Distillery waste management in line with the concept of circular economy

Z Wzorek¹, K Krupa-Zuczek², V Čablík³, A K Nowak⁴ and K Gorazda⁵

¹Professor, Cracow University of Technology, Kraków, Poland
²Ph.D., Cracow University of Technology, Kraków, Poland
³doc. Ing. Ph.D., VSB - Technical University of Ostrava, Faculty of Mining and Geology, Department of Environmental Engineering; Institute of Clean Technologies for Extraction and Utilization of Energy Resources, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic
⁴Ph.D., Cracow University of Technology, Kraków, Poland
⁵Professor, Cracow University of Technology, Kraków, Poland
e-mail: akn@chemia.pk.edu.pl

Abstract. The paper presents physico-chemical characteristic of distillery residue and ashes after its calcination at 650 and 850°C, that may become a potential energy source due to a relatively high heat of combustion and low content of sulphur and moisture. The chemical composition of the obtained ash as well as fresh distillery residue determines its further use for fertilising purposes. Adducing the legislative regulations none of the analysed key heavy metal exceeds norms allowable in the regulation referring to organic and organo-mineral fertilisers. Proposed solution can be considered as waste minimization technology with energy recovery by rational recycling of nutrients. Such an application will exert an additional positive influence on the circular economy potential.

1. Introduction
The legislative changes referring to the distillery sector which were introduced in Poland and the European Union not only led to a considerable decrease in the number of farm distilleries but also resulted in an increase in the amount of waste generated in this industry [1-5]. Farm distilleries in Poland mainly produce ethanol for food industry. The other equally popular area is the utilization of ethanol for energetic purposes – as an additive to biofuels in the form of biocomponent. Up to the year 2005 the production of bioethanol and ethanol was carried out in two stages. The first stage took place in a farm distillery and consisted in the production of agricultural distillate with the infusion mashing process and the second stage, which was carried out along a separate technological line, consisted in dehydration to 99.8% ethanol content. Such a production system resulted in considerable material and energetic losses. After the year 2005 ethanol, and in particular bioethanol for transportation purposes, started to be produced with one-step technologies. The world’s total production of alcohol from cane sugar is more than 13 million litres [6-7]. These are based on an integrated system of producing and dehydrating of the raw material. It is currently estimated that there are around 173 farm distilleries in Poland, which operate periodically [8-9].
Mainly grains are used as the raw material in the production of ethyl alcohol. 227.8 million litres of ethanol are produced from grains. These are followed by molasses – 30.3 million litres, and potatoes – 2.9 million litres of ethanol. Assuming that in order to produce 1 litre of ethyl alcohol one needs 2.9 kg of grains, or 3.3 kg of molasses, or alternatively 12.5 kg of potatoes, such a production level resulted in the necessity for making use of 661,000 tons of grains, 100,000 tons of molasses, and 36,000 tons of potatoes. As an example, in 2011 the total ethanol production in Poland stood at 347.2 million litres, of which 123.2 million litres were aimed at the production of alcohols, 149.6 at the production of fuels and biocomponents, and the remainder was utilized in other industrial sectors [2,6,10-11].

Traditional distillery industries release about 8-15 litres of wastewater for the production of every liter of alcohol during the process. The distillery wastewater is the most complex substrate which leads to pollution in water and environment [12].

At present the Biostil process is the most frequently applied method in the production of ethanol. It is based on continuous removal of ethanol from fermenters and makes use of osmophilic yeast. The application of the Biostil process results in a decrease in the amount of stillage from 11 litres to 0.8 litre per 1 litre of ethanol produced. The stillage is concentrated in an evaporator and is characterized by an extract at the level of 45% dry mass [13].

Such a condition of the distilling sector naturally generates post-industrial organic waste in the form of biomass. The waste, due to its character and biological instability, may become a real threat to natural environment. On the other hand, however, the chemical composition of waste does not allow for treating it as waste designed for depositing in a landfill, particularly when new alternative energy sources are being searched for [14-15].

Distillers industry is focusing not only on reducing of cost production but also on reducing the negative impact on the environment. Such a solution can often be achieved by combining the distillery and cogeneration [16]. Waste from distilleries can also be used to produce hydrogen and thus considered as an alternative fuel [17-18]. Wastewater from alcoholic distillery can be treated in the presence of microorganisms under aerobic thermophilic. In this process organic and inorganic pollutants are transformed into environment-friendly by-products [19-21].

Growing EU environmental demands regarding waste management and an increase in making use of renewable energy sources are an additional aspect supporting the practical application of this type of waste. The European Union, in the perspective of 2020, obliged its member countries to execute the policy described as 3x20% principle referring to 20% reduction of greenhouse gas emissions compared to 1990. Another obligation constitutes lowering of energy consumption by 20% and an increase in making use of renewable energy sources by 15% [7-8,22-23].

2. Distillery waste in the policy of circular economy

The constantly depleting natural resources are the concern of the world community. Hence, there is an increasing emphasis on taking measures which in the long run will allow for substituting fossil raw materials with renewable raw materials – derived from waste. For many years an increase in the amount of generated waste has been observed. It is also known that waste is often a good source of recyclable materials [24]. On the other hand, however, procedures consistent with a waste hierarchy commonly used in the UE, including the recovery of raw materials from waste, bring benefits connected with the reduction of weight and volume of what ultimately has to end up in a landfill.

The EU Member States pursuit of increasing the recycling level in accordance with a long-term perspective promoted within the framework of circular economy, which resulted in the adoption of the document [25], favours the use of different types of waste as an energy raw material [26]. The combustion process itself eliminates only a problem of the amount of generated waste. Different forms of energy recovery from waste give an additional benefit which is crucial in view of the circular economy policy.

The work will additionally present a proposal of further use of waste from the brewing industry. Apart from the advantages resulting from using it for energy purposes it will be proved that the properties of ashes obtained in this process may constitute a potential raw material for further use in the
fertilizer industry. Such an application will exert an additional positive influence on the circular economy potential [21,27-28].

3. Materials and methods
The raw material for research constituted distillery residue and ashes prepared by calcining a sample of the analysed residue in a stationary kiln at temperatures of 650°C and 850°C under oxygen atmosphere for 3 hours.

Total phosphorus content after sample mineralization in a mixture of nitric(V) acid and hydrochloric acid in the ratio 3:1 as well as the content of soluble phosphate forms in 1 mol/dm³ hydrochloric acid in inert ammonium citrate and in water were determined both in the raw material and in ash. The obtained solutions were examined by means of differential photometric method consisting in the formation of a yellow tinted phosphorus-vanadium-molybdenum complex and the photometric measurement of absorbance at a wavelength of 430 nm with the use of Marcel Media apparatus.

Determination of calcium content with a titration method is based on dissolving the sample in nitric(V) acid, precipitation of phosphates in the form of bismuth(III) phosphate(V) and then determining the calcium content during complexometric titration with EDTA in the presence of fluorexon.

Determining the content of potassium in the form of K₂O and heavy metals was performed by an AAS method by means of AAnalyst 300 Perkin Elmer apparatus after former mineralization of the solid sample with concentrated nitric(V) acid.

Moisture content was determined with a RADWAG moisture balance, assuming 5s sampling time and a temperature of 105°C. Heat of combustion was established in accordance with the PN-81/G-04513 norm with the use of an LK-12Mn calorimeter by Precyzja-Bit PPHU Sp. z o.o. The method principle consists in combusting a weighed amount of a substance in a bomb calorimeter under constant pressure and then measuring water temperature increment in a calorimetric vessel.

Sulphur content in the material was determined by Eschka method. The analysis consists in combusting an analytical sample of solid fuel in direct contact with Eschka mixture in an oxidizing atmosphere, followed by the extraction of sulphates with hydrochloric acid solution and gravimetric determination of the precipitated barium chloride.

The content of volatile components was determined by calcining the analysed material at a temperature of 850°C in a closed crucible in the absence of air, whereas the amount of ash was determined by a weight method by calcining the ash at a temperature of 850°C in an oxidizing atmosphere in the presence of oxygen and then establishing weight loss.

Thermal analysis of the material was performed with the use of EXSTAR SII TG/DTA 7300 apparatus, content analysis by the X-ray fluorescence method was carried out on MiniPal4 apparatus by PANalytical. Phase composition was determined by XRD.

4. Results and discussion
At the first step of research fresh distillery residue as well as ashes from its calcination were studied from the point of view of their possible use in fertilizers. The obtained results are shown in Fig. 1 and Table 1. Figures 2-3 show the result of conducted thermal analysis of the residue and ash from its thermal processing.
Fig. 1. Analysis result by X-ray fluorescence of: a) brewers’ spent grain, b) ashes from spent grain’s combustion

Table 1
Physicochemical characteristic of distillery residue and ash obtained by its calcination at temperatures of 650°C and 850°C in a laboratory chamber kiln for 3 hours in air atmosphere

| Studied parameter                                    | Fresh residue | Ash 650°C | Ash 850°C |
|------------------------------------------------------|---------------|-----------|-----------|
| Total phosphorus content [%P]                        | 5.50          | 13.5      | 15.9      |
| Content of HCl - soluble phosphorus [%P]             | 2.30          | 4.44      | 5.56      |
| Content of ammonium citrate - soluble phosphorus [%P]| 2.20          | 3.59      | 4.00      |
| Content of water- soluble phosphorus [%P]            | below LOD*    | below LOD*| 0.10      |
| Calcium content [%Ca]                                | 4.47          | 9.12      | 13.7      |
| Potassium content [%K₂O]                             | 1.19          | 17.8      | 25.0      |

*LOD – limit of detection

The analysis of elemental composition shows the presence in the studied material of elements which are valuable in fertilizing: potassium, phosphorus, calcium and sulphur, as well as manganese and zinc. It should be noted, however, that thermal process significantly impoverishes brewers’ spent grain with
reference to potassium and sulphur content. Research using X-ray diffraction has shown that the analysed material (both residue and ash) does not have a crystalline structure.

![Graph](image)

**Fig. 2. Result of thermogravimetric analysis of fresh brewers’ spent grain**

![Graph](image)

**Fig. 3. Result of thermogravimetric analysis of ashes from the combustion of brewers’ spent grain at a temperature of 850°C**

One of the possible ways of using waste originating from a distillery is the process of making compost. An argument for such a solution is the chemical composition of the analyzed material, with particular reference to the moisture content and the presence of simple sugars. Therefore, heap-composting seems to be one of potential ways of its use. This solution is a relatively long-lasting process and, what is more, may pose a threat of microbiological and odour-forming origin [5, 9, 23].

Due to its chemical composition the distillery waste may also be used, among others, for the production of biogas, the main product of which is e.g. methane. Such a solution, in spite of the fact that it ensures safe waste utilization and may give an energy benefit, does not fully use the potential of the described waste [23, 29].

The direct application of waste in a form of an organic fertilizer, despite supplying available phosphorus and potassium compounds to the soil, is risky due to the microbiological possibility of soil contamination. Moreover, together with provided mineral substances we supply the soil with organic pollutants [29].

Both the biogas production and the use of distillery waste as an organic fertilizer fit entirely into the circular economy trends [29].
However, the best solution to the problem of making use of this type of waste is its thermal utilization which significantly decreases the amount of waste and reduces a potential threat of microbiological origin. Benefits resulting from the application of such a solution also include thermal energy which may be used in a distillery and ash which, in turn, may become a substitute in the production of organo-mineral fertilizers [26-30]. The confirmation of the possibility of using ashes for fertilizing purposes in accordance with the circular economy trend will be high content of nutrients, especially phosphorus and potassium [31-32].

The conducted analysis of distillery residue and ash from its thermal processing has shown also a high content of secondary nutrients like calcium in the studied materials, which may imply their use in fertilizers.

Post-industrial waste from distilleries (brewers’ spent grain) contains 17.5% moisture and within a temperature range exceeding 220°C the combustion of organic fraction occurs. The thermal analysis of ashes from its burning shows that the thermal processing caused the complete removal of the organic fraction - the total weight loss amounted to less than half a per cent (0.45%).

Table 2 shows the contents of heavy metals in fresh residue as well as in ashes obtained by calcining at a temperature of both 650°C and 850°C.

Table 2
Physicochemical characteristic of distillery residue and ash obtained by its calcination at a temperature of 650°C and 850°C in a laboratory chamber kiln for 3 hours in air atmosphere

| Content [mg/kg] | Analysed material | Fresh residue | Ash 650°C | Ash 850°C |
|----------------|-------------------|---------------|-----------|-----------|
| Mg             |                   | 2.94          | 15.1      | 60.2      |
| Fe             |                   | 0.21          | 0.87      | 3.59      |
| Zn             |                   | 61.9          | 330       | 1198      |
| Cr             | below LOD*        | 3.95          | 26.0      |
| Cu             | below LOD*        | 13.6          | 126       |
| Cd             |                   | 13.1          | 14.7      | 18.5      |
| Pb             | below LOD*        | 6.65          | 31.6      |
| Ni             |                   | 39.7          | 39.3      | 60.2      |

*LOD – limit of detection

The data included in Table 2 unambiguously confirms the possibility of using both fresh distillery residue and ashes from its thermal processing for fertilizing purposes. Adducing the Regulation of the Minister for Agriculture and Rural Development of 18 June 2008 [33], none of the key heavy metals exceeds norms allowable in the regulation referring to organic and organic-mineral fertilizers.

An energetic analysis of the examined distillery residue was carried out: moisture content constituted 12.6%, ash content – 4.6%, volatile components content – 83.9%, sulphur content – 0.31%; finally, the heat of combustion was determined at 21,600 kJ/kg. Such a high value of heat of combustion is closely connected with the chemical composition of the residue which contains long-chain sugars in the form of celluloses and hemicelluloses.

5. Conclusions
The studied fresh distillery residue may become a potential energy source due to a relatively high heat of combustion amounting roughly to 21,600 kJ/kg. An additional aspect supporting the thermal usage of the waste is a low content of moisture and sulphur compounds. Thermal processing of brewers’ spent grain causes lowering of sulphur and potassium content. On the other hand, however, the chemical composition of ash obtained by calcination of the waste being discussed determines its further use especially for fertilizing purposes. Phosphorus seems to be a particularly valuable raw material in the ashes. In the case of this type of organic waste, a good solution may be an in situ use of the product as a biomass source and, ultimately, as a substitute for conventional fuels and as a fertilizer.
Further research work aimed at implementation of the ash obtained from distillery waste incineration as a potential raw material for the fertilizers production is fully justified. They are pro-ecological activities that inscribe in the policy of sustainable development and circular economy. Thanks to the proposed solution, the effect of reducing the amount of organic waste, heat recovery and obtaining secondary raw materials for the production of fertilizing substances will be simultaneously achieved.

Acknowledgements
Publication was supported financially under Contract No. 944/P-DUN/2019 from funds of MNiSW intended for dissemination of science (DUN).

References
[1] Sitka A, Jodkowski W and Wójcik K 2013 Archiwum energetyki 1-2 31-40
[2] Golisz E and Wójcik G 2013 Inż. Rol. 2 (143) T1 pp 69-78
[3] Maroun M R and Lèbre La Rovere E 2014 Biomass Bioener. 63 140-155
[4] Elbehri A, Segerstedt A and Liu P 2013 Biofuels and the sustainability challenge: a global assessment of sustainability issues, trends and policies for biofuels and related feedstocks FAO, Rome
[5] Sonobe K, Kobayashi S, Lian F, Asano R and Okazaki K 2012 Waste Biomass Valoriz. 3, 2 207-211
[6] Sridevi K, Sivaraman E and Mullai P 2014 Bioresour. Technol. 165 233-240
[7] Al-Mansour F and Zuwala J 2011 Biopaliwa transportowe na świecie i w UE Gospodarka Materiałowa i Logistyka 6 16-24
[8] Golisz E, Drożdż B, Kupczyk A and Redlarski A 2013 Historia, stan aktualny i perspektywy gorszeli rolniczych w Polsce cz. 1 Przemysł Fermentacyjny i Owocowo-Warzywny 1 23-25
[9] Strąk E and Balcerak M 2015 Acta Sci. Pol., Biotechnologia 14, 1 33-44
[10] Samsudeen N, Radhakrishnan T K and Matheswaran M 2016 Process Biochemistry 51, 11 1876-1884
[11] Milton M A, Knodel J, Kiprop A, Namango S S, Zhang Y and Geißen S 2015 Biomass Bioener. 75 101-118
[12] Mayer F D, Brondani M, Hoffmann R, Feris L A and Baldo V 2016 Biomass Bioener. 93 168-179
[13] Bechard R, Gomez A, Saint-Antonin V, Schweitzer J M and Maréchal F 2016 Energy 117, 2 540-549
[14] Mishra P, Roy S and Das D 2015 Bioresour. Technol. 198 593-602
[15] Samsudeen N, Radhakrishnan T K and Matheswaran M 2015 Bioresour. Technol. 195, 242-247
[16] Krzywonos M, Cibis E, Lasik M, Nowak J and Miśkiewicz T 2009 Bioresour. Technol. 100, 9 2507-2514
[17] Bustamante M A, Paredes C, Morales J, Mayoral A M and Moral R 2009 Bioresour. Technol. 100, 20 4766-4772
[18] Blonska V, Meneret A and Vilu R 2003 Adv. Environ. Res. 7, 3 671-678
[19] Ministry of Economy 2009 Energy Policy of Poland until 2030.
[20] Satyawali Y and Balakrishnan M 2008 J. Environ. Manag. 86 481-497
[21] Álvarez R and Ruiz-Puente C 2017 Waste Biomass Valoriz. 8, 5 1521-1530
[22] Communication From The Commission To The European Parliament, The Council 2017 The European Economic And Social Committee And The Committee Of The Regions, The role of waste-to-energy in the circular economy COM(2017) 34 final, Brussels
[26] Doušková I, Kaštánek F, Maléterová Y, Kaštánek P, Doucha J and Zachleder V 2010 Energy Convers. Manag. 51 606-611
[27] Ghisellini P, Cialani C and Ulgiati S 2016 J. Cleaner Prod. 114 11-32
[28] Peng W and Pivato A 2017 Waste Biomass Valor. First Online: 07 September 2017 1-17
[29] Subhash P, Animesh D, Fantahun D and Brajesh D 2018 Waste Biomass Valoriz. 9, 4 601-611
[30] Guedes P, Couto N, Mateus E P and Ribeiro A B 2017 Waste Biomass Valoriz. 8, 5 1587-1596
[31] Kominko H, Gorazda K and Wzorek Z 2017 Waste Biomass Valoriz. 8, 5 1781-1791
[32] Kominko H, Gorazda K, Wzorek Z and Wojtas K 2018 Waste Biomass Valoriz. 9, 10 1817-1826
[33] Minister for Agriculture and Rural Development 2008 Regulation of the Minister for Agriculture and Rural Development of 18 June 2008 on the implementation of certain provisions of the act on fertilizers and fertilization Official Journal of Law No. 119, item 765