Furthermore, granulation of NPK fertilizer containing biomass ash and sugar factory lime does not require any additional binders or higher moisture content, so the drying time can be reduced considerably as well as the energy consumption.

3.5 Statistical modelling of fertilizer granulation process

It is widely acknowledged that the application of process modelling can bring important rewards leading to better understanding, improved system design, and better control of these systems. One of the typical examples suffering from the insufficient understanding of the process behaviour with a lack of available modelling tools is agglomeration process Complex interrelations between process variables and their strong dependence on properties of process equipment restrict the development of mechanistic (white box) model. However, it is possible to measure, store and retrieve process sensors' data and afterwards perform statistical analysis to "mine" some knowledge. For this purpose, descriptive and inferential statistics need to be used.

Data analysis methods may be divided into graphical and numerical ones. Graphical methods (such as scatter plots, distribution plots, residuals, prediction bounds) are good for visual inspection and interpretation because they allow viewing the entire data set at once and they can easily display a wide range of relationships between the model (fit) and the data. Numerical methods (such as mean, standard deviation, correlation coefficient) have a statistical basis and are narrowly focused on a particular aspect of the data; they often try to compress information into a single number. In practice, with regard to data and analysis requirements, it might be necessary to use methods of both types to determine the best model (fit).

For ash-based agglomeration process experimental data analysis specific software should be used which enables the determination of optimal conditions for granulation, according to the initial material composition, experimental conditions and quality requirements for the final product.

Data analysis software properties should be as follows:

- Experiment data filtering under specified conditions (experiment or recipe numbers, selected parameter value range).
- Visualization of experimental data (initial ash and accumulated size distributions of granulated agglomerates, mutual dependences of parameters visualizing measured data and fitted regression model).
- Extended information for each experiment (recipe, granule distribution by fractions of decomposition of the used materials, the main quality characteristics of the final product).

Standard spreadsheets (e.g. Microsoft Excel) were used for only initial statistical analysis. For better functionality and multiple data analysis the MATLAB software in conjunction with graphical user interface (GUI) builder, which enables a user to perform interactive tasks, was used.

The structure of experimental data visualization and analysis software is presented in Fig. 3.5.

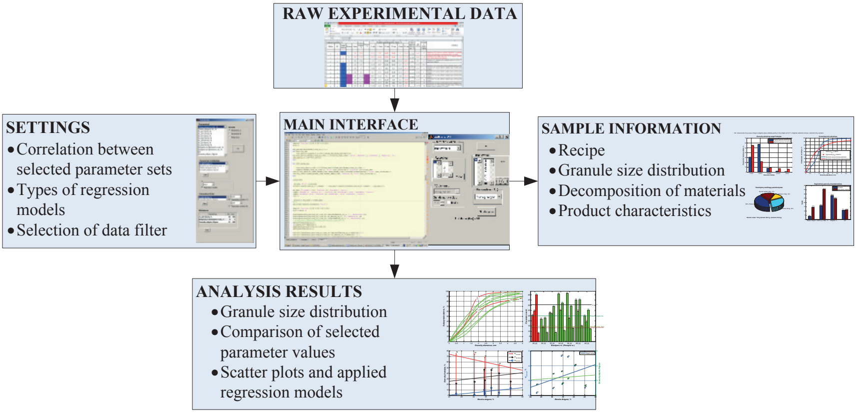

Fig. 3.5. Structure of experimental data visualization and analysis software

The experimental data statistical analysis and modelling tool consists of five parts: raw experimental data loader, parameter settings interface, sample information results, analysis results and main interface.

Raw experimental data loader uses the Microsoft Excel format data and prepares it for future processing in Matlab environment. Parameter setting interface is used for parameterization of regression analysis (parameter sets, types of models) and advanced filtering and sorting (using defined conditions). User defined graphical and numerical information concerning the recipe, granule size distribution, decomposition of materials and product characteristics is provided in the sample information window. According to the settings defined, analysis results window provides granule size distributions, comparison of selected parameter values, scatter plots and applied regression models. The main interface (programme code) is used to coordinate information exchange between different parts of the software tool and initiate data visualization and analysis form different points of view.

3.6 Production of compound fertilizers with biomass ashes

3.6.1 Technological scheme

The obtained results under laboratory conditions and conclusions of the granulation process modeling allow creating the production technology of compound fertilizers granulated with biomass ash, determining optimal technological parameters, calculating material balances for different fertilizers as well as selecting the most suitable technological equipment. The principal technological scheme is presented in Fig. 3.6.

Powdered or granular simple (ammonium sulfate, potassium chloride, urea, etc.) and/or compound (ammonium dihydrophosphate and diammonium phosphate) fertilizers are supplied by railway, unloaded by automated discharge line and stored in separate bins of raw materials warehouse. Biomass ash and other raw materials are packed in bags of 50 kg and 500 kg can be supplied by rail or road, unloaded by fork-lift truck and stored in bins.

From the bins, mobile bucket loader transports raw materials to the hopper (1) of the fertilizer manufacturing plant where they are transported by bucket elevator (2) and a screw conveyor (3) into the container (4) and belt scales-dispensers (5). The dispenser’s capacity is 2–12 tons/h, dosing error – 1.0 %. The ratio of raw materials provided into dispensers depends on the formula of produced fertilizers and their purpose. Raw materials are shredded by rotary mills (6) and are fed into high-intensity paddle mixer (7). Heated with steam and irrigated with water from the scrubber (19), the mass of dry raw material is fed into a rotary drum granulator (8). Granulator is also supplied with steam (130–140 °C; 3–4 bar) and irrigation water, and while it rotates, particle agglomeration takes place and granules form.

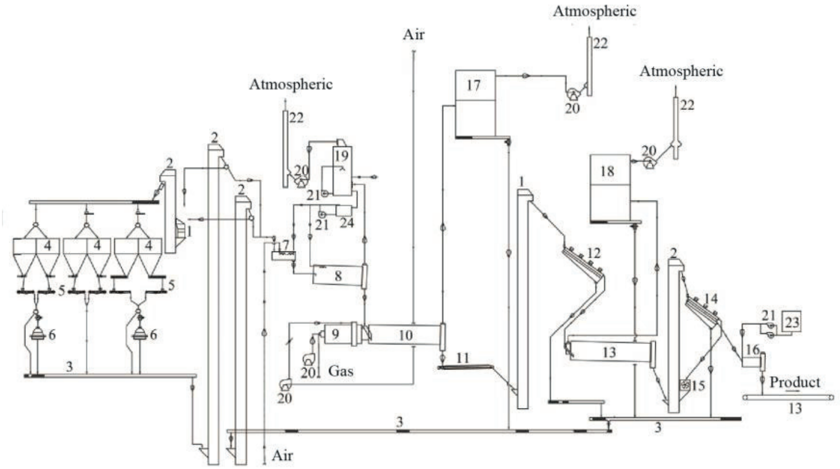

Fig. 3.6. Principal technological scheme for fertilizer production from biomass ash: 1 – hopper; 2 – bucket elevators; 3 – screw conveyor; 4 – container of raw materials; 5 – belt scales-dispensers; 6 – rotary mill; 7 – mixer; 8 – granulator; 9 – combustion chamber (furnace); 10 – dryer; 11 – belt conveyor; 12 – single-meshed sieves; 13 – cooler; 14 – double-meshed sieves; 15 – hammermill crusher; 16 – coating drum; 17 – bag filter (hot); 18 – bag filter (cold); 19 – scrubber; 20 – fan; 21 – pump; 22 – chimney; 23 – wax container; 24 – acidic water tank

Granular product is then transported to the dryer (10), where the heat, originating from combustion chamber (9) by burning natural gas, heats the granules and evaporates the remaining moisture. The remaining moisture content of the dry granulated product is less than 2 %. Hot dried product is transported by belt conveyor (11) and the bucket elevator to the single meshed sieves (12) where the smaller than 2 mm fraction is separated and returned back to the mixer. Larger than 2 mm in diameter granules are cooled (13) to 40 °C and fractioned on the double meshed sieves (14) where the smallest fraction is returned to the mixer and larger than 5 mm granules are crushed by hammermill crusher (15) and returned to the double-meshed sieves. The marketable fraction (2–5 mm) is supplied to a coating drum (16) where granules are coated with special wax. Waxed granules are supplied by belt conveyors are supplied to the bins of product warehouse. Mobile bucket loader is used to load bulk product to packing facilities or railway wagons. Fertilizers are packed in bags of 50 kg and 500 kg which can be stored in the company's territory.

Vapours originating from granulator is contaminated with dust and ammonia so they are fed to the wet scrubber (19), irrigated with acidified water (pH <5) containing phosphoric acid. Water from the scrubber is returned to the production process – granulator or mixer. Decontaminated air is removed to the environment by the fan (20) through the chimney (22). Air originating from the dryer is cleaned in the hot bag filter (17) and the cold bag filter (18). Cleaned air is discharged into the environment. Accumulated fertilizer dust in the bag filters is returned to the mixer and further processed. This technological process is free from waste.

With all the ash received from biomass waste in Lithuania it is possible to produce about 100 thousand tons of compound fertilizers of various formulas.

Considering the fact that the network of biomass boilers is constantly increasing, there might be increase in the amount of biomass ash in the near future, so capacity of proposed technological line could reach 120 thousand tons/year. Having in mind the trends of latest global technology schemes and equipment, the most advanced technological equipment was selected with the help of latest world-class chemical engineering companies such as “Sackets & Sons Co.”, “SCHENCK”, “RHEWUM” and others.

3.6.2 Parameters of pilot production and their evaluation

Fertilizer company CSC “Arvi fertis” produced popular compound NPK fertilizers of 5-15-25 and 10-10-20 formula with trace elements while using existing equipment and adding biomass ash and sugar factory lime. The obtained products were analyzed according to the EC Regulation No. 2003/2003 and physicochemical parameters of products were determined. Tables 3.10 and 3.11 contain raw materials balance sheets of different formula fertilizers, while Table 3.12 presents the optimal parameters of the production process. Physicochemical parameters of fertilizers are presented in Table 3.13.

Table 3.10. Raw materials balance sheet of NPK 5-15-25 fertilizer

Component	Formula	Amount of nutrients, kg						Amount, kg/ton
		N	P_2O_5	K_2O	CaO	MgO	S	
Ammonium sulphate (AS)	20.5–0–0	15.0	–	–	–	–	17.0	73.1
Diammonium phophate (DAP)	17.5–46–0	17.8	46.7	–	–	–	3.0	101.5
Ammonium phosphate (MAP)	11.5–52–0	17.2	78.0	–	–	–	–	150.0
Superphosphate (SSP)	0-18-0	–	20.0	–	–	–	13.3	111.0
Potassium chloride (MOP)	0–0–60.5	–	–	219.3	–	–	–	362.4
Sugar factory lime	40.75 % CaO	–	–	–	40.7	–	-	100.0
Biomass ash	0–5.3–30.7 12.0 % CaO	–	5.3	30.7	12.0	6.0	–	100.0
Wax	–	–	–	–	–	–	–	2.0
Total:		50	150	250	52.7	6	33.3	1000

Table 3.11. Raw materials balance sheet of NPK 10-10-20 fertilizer

Component	Formula	Amount of nutrients, kg						Amount, kg/ton
		N	P_2O_5	K_2O	CaO	MgO	S	
Ammonium sulphate (AS)	20.5–0–0	71.9	–	–	–	–	81.0	350.5
Diammonium phosphate (DAP)	17.5–46–0	17.2	45.3	–	–	–	3.0	98.5
Ammonium phosphate (MAP)	11.5–52–0	10.9	49.4	–	–	–	–	95.0
Potassium chloride (MOP)	0–0–60.5	–	–	169.3	–	–	–	279.8
Sugar factory lime	40.75 % CaO	–	–	–	30.0	–	–	74.2
Biomass ash	0–5.3–30.7 12.0 % CaO	–	5.3	30.7	12.0	3.6	–	100.0
Wax	–	–	–	–	–	–	–	2.0
Total:		100	100	200	42	3.6	84	1000

Table 3.12. Optimal parameters for the production of NPK 5-15-25 and 10-10-20 fertilizers with microelements

Equipment Parameters	Maišytuvas	Granulator	Combustion chamber/dryer	Cooler	Warehouse
NPK 5–15–25 with biomass ash and SFL, capacity 15 ton/h					
Temperature, °C	58–61	55–58	240–255 /88–92	32–35	±10% env.
Moisture, %	4.2–5.0	3–6	up to 2	up to 2	up to 2
pH	5.9–6.3	5.9–6.3	5.9–6.3	5.9–6.3	5.9–6.3
NPK 10–10–20 with biomass ash and SFL, capacity 16 ton/h					
Temperature, °C	58–61	60–62	240–255/ 88–92	32–35	±10% env.
Moisture, %	3.2–5.0	3–4.5	up to 2	up to 2	up to 2
pH	6.2–6.5	6.5–7.0	6.2–6.5	6.0–6.5	6.0–6.5

Table 3.13. Physicochemical parameters of NPK 5-15-25 and 10-20-20 fertilizers with microelements

Content of nutrients, %							Parameters						
K_2O	P_2O_5 total	P_2O_5 assimilated	P_2O_5 soluble H_2O	N ammoniacal	N amidic	N total	>5.00, %	<5.00 >2.00, %	<2.00, %	Moisture, %	pH	Strength, MPa	SGN
NPK 5–15–25 with biomass ash and SFL, capacity 15 ton/h													
25.2	14.5	14.4	13.3	4.8	–	4.8	0.4	98.2	1.4	1.26	5.71	6.7	333
NPK 10–10–20 with biomass ash and SFL, capacity 16 ton/h													
19.8	10.1	9.9	9.3	9.7	–	4.8	0.6	99.2	0.2	0.98	6.25	7.2	340

The results show that the production of NPK 10-10-20 and 5-15-25 fertilizer with microelements, biomass ash and sugar factory lime results in quality product, which meets the requirements of CSC “Arvi fertis” standards. However, the dosing of sugar factory lime becomes problematic task during the production of fertilizers, because it contains about 30 % of water, is adhesive and not bulk material. Therefore, industrial tests were carried out with dried (3–4 % of moisture content) sugar factory lime. Although such preparations of sugar factory lime increases the product cost and solving of this problem is needed to streamline the process. In this case the use of sugar factory lime paste, which could be produced using water from the scrubber, was proposed. Of course, suitable nozzle system would be needed to dispense the paste into the mixer. This would allow using larger amounts of sugar factory lime more efficiently.

In order to fulfill market demand, it was decided to perform industrial experiment production of fertilizers with low content of chlorine – instead of potassium chloride using potassium sulphate as the raw material. Material balance sheet of this chlorine-free 11-10-16+MgO+S+B fertilizer is presented in Table 3.14.

Table 3.14. Raw materials balance sheet of NPK 11-10-16+MgO+S+B fertilizer

Komponentas	Formula	Amount of nutrients, kg							Amount, kg/ton
		N	P_2O_5	K_2O	CaO	MgO	S	B	
Ammonium sulphate (AS)	20.5–0–0	64.8	–	–	–	–	73.0	–	315.8
Urea	46–0–0	10.2	–	–	–	–	–	–	22.3
Diammonium phosphate (DAP)	17.5–46–0	35.0	92.0	–	–	–	6.0	–	200.1
Potassium sulphate (SOP)	0–0–54 18 % S	–	–	95.8	–	–	–	–	191.6
Kizerite	15.5 % MgO 22 % S	–	–	–	–	21.3	19.0	–	85.0
Potassium chloride (MOP)	0–0–60.5	–	–	18.1	–	–	–	–	30.0
Biomass ash	0–5.3–30.7 12.0 % CaO	–	8.0	46.1	18.0	3.7	–	–	150.0
Sodium tetraborate	15.3 % B	–	–	–	–	–	–	0.5	3.2
Wax	–	–	–	–	–	–	–	–	2.0
Total:		110	100	160	18	25	97	0.5	1000

Table 3.15 shows optimal parameters of aforementioned process. Physicochemical parameters of fertilizers produced under laboratory conditions are presented in Table 3.16.

Table 3.15. Optimal parameters for the production of NPK 11-10-16+MgO+S+B fertilizer with microelements

Equipment Parameters	Maišytuvas	Granulator	Combustion chamber/dryer	Cooler	Warehouse
NPK 11–10–16+MgO+S+B with biomass, capacity 15 ton/h					
Temperature, °C	65–68	60–62	220–255/ 88–95	32–35	$\underline{+}$10% env.
Moisture, %	6.4–7.8	8.4–10.2	up to 2	up to 2	up to 2
pH	6.2–6.8	6.3–7.0	6.3–7.0	6.3–7.0	6.3–7.0

Table 3.16. Physicochemical parameters of NPK 11-10-16+MgO+S+B fertilizer with microelements

Content of nutrients, %							Parameters						
K_2O	P_2O_5 total	P_2O_5 assimilated	P_2O_5 soluble H_2O	N ammoniacal	N amidic	N total	>5.00, %	<5.00 >2.00, %	<2.00, %	Moisture, %	pH	Strength, MPa	SGN
NPK 11–10–16+MgO+S+B with biomass ash. capacity 15 ton/h													
15.8	10.1	9.2	9.1	10.2	1.0	11.2	0.2	98.6	1.2	1.76	6.72	7.5	325

The parameters of industrial process show, because of increasing amount of biomass ash, more water is used and this increases the moisture content in the granulator. However, laboratory studies that were performed in the company suggest, those both chemical and physical parameters of produced granular compound NPK 11-10-16+MgO+S+B fertilizer with trace elements remains good and fully complies with the requirements for bulk fertilizers. Examples of granular compound NPK 11-10-16+MgO+S+B fertilizer with trace elements with and without additive are presented in the Fig. 3.7.

Fig. 3.7. NPK 11-10-16+MgO+S+B fertilizer granulated under industrial conditions: 1 – without biomass ash; 2 – with biomass ash

4. CONCLUSIONS

1. It was determined, that all (RSL, RSI, USH and MSH) biomass ashes contain primary and secondary nutrients as well as micronutrient, and they free of heavy metals. The highest content of P_2O_5 is 10.94 % in MSH; K_2O – 30.68 % in USH; CaO – 23.24 % in RSL; MgO – 18.58 % in MSH ashes. Maximum concentrations of microelements: Fe (7369.35 mg/kg) and Mn (998.24 mg/kg) is in RSI ash; Mo (806.80 mg/kg) – RSL ash; Cu (405.61 mg/kg) in MSH ash; Zn (463.02 mg/kg) – USH ash. Low concentrations of Na and Co as well as some heavy metals Pb, Cd, Hg were determined, but they do not exceed permissible limits. Sugar factory lime from CSC "Arvi" ir ko sugar factory contains mostly CaO (40.75 %) while concentrations of MgO (1.97 %), P_2O_5 (1.3 %) and micronutrients (Fe, Cu, Zn, Mn, Co and Mo) are significantly lower. The pH of 10 % solutions of various ashes is alkaline and differs only slightly (from 10.37 to 12.16) while the granular product is predominantly composed of granules, which are less than 2 mm in size. The pH of 10 % solution of sugar factory lime is 8.68. Biomass ash and sugar factory lime are suitable as raw materials for fertilizer manufacturing.

2. Granulation of biomass ashes without additives, regardless of their origin, amount of recycle, moisture content, results in bad quality products, which strength varies between 1.7 N/gran. and 19.9 N/gran., yield of marketable fraction – from 5 % to 46 %, SGN is 40–669.

3. Granulation process of biomass ash and quality of the product can be improved with plasticity-enhancing substances, such as molasses, urea-formaldehyde resin, sugar factory lime and addition of recycle.

3.1. With the addition of molasses aqueous solution (ratio 1:1 or 1:2) during granulation, the static strength of granules increases and ranges from 6.6 to 64.5 N/gran., the yield of marketable fraction is 6–65 % (SGN = 178–1105), pH of 10 % solution is 10.4 to 12.4. Urea-formaldehyde resin additive (up 2 %), does not increase the strength of granules significantly (from 8.3 to 23.5 N/gran.), but improves granulometric composition of the product (marketable fraction 22 % to 53 %) while the value of SGN is 119–1062, pH of 10 % solution 10.7–12.99.

3.2. Mixing biomass ashes with sugar factory lime (1:1) while irrigating with water resulted in low strength granules (3.2–10.8 N/gran.) and small-fraction product (SGN 39 – 769). Irrigation with MWS and UFR improves parameters of the product. Addition of MWS: marketable fraction – 12–55 % (SGN 199–1093), static strength – 8.0 – 33.9 N/gran., pH of 10 % solution 10.3–12.1 and addition of UFR: marketable fraction – 23–59 % (SGN 144–1039), static strength – 7.2–37.29 N/gran., pH of 10 % solution 10.6–12.4.

3.3. The addition of 50 % of recycle to the mixture of raw materials does not show the significant improvement of granular product quality, but values of parameters are changing in more narrow limits: marketable fraction – 22–48 %

(SGN 251–1062), static strength – 11.9–24.4 N/gran., pH of 10 % solution 10.9–11.7.

4. Based on experimental results, the mathematical model of biomass ash granulation process was created, which complexically describes the dependency of product characteristics on the process parameters. The best quality granular product is obtained when: ash and sugar factory lime ratio is 1:1; mixture of raw materials is irrigated with molasses solution (1:1 or 1:2) and moisture content is 20–30 %.

5. Under optimal conditions, while granulating biomass ashes with sugar factory lime and molasses, quality products can be obtained containing: K_2O, P_2O_5, MgO, CaO and microelements (Fe, Cu, Zn, Mn, Co and Mo) with heavy metal (Cd and Hg) concentrations below the permissible limits. These products comply with fertilizer formulas: 0-4-10+26CaO+2MgO+ME (RSH ash), 0-3-15+21CaO+8MgO+ME (USH ash) and 0-6-13+24CaO+10MgO+ME (MSH ash). Principal technological scheme for biomass ash granulation was proposed.

6. The biomass ash can be used for the production of mineral compound fertilizers.

6.1. While using technical salts, biomass ash (USH), sugar factory lime and recycle, fertilizers 8-20-25+3CaO+2S were granulated under laboratory conditions, which best physical and chemical parameters are: 74 % of marketable fraction (SGN 261); strength of granules 11.98 N/gran., pH of 10 % solution is 6.6.

6.2. Under industrial conditions, while using biomass ash and sugar factory lime made NPK 5-15-25+5.3CaO+3.3S and NPK 10-10-20+4.2CaO+8.4S as well as chlorine-free NPK 11-10-16+1.8CaO+2.5MgO+9.7S+B compound fertilizer were produced, which chemical characteristics are in compliance with requirements of technical standards.

LIST OF PUBLICATIONS AND PROCEEDINGS ON THE THEME OF DISSERTATION

Publications corresponding to the list of Thompson Reuters Web of Science database

1. Paleckienė R., Sviklas A. M., Šlinkšienė R., Štreimikis V. Processing of rape straw ash into compound fertilizers using sugar factory waste // Polish Journal of Environmental Studies. Olsztyn : HARD Publishing Company. ISSN 1230-1485. 2012, Vol. 21, no. 4, p. 993-999. [ISI Web of Science; Academic Search Premier; BIOSIS; CAB Abstracts]. [IF: 0,462, AIF: 2,678 (E, 2012)]. [M.kr. 05T].

2. Paleckienė R., Sviklas A. M., Šlinkšienė R., Štreimikis V. Complex fertilizers produced from the sunflower husk ash // Polish Journal of Environmental Studies. Olsztyn : HARD Publishing Company. ISSN 1230-1485. 2010, Vol. 19, no. 5, p. 973-979. [ISI Web of Science; Academic Search

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1. Paleckienė R., Sviklas A. M., Šlinkšienė R., Štreimikis V. Получение гранулированных удобрений из золы биомассы // VI Міжнародна науково-технічна конференція "Новітні енерго-та ресурсозберігаючі хімічні технологіі без екологічних проблем", 9-13 вересня 2013 р, Одеса, Украіна : збірник науковых праць. Т. 1. Одеса : Екология, 2013. ISBN 9786177046003. p. 128-133. [M.kr. 05T].
2. Sviklas A. M., Paleckienė R., Šlinkšienė R., Štreimikis V. Influence of raw material particles size to properties of granulated fertilizers // Chemistry and chemical technology of inorganic materials : proceedings of scientific conference chemistry and chemical technology / Kaunas university of technology. Kaunas : Technologija. ISSN 2029-9222. 2012, p. 31-37. [M.kr. 05T].
3. Sviklas A. M., Paleckienė R., Šlinkšienė R., Štreimikis V. Influence of raw material particles size to properties of granulated fertilizers // 5th International Granulation Workshop : Granulation conference, Lausanne, Switzerland, 20-22 June 2011. [S.l. : s.n.], 2012. p. 240. [M.kr. 05T].

Patents

1. LT 5974B. A.M. Sviklas, V. Kučinskas, V. Štreimikis “Sudėtinių trąšų gamybos būdas“. 2013 m.
2. LT 5329B. A.M. Sviklas, R. Šlinkšienė, R. Paleckienė, M. Krasauskas, V. Štreimikis. „Biriųjų sudėtinių trąšų gamybos būdas“. 2005 m.

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Employment	1985–1992 “Vyris” engineer-chemist technologist 1994–1996 CSC “Tex Color” engineer-chemist technologist 1998–2000 CSC “MANTINGA” manager 2000– CSC “ARVI” engineer technologist, director of technological processes, director of production

REZIUMĖ

Temos aktualumas. Tradicinių energetikos šaltinių Lietuvoje bei iš dalies visoje Europoje priklausomybė nuo vienintelio tiekėjo sukelia rimtų ekonominių ir politinių problemų. Tradicinės energetikos žaliavų – gamtinių dujų bei akmens anglies degimo produktai smarkiai veikia pasaulio ekologinę pusiausvyrą, teršia aplinką, didina klimato atšilimą. Todėl pastaruoju metu vis svarbesniais tampa alternatyvūs energetikos šaltiniai – saulės ir vėjo energija, hidroenergetika bei biokuras. Biokuro rezervai Lietuvoje yra ganėtinai dideli – nepakankamai organizuotai tvarkomos ir naudojamos menkavertės medienos atliekos, pjuvenos, be to, galima deginti daugelio augalų atliekas – šiaudus. Remiantis Lietuvos statistikos departamento 2012–2013 m. duomenimis apie grūdų derlių ir vertinant jų santykį su šiaudais, Lietuvoje buvo gauta apie 4 mln. tonų šiaudų (daugiausia auginant žieminius kviečius, miežius ir žieminius bei vasarinius rapsus). Laukų tręšimas ant dirvos likusiais šiaudais, juos apariant, nėra efektyvus, todėl bioenergetikai siūlo šiaudus naudoti biokatilinėse, kaip alternatyvą medienai. Sudeginus šiaudus susidarytų apie 60 tūkst. t pelenų. Plačiai diskutuojama apie tokio biokuro naudojimo galimybes šilumos ūkyje, tačiau kol kas šiaudų ir jų pelenų naudojimas nėra racionalus. Tiek medienos, tiek žemės ūkio augalų šiaudų pelenai yra vertingas agrocheminis produktas. Juose randama įvairių augalų mitybai reikalingų pagrindinių elementų: 1–3 % fosforo, 10–25 % kalio; antrinių elementų: – 5–20 % kalcio 1–2 % magnio bei kai kurių mikroelementų. Priklausomai nuo augalų rūšies, dirvožemio, tręšimo ir biokuro deginimo sąlygų pelenuose gali būti sunkiųjų metalų (kadmio, švino). Tačiau dažniausiai jų kiekiai yra tokie maži, kad neturi jokios neigiamos įtakos. Be to, kad pelenuose yra augalų maisto medžiagų, jie pasižymi šarminėmis savybėmis, jie gali būti naudojami ne tik kaip trąšos, bet ir kaip kalkinimo medžiaga, skirta rūgščioms dirvoms neutralizuoti. Biomasės pelenų naudojimas be specialaus apdorojimo agrocheminiu požiūriu nėra efektyvus, nes sausų pelenų dalelių dydis ir forma labai skiriasi, išbarstant į dirvą jie dulka ir pasiskirsto netolygiai. Tinkamiausias būdas pelenų fizikinėms-mechaninėms savybėms pagerinti yra granuliavimas, kai aglomeracijos būdu dalelės gaunamos norimo (beveik vienodo) skersmens ir pakankamo stiprio. Išbarstant į dirvą granuliuotą produktą, jis pasiskirsto tolygiau, ir augalai patręšiami vienodai. Kadangi biomasės pelenų plastiškumas labai mažas, jų granuliavimui reikalingos rišamosios medžiagos, tokios kaip molis, kizelgūras, įvairūs organiniai priedai.

Literatūroje randama duomenų, kad mineralinių trąšų plastiškumą padidina cukraus gamybos iš cukrinių runkelių atlieka – defekatas. Ši atlieka gali būti naudojama ir kaip kalkinimo medžiaga, nes joje yra apie 40 % CaO, o taip pat nedideli kiekiai augalų maisto makro ir mikroelementų (Fe, Cu, Zn, Mn, Co, Mo). Kadangi defekatas klasifikuojamas kaip atliekos, kurios kaupiasi cukraus pramonės gamyklose, tai jo panaudojimas būtų racionalus ir ekologiniu požiūriu.

Cukraus pramonėje susidaro ir kitas šalutinis produktas – melasa, kuri nedideliais kiekiais naudojama kai kuriose pramonės šakose (maisto, gyvulių pašarų gamyboje ir t.t.). Ji pasižymi didele klampa todėl gali būti naudojama kaip rišanti (plastiškumą didinanti) medžiaga.

Pelenų granuliavimo su defekatu ir melasa duomenų nėra. Tokie tyrimai yra svarbūs, nes jų rezultatai leistų gaminti draugiškas aplinkai sudėtines mineralines trąšas, kuriose yra fosforo, kalio, kalcio ir kai kurių mikroelementų bei sumažinti kitose Lietuvos pramonės šakose (energijos, cukraus gamybos) susidarančių atliekų kiekį. Iš minėtų žaliavų pagamintas produktas galėtų būti naudojamas ir kaip trąšos, ir kaip kalkinimo medžiaga. Be to tikėtina, kad biomasės pelenai ir defekatas galėtų būti naudojami kaip kalio žaliava gaminant bechlores sudėtines NPK trąšas.

Darbo tikslas – nustatyti teorinius ir technologinius aspektus bei sukurti sudėtinių trąšų, gaunamų naudojant biomasės pelenus ir kitas atliekines medžiagas, gamybos technologiją.

Siekiant užsibrėžto tikslo reikėjo išspręsti šiuos uždavinius:

1. Nustatyti biomasės – rapsų stiebelių, saulėgrąžų lukštų pelenų ir cukraus pramonės atliekos – defekato chemines fizikines savybes bei įvertinti jų tinkamumą trąšoms gaminti.
2. Ištirti ir įvertinti sugranuliuotų biomasės pelenų su priedais fizikines chemines savybes (granulių stiprį, granuliometrinę sudėtį, drėgmę, pH) bei nustatyti šių žaliavų granuliavimo technologinius parametrus.
3. Naudojant programinę įrangą išanalizuoti eksperimentinius rezultatus ir patikslinti nustatytus biomasės pelenų granuliavimo technologinius parametrus bei sukurti principinę technologinę schemą, skirtą biomasės pelenams granuliuoti.
4. Naudojant biomasės pelenus ir defekatą pagaminti sudėtines NPK trąšas bei, įvertinant gauto produkto fizikinius cheminius

rodiklius, pateikti technologines prielaidas sudėtinėms trąšoms gaminti.
5. Įvertinant gautus rezultatus, sukurti technologiją NPK trąšoms, naudojant biomasės pelenus ir defekatą, gaminti ir įdiegti ją pramoninėje gamyboje.

Mokslinis naujumas

1. Nustatyta, kad granuliuojant pelenus defekato, melasos ir karbamido formaldehidinės dervos priedai suaktyvina granuliavimo procesą ir pagerina kai kuriuos produkto fizikinius mechaninius rodiklius (granuliometrinę sudėtį ir granulių stiprį) arba prekinės išeigos (frakcijos) kiekį.
2. Naudojant programinę įrangą sudarytas biomasės pelenų granuliavimo proceso matematinis modelis, kompleksiškai aprašantis produkto parametrų (granuliometrinės sudėties, statinio granulių stiprio, drėgmės) kitimo priklausomybę nuo eksperimento sąlygų (žaliavų sudėties ir drėgmės, returo kiekio).

Praktinė vertė

1. Nustatyti biomasės pelenų granuliavimo su defekatu optimalūs technologiniai parametrai ir pateikta galima sudėtinių (PK) trąšų su mikroelementais formulė.
2. Sukurta sudėtinių (PK) trąšų, gaunamų naudojant biomasės pelenus ir defekatą principinė schema.
3. Laboratorinėmis sąlygomis sukurta sudėtinių NPK trąšų gamyba išbandyta pramoninėmis sąlygomis ir gautas kokybiškas produktas, kuris realizuojamas trąšų rinkoje.

Darbo aprobavimas ir publikavimas

Disertacinio darbo tema paskelbti 4 recenzuojami straipsniai, iš jų 2 Thompson Reuters Web of Knowlwdge duomenų bazės leidiniuose, turinčiuose citavimo indeksą, 3 publikacijos konferencijų, 2 iš jų tarptautinės, pranešimų medžiagoje ir kartu su bendraautoriais gauti 2 patentai.

Darbo apimtis

Disertaciją sudaro įvadas, literatūros duomenų analizė, metodinė dalis, tyrimų rezultatai ir jų apibendrinimas, išvados, 176 literatūros šaltinių sąrašas, publikacijų sąrašas ir priedai. Pagrindinė medžiaga išdėstyta 96 puslapiuose, įskaitant 35 lenteles ir 36 paveikslus.

Ginamieji disertacijos teiginiai

1. Defekatas ir melasa teigiamai veikia biomasės pelenų granuliavimo procesą, pagerina produkto fizikines mechanines savybes:

granuliometrinę sudėtį ir granulių stiprį bei padidina prekinės išeigos kiekį.

2. Naudojant matematinį modelį galima kompleksiškai įvertinti produkto kokybės rodiklių priklausomybę nuo pasirinktų granuliavimo proceso parametrų, o nustatyti dėsningumai leidžia parinkti optimalias granuliavimo sąlygas ir kokybiškai valdyti technologinį procesą.
3. Pramoninėmis sąlygomis, naudojant biomasės pelenus, galima pagaminti sudėtines mineralines trąšas, kurių fizikinių cheminių savybių rodikliai atitinka biriosioms trąšoms keliamus kokybės reikalavimus.

IŠVADOS

1. Nustatyta, kad visuose (RSL, RSP, USL ir MSL) biomasės pelenuose yra pagrindinių ir antrinių augalų maisto medžiagų bei mikroelementų, ir praktiškai nėra sunkiųjų metalų. Didžiausias P_2O_5 kiekis 10,94 % yra MSL; K_2O – 30,68 % USL; CaO – 23,24 % RSL; MgO – 18,58 % MSL pelenuose. Mikroelementų didžiausia koncentracija: Fe (7369,35 mg/kg) ir Mn (998,24 mg/kg) – RSP; Mo (806,80 mg/kg) –RSL; Cu (405,61 mg/kg) MSL; Zn (463,02 mg/kg) – USL pelenuose. Taip pat rastos nedidelės Na bei Co ir mažesnės už leistinas sunkiųjų metalų (Pb, Cd, Hg) koncentracijos. UAB „Arvi cukrus“ fabriko cukraus gamybos atliekose – defekate daugiausia (40,75 %) yra CaO, gerokai mažiau MgO (1,97 %) ir P_2O_5 (1,3 %) bei mikroelementų (Fe, Cu, Zn, Mn, Co ir Mo). Skirtingų pelenų 10 % tirpalų pH yra šarminis ir skiriasi nežymiai (10,37–12,16), o pagal granuliometrinę sudėtį – visais atvejais vyrauja mažesnės nei 2 mm dydžio dalelės. Defekato 10 % tirpalo pH vertė yra 8,68. Tirti biomasės pelenai ir defekatas yra tinkamos žaliavos trąšoms gaminti.
2. Granuliuojant vienus biomasės pelenus nepriklausomai nuo jų kilmės, drėgmės ir returo kiekio, granuliavimo procesas vyksta blogai ir gaunamas nekokybiškas produktas: granulių statinis stipris kinta ribose nuo 1,7 N/gran. iki 19,9 N/gran., prekinės frakcijos išeiga – nuo 5 % iki 46 %, o SGN – nuo 40 iki 669.
3. Biomasės pelenų granuliavimo procesą ir produkto kokybinius rodiklius gerina plastiškumą didinančios medžiagos – melasa, karbamido formaldehidinė derva, defekatas bei returo pridėjimas.
    3.1. Į granuliuojamus skirtingus pelenus įdėjus melasos vandens tirpalo (MVT) (santykiu 1:1 arba 1:2), granulių statinis stipris padidėja ir kinta ribose (6,6–64,5 N/gran., o prekinės frakcijos išeiga – 6–65 % (SGN 178–1105), 10 % tirpalo pH 10,4–12,4. Karbamido formaldehidinės dervos (KFD) priedas (iki 2 %), mažai padidina skirtingų biomasės pelenų granulių stiprį (8,3–23,5 N/gran.), tačiau pagerina produkto granuliometrinę sudėtį

(prekinės frakcijos išeiga – nuo 22 % iki 53 %, o SGN vertės – 119–1062), 10 % tirpalo pH 10,7–12,99.

   3.2. Skirtingus biomasės pelenus maišant su defekatu (santykiu 1:1) ir drėkinant vandeniu, gaunamas mažas granulių stipris (3,2–10,8 N/gran.) ir daug smulkiosios frakcijos (SGN 39–769). Drėkinant MVT arba KFD tirpalu, produkto rodikliai pagerėja. Su MVT: prekinės frakcijos kiekis – 12–55 % (SGN – 199–1093), statinis stipris – 8,0–33,9 N/gran., 10 % tirpalo pH 10,3–12,1, o su KFD tirpalu: prekinės frakcijos kiekis – 23–59 % (SGN – 144–1039), statinis stipris – 7,2–37,29 N/gran., 10 % tirpalo pH 10,6–12,4.
   3.3. Į žaliavų mišinį įdėjus 50 % returo iš esmės granuliuoto produkto kokybė nepagerėja, tačiau rodiklių vertės kinta siauresnėse ribose: prekinės frakcijos kiekis – 22–48 % (SGN – 251–1062), statinis stipris – 11,9–24,4 N/gran., 10 % tirpalo pH 10,9–11,7.
4. Remiantis eksperimento rezultatais, sudarytas biomasės pelenų granuliavimo matematinis modelis, kompleksiškai aprašantis produkto rodiklių priklausomybę nuo proceso parametrų. Geriausi granuliuoto produkto rodikliai gaunami kai: pelenų:defekato santykis – 1:1; žaliavų mišinys drėkinamas melasos vandens tirpalu (santykiu 1:1 arba 1:2); drėgmės kiekis – 20–30 %.
5. Nustatytomis optimaliomis sąlygomis granuliuojant skirtingus biomasės pelenus su defekatu ir melasa, galima gauti produktus, kuriuose yra: K_2O, P_2O_5, MgO, CaO bei mikroelementų (Fe, Cu, Zn, Mn, Co ir Mo), o sunkiųjų metalų (Cd ir Hg) koncentracija nesiekia leistinos ribos. Tokie produktai atitiktų trąšų formules: 0–4–10+26CaO+2MgO+ME (RSL pelenų), 0–3–15+21CaO+8MgO+ME (USL pelenų) ir 0–6–13+24CaO+10MgO+ME (MSL pelenų). Pasiūlyta biomasės pelenų granuliavimo principinė technologinė schema.
6. Biomasės pelenai gali būti naudojami sudėtinėms mineralinėms trąšoms gaminti.
   6.1. Naudojant technines druskas, biomasės pelenus (USL), defekatą bei returą laboratorijoje sugranuliuotos 8–20–25+3CaO+2S trąšos, kurių geriausi fizikinių cheminių savybių rodikliai yra: 74 % prekinės frakcijos (SGN 261); granulių stipris 11,98 N/gran., 10 % tirpalo pH 6,6.
   6.2. Pramoniniu būdu naudojant biomasės pelenus ir defekatą pagamintos biriosios sudėtinės NPK 5–15–25+5,3CaO+3,3S ir NPK 10–10–20+4,2CaO+8,4S markių bei naudojant biomasės pelenus bechlorės NPK 11–10–16+1,8CaO+2,5MgO+9,7S+B markės trąšos, kurių fizikinių cheminių savybių rodikliai atitinka ĮST kokybės reikalavimus.

UDK 66.099.2+631.812](043.3)
SL344. 2015-08-25. 2,75 leidyb. apsk. l. Tiražas 40 egz. Užsakymas 308.
Išleido Kauno technologijos universitetas, K. Donelaičio g. 73, 44249 Kaunas
Spausdino leidyklos „Technologija“ spaustuvė, Studentų g. 54, 51424 Kaunas