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Original Research

Processing of Rape Straw Ash into Compound Fertilizers Using Sugar Factory Waste

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Abstract

Rape straw is a waste product of rapeseed oil production that can be processed for use by burning. This study examined the processing of rape straw ash into compound fertilizers containing phosphorus, potassium, calcium, magnesium, and microelements by granulation using additives from sugar factories, such as sugar factory lime and molasses. Rape straw ash was examined by chemical analysis, differential scanning calorimetry-thermogravimetry, infrared spectroscopy, and x-ray diffraction analysis. The optimum parameters of compound fertilizer granulation and the main physicochemical properties of the product, such as particle size distribution, moisture content, pH, and particle-crushing strength were determined using standard methods. The results of our investigation show that compound fertilizers of 0-6-21-23CaO-2MgO grade can be obtained from rape straw ash using sugar factory lime and molasses.

Keywords: waste, utilization, rape straw ash, sugar factory lime, molasses, fertilizers, granulation

Introduction

The high demand for alternative and renewable sources of energy presents a suitable alternative for utilization of part of the straw produced in Lithuania. Biodiesel fuel is one option for reducing consumption of petroleum, as well as energy dependence on imported mineral oil sources, and rapeseed oil can be used as such. Methyl and ethyl esters can be extracted from rapeseed oil by treatment with alcohols [1]. It has been reported that a blend of 30% biodiesel and 70% mineral diesel is optimal for diesel engines [1, 2]. Biomass is a renewable resource whose utilization has received great attention because of environmental considerations and the increasing demand for energy worldwide [1, 3]. Various types of straw are a byproduct of grain production. Approximately 10% of the straw produced in Lithuania comes from summer and winter rape straw (Fig. 1), but crop production is expected to increase rapidly with the rising demand for biofuel production [4]. Growing rapeseed for biofuel will also generate large amounts of rape straw, which can be used to replenish soil organic carbon, or recycled back into the atmosphere and in the process producing energy [4].

One alternative to chemical fertilizers is the use of biomass ash [5, 6]. Different investigations of ash used as fertilizer have shown beneficial effects [5-10]. The ash improves the soil structure and supplie plants with nutrients [5-15]. Straw ash and wood ash (especially hardwood ash) are the types best suited to fertilization [5, 10, 12-16].

Rape straw ash (RSA) contains a significant amount of plant nutrients such as phosphorus (P), potassium (K), calcium (Ca), and magnesium (Mg), plus microelements such as zinc (Zn), copper (Cu), cobalt (Co), manganese (Mn), and iron (Fe), which makes RSA a valuable alternative fertilizer option. The chemical composition and nutrient ratio of rape straw ash will depend not only on soil fertility dur-

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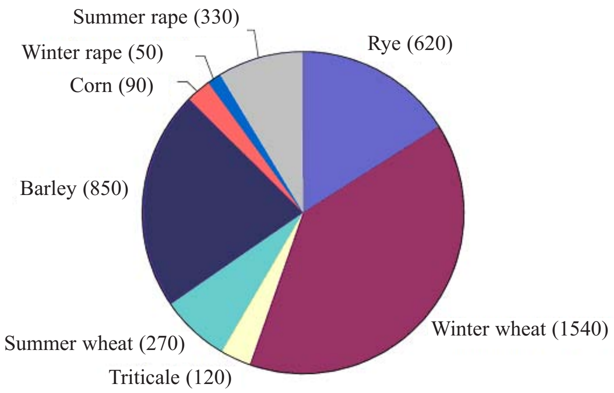

Fig. 1. Average straw yield in Lithuania (×10³ tons) [1].

ing the growth season, but also on combustion conditions, such as temperature interval, excess air ratio, and furnace design [10, 11, 15]. Therefore, the use of ashes as fertilizers without special treatment is problematic.

The use of RSA as fertilizer could be improved if the product is granulated and particle size is kept uniform. Unprocessed RSA particles differ widely in size distribution and during storage the particles might form hardened larger aggregates due to changes of moisture. Therefore, if RSA is applied to the soil, it may be unevenly distributed, resulting in uneven levels of fertilizer throughout the landscape. The alternative option is to aggregate the RSA into uniform grains. No found data on RSA granulation process, only certain results of fly ash granulation is known. One problem associated with granulation of RSA is the lack of plasticity, which makes its aggregation by agglomeration difficult. What is known is that ash granulation in drum granulators is more effective, and a more uniform particle size can be obtained when binding materials are used. Formulations that are lacking in plasticity can be granulated using additives of binders such as clay at low moisture content. It has also been reported that the presence of organic additives in the mix can increases the compressive strength of the grains, making it more suitable for use as a fertilizer [3, 17]. Some authors have used polyamine alkylol or dolomite to improve the ash granulation process and product quality parameters [17, 18]. The equipment for the ash granulation process is developed and analyzed by American, Japanese, Chinese, Australian, and German companies [19-24]. Previous studies have reported positive results from granulation of sunflower ash using additives such as sugar factory lime and molasses [25, 26]. The plasticity of the granulation mixture and the commercial grade of product indicators such as particle size distribution, crushing strength of grains, were all increased.

The composition of sugar factory lime (SFL) varies in accordance with that of the limestone used in the manufacture of lime milk and the chemical composition of the beets used for sugar [27, 28]. Most of this waste consists of calcium carbonate containing up to 50% CaO. Molasses is also a byproduct of the sugar industry and is a useful material for the production of fertilizers due to its potential to increase plasticity for ash granulation [29]. A small concentration of macroelements, such as N, P, K, Mg, and Na, is also present in SFL and molasses. SFL and molasses also contain microelements such as Fe, Cu, Zn, Mn, Co, and Mo, making them potential micronutrient sources in fertilizers.

The purpose of this study was to determine the opportunities for RSA granulation in a drum granulator when sugar factory wastes, such as SFL and molasses, were used as binders for granulation. The rape straw ash granulation parameters were determined and the physical and chemical properties of the final product were evaluated.

Materials and Methods

RSA and two types of waste from a sugar factory in Marijampolė, Lithuania, SFL and molasses (M), were used for the granulation process. Sugar factory lime and molasses were chemically analyzed previously and results can be found at [25, 29]. RSA was obtained by burning straw in a laboratory furnace at 400-500ºC. Ground water (W) was used for moistening the granulation mixture.

In this work, nitrogen, phosphorus, magnesium, calcium, potassium, and sodium content were determined by the standard methods [30-32]. Microelement content was analyzed by the atomic absorption spectrometry method with the A Analyst 400 device from PerkinElmer [33-35]. Ash x-ray radiation diffractive analysis [34, 36] was carried out using the Dron-6 x-ray difractometer. Infrared spectroscopy (IR) spectra [35, 36] were obtained on a PerkinElmer FT-IR

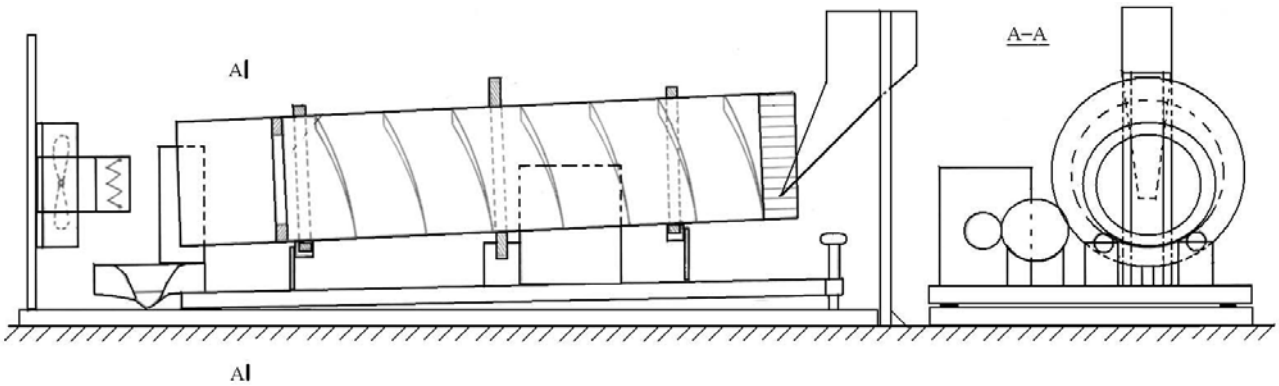

Fig. 2. Laboratory drum granulator-dryer.

spectrometer. The samples were produced by the standard method with KBr. Simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) [36] was carried out using the Netzch Sta 409 PC Luxx thermal analyzer. Samples were heated to 600ºC.

Rape straw ash was granulated in an upgraded laboratory drum-type granulator-dryer at 3 degrees of tilt angle and a constant (26 rpm) rotation speed (Fig. 2). The operating principle of this device is described in the literature [3, 37]. For drying the mixture, hot air, preheated up to 70ºC, was supplied to the granulator. The 1-20 samples of RSA (fraction <2 mm) with sugar factory waste (SFL and M in the laboratory technique) were granulated. The resulting granular product was dried for 7 to 21 hours at 60-70ºC (depending on the content of SFL, M, and W), and then its physical and chemical properties were identified.

Crushing strength of grains is expressed as the force necessary to destroy the grain as such N/grain [38]. The strength of grains, as the average value of 20 grains (fraction 2-5 mm) subjected to crushing, was determined by using an IPG-2 device under standard conditions [31]. The hygroscopic moisture of granulated fertilizer, pH, granulometric composition, and bulk density of ash were determined using standard procedures [31].

Some experimental results (granulometric composition of product and crushing strength of grains) were estimated by statistical methods. The calculations of the experimental data were carried out on the basis of three replicates [31, 38]. Experimental results are given in Tables 1-4 as arithmetic means.

Table 1. Chemical composition of rape straw ash.

Element or element oxide	Concentration, %	Element	Concentration, mg/kg
N	0.01	Fe	1201.87
P_2O_5	6.23	Cu	7.03
K_2O	20.72	Zn	125.06
CaO	23.24	Mn	475.88
MgO	2.12	Co	90.40
Na_2O	0.19	Mo	806.80

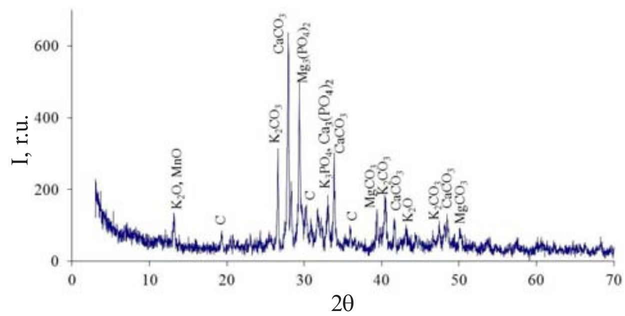

Fig. 3. X-ray diffractive curve of rape straw ash.

Results and Discussion

Chemical analysis (Table 1) of rape straw ash showed that it is composed of 20.7% K_2O, 23.2% CaO, 6.2% P_2O_5, and 2.1% MgO, as well as trace amounts of Na_2O and N. Microelement concentration was found to vary and the most abundant elements were iron (1202 mg/kg), Mo (807 mg/kg), Mn (476 mg/kg), and Cu (406 mg/kg); with lower amounts of Zn (125 mg/kg) and Co (90 mg/kg). Chemical composition exspresed in elements or element oxides as is done in European Fertilizers Reglament [31]. The obtained results are similar as published [10]. For example, the chemical composition of rape ash from Poland is as follows: phosphorus, 15.1 g/kg; potassium, 155.7 g/kg; calcium, 124.0 g/kg; magnesium, 7.3 g/kg; copper, 34.3 mg/kg; manganese, 836.4 mg/kg; zinc, 185.0 mg/kg; and iron, 3661.7 mg/kg [10].

The x-ray diffractive analysis curve (Fig. 3) shows peaks that correspond to calcium carbonate, potassium car-

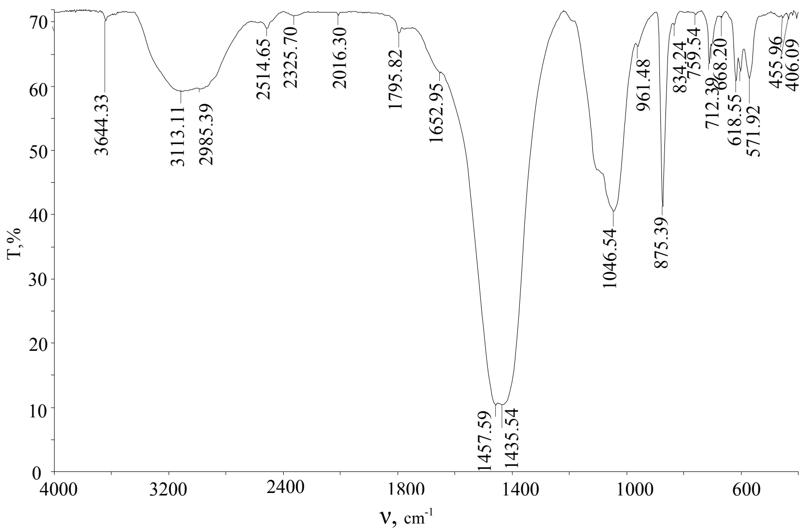

Fig. 4. IR spectrum of rape straw ash.

Table 2. Physical properties of rape straw ash.

pH	Bulk density, kg/m^3	Granulometric composition, %				
		<1 mm	1-2 mm	2-3 mm	3-5 mm	>5 mm
10.5	618	31.09	57.44	8.00	2.31	1.16

Table 3. Quantities of components (%).

Sample	Ash	SFL	Molasses	Water	Recycle
1	75.00	0.00	0.00	25.00	0.00
2	60.00	0.00	0.00	40.00	0.00
3	33.33	0.00	0.00	33.33	33.33
4	31.25	0.00	0.00	37.50	31.25
5	0.00	0.00	0.00	37.50	62.50
6	0.00	0.00	0.00	28.57	71.43
7	41.67	41.67	0.00	16.67	0.00
8	17.86	17.86	0.00	28.57	35.71
9	58.82	0.00	41.18	0.00	0.00
10	50.00	0.00	25.00	25.00	0.00
11	58.82	0.00	30.88	10.29	0.00
12	58.82	0.00	27.41	13.76	0.00
13	58.82	0.00	13.76	27.41	0.00
14	35.71	0.00	14.29	14.29	35.71
15	35.71	35.71	28.57	0.00	0.00
16	35.71	35.71	14.29	14.29	0.00
17	35.71	35.71	21.43	7.14	0.00
18	35.74	35.74	19.01	9.51	0.00
19	35.74	35.74	9.51	19.01	0.00
20	19.23	19.23	11.54	11.54	38.46

bonate, magnesium carbonate, sodium and potassium sulfate, calcium, magnesium, phosphorus oxide, and diffractive reflexions characteristic of elemental carbon [34]. In the spectrum obtained during the IR spectral analysis (Fig. 4), in the area of approximately 3600-3400 cm^{-1} the low intensity typical of OH connection valentic vibration of water molecules can be distinguished [35]. Oscillations in the frequency range of approximately 3200-2800 cm^{-1} can be attributed to the CH group, and nonintensive vibrations in the range of 2500-1600 cm^{-1} are typical of the CO connection [35]. The spectrum has a very pronounced vibration of the CO_3^{2-} functional group in the frequency range of approximately 1400-800 cm^{-1} [36]. The vibration in the frequency range of 800-700 cm^{-1} corresponds to the SO_4^{2-} functional group, and that in the range of 600-500 cm^{-1} corresponds to PO_4^{3-} [35]. The data from the simultaneous DSC-TG analysis (Fig. 3) indicated that at 150ºC, the DSC curve displays an insignificant endothermic effect, and in the TG curve it corresponds to the mass loss, which is attributed to the adsorptive water removal in ashes. The significant exothermic peak at 470ºC corresponds to the mass loss (3.56%) in the TG curve. The mass decrease is obtained due to incompletely burnt straw at a low combustion temperature [36].

The ash properties (pH, bulk density, and granulometric composition) were measured and are presented in Table 2. The pH value of 10% aqueous ash solution was 10.5 at 20ºC. The bulk density of rape straw ash was 618 kg/m^3. The majority of ash consists of particles less than 2 mm in diameter.

The composition of the granulated mixture (1-20 samples) with RSA, SFL, M, W, and recycling part is given in Table 3. Rape straw ash was granulated by moistening with water in samples of pure RSA, (samples 1 and 2), RSA with

Table 4. Rape straw ash granulating conditions and product indicators.

Sample	Humidity of raw materials, %	Quantity of recycle, %	Granulometric composition of product, %			Mass change after drying, %	pH (10%)	Crushing strength, N/grain
			>5 mm	2-5 mm	<2 mm			
1	25.00	–	10.28	14.54	75.19	15.184	10.27	2.2
2	40.00	–	44.42	29.77	25.81	32.333	10.46	6.0
3	33.33	50	3.68	15.59	81.73	15.685	10.85	1.9
4	37.50	50	6.13	18.49	75.38	20.420	10.55	3.8
5	37.50	100	4.85	4.99	90.16	24.970	10.75	3.4
6	28.57	100	4.74	9.42	85.84	23.978	10.56	3.3
7	28.20	–	6.18	16.52	77.30	11.510	11.04	3.8
8	33.51	50	8.81	24.64	66.54	23.491	10.65	3.2
9	24.71	–	61.35	33.44	5.21	8.815	10.89	38.5
10	30.00	–	25.46	30.05	44.49	17.282	10.48	6.6
11	16.47	–	39.39	44.71	15.89	11.317	10.89	64.5
12	19.25	–	25.52	45.15	29.33	7.259	10.86	19.6
13	30.16	–	22.84	30.87	46.29	15.765	11.33	20.4
14	17.14	50	42.90	22.06	35.04	0.455	11.19	24.4
15	15.60	–	81.05	17.22	1.72	14.163	10.64	30.4
16	27.03	–	16.55	33.27	50.18	15.051	10.25	8.0
17	21.31	–	48.43	44.47	7.10	14.934	10.84	28.0
18	23.20	–	44.89	46.43	8.68	15.672	10.46	33.9
19	30.80	–	24.77	54.58	20.66	24.231	10.74	8.4
20	19.17	50	25.81	32.44	41.73	11.914	10.88	20.5

50% recycle (samples 3 and 4), and pure recycle (samples 5 and 6). After primary agglomeration of raw material particles by drum granulation, the granulated product is sieved, a small fraction (less than 1 mm in diameter) is returned into the granulator as recycle. In practice, for fertilizer granulation, the ratio of recycle to raw material may range from 2:1 to 1:2. The content of recycle in a granulator depends on the physical and chemical properties of materials, such as plasticity, moisture content, and chemical composition, for example. During this investigation, the raw materials, pure recycle, and a mixture of raw materials with 50% recycle were granulated.

The product was obtained by granulating, drying at 60-70ºC, and fractionating. The results for humidity, granulometric composition, mass change after drying, pH of 10% solution, and static crushing strength of 3 to 5 mm fraction for the grains are presented in Table 4.

The static strength of grains depends on the quantity of water and recycle and varies from 1.9 N/grain to 3.6 N/grain. Compared with pure ash granulation, a smaller (approximately 5%) marketable fraction of product (grain diameters of 2-5 mm) was obtained when recycle was used in the granulation process.

The influence of recycle on granulometric composition of the rape straw ash is shown in Fig. 6. Granulation of pure ash with lower moisture content (30%) (Fig. 6a) and the use of recycle slightly changed the granulometric composition. In all cases (using 0%, 50%, and 100% recycle), the ashes with lower moisture produced a greater proportion of small

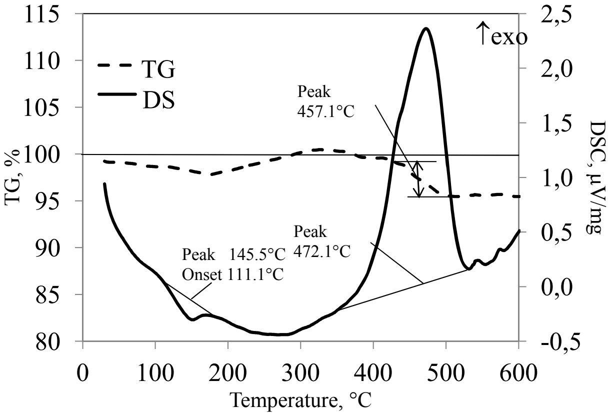

Fig. 5. DSC-TG analysis curves of rape straw ash.

(<2 mm) fraction and a lower amount of large (>5 mm) fraction. The use of recycle worsened the granulometric composition of products when the moisture content was increased to approximately 40% (Fig. 6b). The content of marketable fraction decreased from 29.77% without recycle to 9.42% with 100% recycle. When the RSA and SFL at a ratio of 1:1 using water (sample 7) were granulated, a low strength of grains was observed (3.8 N/grain). When 50% recycle was added to the RSA and SFL mixture, the strength of grains was decreased even further, but the marketable fraction was increased from 16.52% (sample 7) to 24.64% (sample 8).

As an attempt to improve the physical properties of the grains, RSA was mixed with molasses (sample 9) or with a solution of molasses in water at different concentrations (samples 10-14). Molasses content in the mixtures prepared for granulation varied from 14% to 41%. The data show that the physical properties of the grains were improved by the addition of molasses. When molasses content was greater than 31%, the mixture becomes very sticky, and the drying time of the grains was significantly extended. Increased grains characteristics – such as marketable product yield of approximately 45% and a grain crushing strength of 64.5 N/grain were obtained with the addition of 30.9% molasses. When the mixture of ash with SFL (ratio of 1:1) containing 28.7% molasses was granulated (sample 15), a grain strength was sufficiently high and equal to 30.4 N/grain, but only a very low proportion of marketable material – approximately 17% – was obtained. Better grain

a)

b)

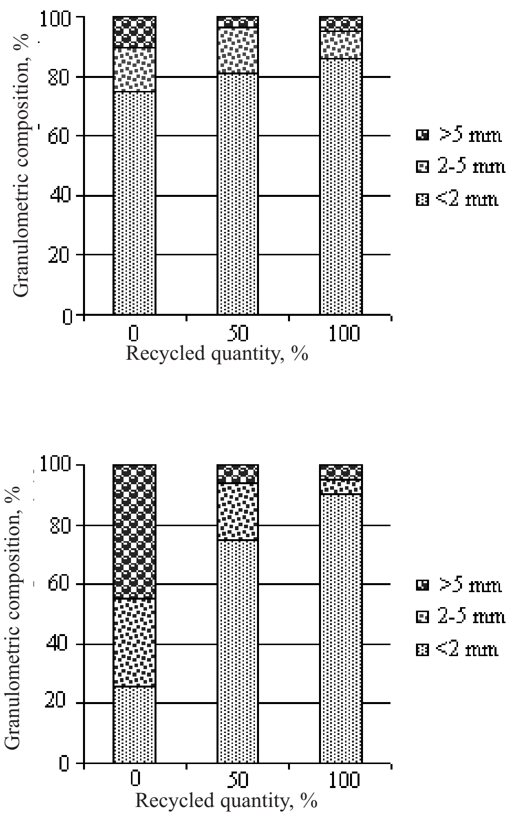

Fig. 6. Dependence of RSA granulometric composition on recycled quantity for ~30% (a) and ~40% (b) moisture content.

properties were obtained by granulation of an RSA and SFL mixture with a solution of molasses in water (samples 16-19). However, the static strength of the resulting grains depended on the quantity of molasses added. When the ash was granulated using 40% water (sample 2), the grain strength was 6.0 N/grain. The addition of similar quantities of molasses (sample 9) increased the grain strength to 38.5 N/grain. The best grain strength and product marketable proportion was obtained at a 2:1 ratio of M:W (sample 18). The static strength of grains was 33.9 N/grain, and the quantity of marketable fraction was approximately 46%.

The results obtained by granulation of rape straw ash, sugar factory lime, and molasses-water solution mixture using 50% recycle (sample 20) show that characteristics of granulated product were lower than those of sample 18. This means that using recycle slightly improved granulation parameters and properties of granulated ash.

Conclusions

The chemical composition and the physical and chemical properties of rape straw ash were determined by chemical and instrumental methods. The most abundant nutrients in the ash were found to be phosphorus (6.2% P_2O_5), potassium (20.7 K_2O %), calcium (23.2% CaO), and magnesium (2.1% MgO) in addition to smaller amounts of micronutrients: Fe (1202 mg/kg), Mo (807 mg/kg), Mn (476 mg/kg), Cu (406 mg/kg), Zn (125 mg/kg), and Co (90 mg/kg). This study showed that a granular product could be obtained by granulation of rape straw ash and certain grain properties were improved by granulation of ash and a sugar factory lime mixture. The granulation process and the parameters of the marketable product were improved by the addition of molasses. The best physic-chemical and marketable properties were obtained by granulation of rape straw ash with sugar factory lime (ratio of 1:1) and a solution of molasses in water (ratio of 2:1). This mixture resulted in a product with a static strength of grains of 33.9 N/grain and 46% of marketable fraction. Using recycle slightly improved the properties of the granulation product. The results of granulating the RSA and SFL mixture with a solution of molasses in water showed that fertilizer of 0-6-21-23Ca-2MgO grades with suitable marketable parameters could be obtained.

References

1. SPEIGHT J. Synthetic fuels handbook. New York, NY: McGraw-Hill, 221, **2008**.
2. JANULIS P., MAKAREVIČIENĖ V. Using of biofuel and biooil in Lithuania. Vilnius. 71, **2004** [In Lithuanian].
3. Ullmann's Encyclopedia of Industrial Chemistry. A **10**, 374, **1983**.
4. GENUTIS A. Straw fuel resources, using and forecast. Therm. Technol. **2**, (24), 10, **2005** [In Lithuanian].
5. OLANDERS B., STEENARI B.-M. Characterization of ashes from wood and straw, Biomass Bioenerg., **8**, (2), 105, **1995**.

6. CIARKOWSKA K. Effect of fertilization on the structure of upland grassland soil. Pol. J. Environ. Stud., **19**, (4), 693, **2010**.
7. http://lt.lt.allconstructions.com/portal/categories/309/1/0/12/article/9175/pelenai-ir-darzui-ir-gelynui [In Lithuanian].
8. http://www.lzuu.lt/nm/l-projektas/augalu-mityba/53.htm [In Lithuanian].
9. ZHANG F.-S., YAMASAKI S., KIMURA K. Rare earth element content in various waste ashes and the potential risk to Japanese soils. Environ. Int. **27**, (5), 393, **2001**.
10. PIEKARCZYK M., KOTWICA K., JASKULSKI D. The elemental composition of ash from straw and hay in the context of their agricultural utilization. Acta Sci. Pol. Agricultura **10**, (2), 97, **2011**.
11. Conference on Recycling of Biomass Ashes. Innsbruck, Austria. Program and abstract book. 47, **2010**.
12. SCHIEMENZ K., KERN J., PAULSEN H.M., BACHMANN S., EICHLER-LÖBERMANN B. Phosphorus fertilizing effects of biomass ashes. In Recycling of Biomass Ashes, **VIII**, 17, **2011**.
13. SCHIEMENZ K., EICHLER-LÖBERMANN B. Biomass ashes and their phosphorus fertilizing effect on different crops. Nutr Cycl Agroecosyst. **87**, (3), 471, **2010**.
14. SANDER M.-L., ANDRÉN O. Ash from cereal and rape straw used for heat production: liming effect and contents of plant nutrients and heavy metals. Water Air Soil Pollut. **93**, (1-4), 93, **1995**.
15. STEENARI B.M., SCHELANDER S., LINDQVIST O. Chemical and leaching characteristics of ash from combustion of coal, peat and wood in a 12 MW CFB: a comparative study. Fuel **78**, (2), 249, **1999**.
16. http://gardening.about.com/od/soil/f/Wood_Ash.htm
17. MARRUZZO G., MEDICI F., PANEI L., PIGA L., RINALDI G. Characteristics and properties of a mixture containing fly ash, hydrated lime, and an organic additive. Environ. Eng. Sci., **18**, (3), 159, **2004**.
18. SVANTESSON T. Automated manufacture of fertilizing granules from burnt wood ash. Lund University, 117, **2000**.
19. RAISON R. J., MCGARITY J. W. Soil. Sci. Soc. Am. J., **42**, 140, **1978**.
20. GOTO S., AOKI M., TAKADA C., HAYASHI H., CHINO M., CAI D.L. Jpn J. Soil Sci. Plant Nutr., **71**, (3), 378, **2000**.
21. http://www.loedige.de/uploads/_downloads/BR-IND-GB-BUILDING-GLP200107.pdf
22. http://en.cnki.com.cn/Article_en/CJFDTOTAL-HNKX200404019.htm
23. YUSIHARNI B.E., ZIADI H., GILKES R.J. A Laboratory and glasshouse evaluation of chicken litter ash, wood ash, and iron smelting slag as liming agents and P fertilizers. Soil Res., **45**, (5), 374, **2007**.
24. CLARHOLM M. Granulated wood ash and a "N-free" fertilizer to a forest soil-effects on P availability. For. Ecol. Manag., **66**, 127, **1994**.
25. PALECKIENĖ R., SVIKLAS A. M., ŠLINKŠIENĖ R. The role of sugar factory lime on compound fertilizers properties. Pol. J. Environ. Stud., **16**, (3), 423, **2007**.
26. PALECKIENĖ R., SVIKLAS A. M., ŠLINKŠIENĖ R., ŠTREIMIKIS V. Complex fertilizers produced from the sunflower husk ash. Pol. J. Environ. Stud., **19**, (5), 973, **2010**.
27. GONZÁLEZ-FERNÁNDEZ P., ESPEJO-SERRANO R., ORDÓÑEZ-FERNÁNDEZ R., PEREGRINA-ALONSO F. Comparative studies of the efficiency of lime refuse from sugar beet factories as an agricultural liming. FAO European Cooperative Research. Material Nutrient and Carbon Cycling in Sustainable Plant-Soil Systems, 157, **2004**.
28. MESIC M., BUTORAC A., BAŠIC F., KISIC I. The influence of sugar factory waste lime and phosphogypsum upon selected chemical properties of an acid semigley. 16th World Congress of Soil Science, Symposium 21, **1998**.
29. NAVICKAITĖ G., PALECKIENĖ R., SVIKLAS A.M., ŠLINKŠIENĖ R. Molasses influence on ash granulation process and quality parameters. Mater. Sci., **16**, (4), 373, **2010**.
30. POKHODENKO L. A. Methods for determining various forms of nitrogen in mineral nitrogen fertilizer. Instruction, Lvov, LPI, **1986** [In Russian].
31. Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 Relating to Fertilizers. Official Journal. 304-1, **2003**.
32. ZOLOTOV J. A. Fundamentals of analytical chemistry. Moscow. 464, **2001** [In Russian].
33. PENTIN J. A., VILKOV L. V. Physical Methods of Chemical Analysis. Moscow, 684, **2003** [In Russian].
34. YUNG G. Instrumental Methods of Chemical Analysis; Moscow, 608, **1989** [in Russian].
35. NAKAMOTO K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed.; New York, 536, **1986** [In Russian].
36. ŠIAUČIŪNAS R., BALTAKYS K., BALTUŠNIKAS A. Instrumental Analysis of Silicates Materials. Kaunas, 244, **2007** [In Lithuanian].
37. PALECKIENĖ R., SVIKLAS A. M., ŠLINKŠIENĖ R. Compound Fertilizer; Vilnius, 197, **2008** [In Lithuanian].
38. CEN REPORT. Fertilizers – Crushing strength determination on fertilizer grains. LST CR 1233:**2006**.