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Traditional and new raw materials for spirit beverage production BIOOPEN 2021 – POST-CONFERENCE ARTICLE

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ABSTRACT

The ethanol production industry is a fast growing branch of the economy in many countries, and there is a rich tradition of spirit beverage production of many unique drinks such as Polish vodka and Starka or Irish and Scotch whisk(e)y, all of which have unique organoleptic features. This variety is possible thanks to different raw materials used for production such as rye, barley or corn and potatoes, as well as technological solutions developed over the generations of manufacturing. Rye deserves a closer look due to its low growth requirements and many different uses as well as its long tradition of cultivation, especially in Poland. On the other hand, manufacturers are currently interested in using new, original raw materials for the production of so-called craft alcohols. Buckwheat is an example of a raw material that can be successfully used in the production of original spirits.

KEYWORDS: cereal grain, pseudo-cereals, starch, fermentation, agricultural distillate, vodka

Introduction

For centuries, the production of spirit drinks has been an important branch of the economy of many countries around the world. In Poland, the production of drinks as vodka and Starka has a long tradition. Countries such as Scotland and Ireland are known for whisk(e)y production, France is known for cognac and calvados, Italy is known for grappa and the United States is known for bourbons, among others. In Asian countries, strong spirit beverages with high ethanol content are also produced. The typical products of this region are drinks such as arak, rum or Japanese whisky, which is based on the production technology of traditional Scotch whisky and has become popular in recent years. These ethanol beverages have unique sensory features that are directly connected to the wide range of raw material used for their production. These features are a direct consequence of intricate, unique procedures included in their production, for example, the use of smoke created from burning peat to dry malt during Scotch whisky production, while in Irish whiskey smokeless hot air is used in this process, resulting in more a delicate flavour of the finished beverage (Cieślak and Lasik 1979).

The Polish spirits industry is a crucial part of the economy. Poland is the largest manufacturer of vodka in the European Union and the fourth largest vodka producer in the world, just behind Russia, Ukraine and the United States. Significant volumes of exports contribute to the improvement of the country's trade balance. For several years, the largest importers of Polish spirit drinks have been France and the United States. Other important export destinations are Hungary, Germany, Italy, Bulgaria and Canada. Besides. Polish spirit drinks are sold in such distant markets as Singapore, Hong Kong and Chile. The estimated demand for starchy raw materials for the annual production of ethanol amounts to an average of 420,000 tons of grain and 80,000 tons of potatoes. It should be emphasised that approximately 94% of used raw materials are from Poland.

In Poland, 320 million litres of spirit beverages are produced each year, and up to 57.75 million litres are exported from Poland all around the world. These exports bring a total revenue of 151.3 million EUR. The ethanol production industry in Poland generates 4009 direct jobs and up to 89,000 indirect jobs. In 2013, the excise tax generated 10.1 million PLN (Związek Pracodawców Polski Przemysł Spirytusowy n.d.) in revenue.

Starchy raw material used for the production of spirits

Currently, the most commonly used basic raw materials for spirit beverage production are potatoes and cereal grains such as rye, wheat, and maize. Manufacturers are searching for new cultivars of plant raw materials, with appropriate physicochemical properties, such as starch, protein content (Pietruszka and Szopa 2014) and moisture content as basic indicators of the storability of cereal grains. Indeed, the levels of these factors indicate the risk of mould formation and the growth of other undesirable microorganisms while the material is being stored (Wilkin and Stenning 1989). Moreover, it is important that the processed raw materials allows the manufacturers to obtain desirable organoleptic properties in the finished products, such as smoothness and delicate smell and flavour.

Rye grain – a traditional raw material in the Polish spirits industry

Rye (Secale L.), as most cereal crops, belongs to the class of monocotyledons plants (Monocotyledoneae) from the family Poaceae. Rye originally entered Polish territory from central Asia in the 5th century, where it was commonly growing and was treated as a weed on farmlands. This cereal has low soil requirements and can be grown on almost every kind of existing soil type. The rooting system of rye enables it to draw water, essential minerals and substances needed for growth even from layers of soil in which other plants cannot grow. Even without additional supplementation, rye has shown higher yields than other cereals planted on the same field. A high yield is guaranteed by supplementation of the soil with three basic minerals: nitrogen, phosphorus and potassium. Rye also has low heat requirements - thus it can start to grow early in spring - and it is immune to low temperatures (even -25 °C) in harsh winter conditions. However, the yield is determined mostly by weather and the level of agrotechnology involved in the growing process (Ludwicka 2007, Buksa et al. 2012).

The main product in rye farming is its grain, which is used in numerous industries, such as baking, milling or ethanol and spirit beverage production. Rye grain is also used as animal feed, but farmers have gradually lost interest in it because of its low caloric value. Besides the main product (the grain), other parts of the plant can be used in numerous ways. Indeed, straw can be also used as animal feed but also as lignocellulose raw material in the production of secondgeneration bioethanol. which is becoming more popular every year, for energy production purposes (Kapusta 2016).

Among many different species of rye from *Secale* L., only one (*Secale cereale* L.) is suitable for cultivation; others have not found application in industry. However, within this species there are many cultivars – natural and manmade – that differ in their physicochemical composition and suitability for industrial applications (Jarosz and Jarociński 1980; Górny 2004; Kapusta 2016).

Besides its basic components such as starch (on average 60%), protein (about 12%) and fat (about 2%), rye grain is also rich source of dietary fiber (Figure 1), of which the main part comprises fructans, pentosans and β -glucans, which are soluble in water fractions and have proven pro-health features. Moreover, rye grain also contains phenolic compo-unds (ferulic acid, 3,4-dihydroxycin-namic acid) phytoestrogens and vitamins.

Most of these pro-health components are found in the external layers and not in the endosperm (Gąsiorowski 1994; Michniewicz and Gąsiorowski 1994; Michniewicz 1995; Vinkx and Delcour 1996; Nilsson *et al.* 1997; Heinonen *et al.* 2001).

The characteristic features of soil in Poland are light and very light, which makes rye still one of most popular grown cereals in the country; however, in recent decades its growth acreage has decreased systematically. In 2015, GUS (Główny Urząd Statystyczny) reported that rye in Poland comprised 725,000 ha of land, representing 10.7% of all cultivated cereals, while in the 1980s and 1990s, it had been grown on markedly more land. Among rye cultivars grown in Poland are so-called population and hybrid cultivars. The hybrid cultivars differ from the population cultivars by seed material, which in the case of hybrids needs to be specially cross-bred every time. The main difference between the population and hybrid cultivars is their fertility. Researchers have shown that yield of the hybrid cultivar crops are 17%–19% higher than the population cultivar crops. This difference is directly connected to the heterosis effect obtained by cross-breeding male forms and pollinators with a broad genetic basis. This heterosis effect is only valid through



Figure 1. Average composition of rye grain (adapted from Gąsiorowski 1994).

the first generation (F1); hence, farmers need to purchase the hybrid seed material every year. In the case of the population cultivars, farmers can use the grain grown in the previous year without significant difference in yield height for 2-4 years (Grabiński 2016). The Polish National List (NLI n.d.) currently has 65 registered cultivars of winter rye. Among them are 50 intended for harvesting grain (26 population and 24 hybrid cultivars). Since 2008, the total sugar content of grains from each cultivar has been recorded, information that should be helpful to indicate the cultivars suitable for ethanol production.

Cereal-grain-based spirit beverages

Whisk(e)y

Whisk(e)y is a popular spirit beverage around the world. As defined by Lyns (2003), whisk(e)y is a spirit drink prepared by fermentation of mashes prepared with the use of barley malt and the addition of other cereal grains. The bioconversion process is carried out with use of the yeast Saccharomyces cerevisiae. However, there are many types of whisk(e)y produced outside the United Kingdom, from where most popular whiskies (Scotch and Irish whiskey) have originated, but also similar drinks are produced in the United States and even in Japan, where manufacturers produce whiskies with pleasant taste and aroma, such as Scotch whisky.

Scotch whisky

Scotch whisky is a spirit drink produced with the use of barley malt and often with the addition of other cereal grains, mostly wheat and corn. This addition can even reach up to 90% of the total mash mass. Current, wheat is the most used additional raw material. Traditional Scotch whisky is produced in small distilleries all around Scotland, and a number of rigorous requirements need to be fulfilled so that the beverage can be called a 'Scotch whisky'. First, all stages of the production process need to be carried out on Scottish territory from mashes prepared with use of barley malt, the presence of which is crucial. Sweet mashes need to be prepared with only the use of enzymes from malt and fermented only with yeast. Scotch whisky is matured in oak barrels not larger than 700 litres for at least 3 years, but it is commonly aged for at least 8 years. The ageing process also needs to be carried out in Scotland. The finished products should feature the taste and smell of the used raw material and cannot include any other additives than water and caramel (Dunnett 1953; Daiches 1969; Brander 1975).

Irish whiskey

In comparison to Scotch whisky, Irish whiskey has a less of a smoky taste, and more of a rich taste and flavour. A law from the 1980s states that the name 'Irish whiskey' can only apply to beverages that originate from Northern Ireland, obtained after fermentation of mashes prepared with malts and cereals, in contrast to Scotch whisky, the production of which allows the use of an enzymatic preparation. Irish whiskey is also triple distilled to obtain a much smoother and delicate taste, and malt used for the production is dried with use of smokeless hot air. Irish whiskey also needs to be maturated in wooden barrels, not necessarily oak, for at least 3 years (Court and Bowers 1970; McGuire 1973).

American spirit beverages

Spirit drink production – bourbons, rye and wheat-based whiskey as well as Tennessee whiskey – in the United States began in the 18th century. American whiskey is produced similarly to beverages created on the British Isles, however, like in the case of Irish and Scotch whisk(e)v, the American beverages have some unique sensory qualities due to differences in raw materials and technology. Bourbon is produced with the use of corn as a raw material; the corn grain share should be between 51% and 79% of the overall mash composition. After fermentation, the mash is distilled to not higher than 80% (v/v)alcohol content. The obtained distillate is matured in burned oak barrels: during this process, alcohol content cannot be higher than 62.5% (v/v). Rye and wheat whiskey are produced in a similar fashion: the rye and wheat grains, respectively, need to comprise at least 51%. Tennessee whiskey falls under the same regulation, but to receive the name 'Tennessee whiskey', the production and maturation need to be conducted in the state of Tennessee, and the wood from which barrels for maturation are made also needs to be from Tennessee (Ralph 2003).

Polish vodka

The production of spirit beverages in the Polish territory had been recorded as early as the 14th and 15th centuries. Currently, vodka is defined as a spirit drink created out of ethyl alcohol of agricultural origin, that is, rectified spirits obtained from agricultural distillate, which is produced via fermentation and distillation process from mashes prepared with use of potatoes or cereal grains, such as rye, wheat, triticale, barely, oat or corn. 'Polish vodka' is safeguarded with a protected geographical indication (PGI), which identifies products with a quality or reputation linked to the region where it is produced, and the finished product needs to meet certain requirements. The most basic criteria is that Polish vodka cannot have any additives besides water (in case of so-called pure vodkas) and needs to be produced entirely on Polish soil. Raw materials

that can be used for the production of Polish vodka are: rye, wheat, triticale, barely, oat and potatoes, all of which must also be grown on Polish soil. Polish vodka can be matured to obtain the required unique organoleptic properties. This definition is formulated in article 38 of the Act on spirit drinks and registration, and protection of geographical indications for spirit drinks (2006).

Starka

Starka is a natural cereal vodka (okowita), the production of which dates back to the 16th century. According to the historians of the traditional production of Starka, distillate with 55% alcohol content was used, it was placed in oak barrels and later buried in sandy ground for 15-20 years to gain its unique organoleptic features. Currently, for Starka production raw rye distillate with a 91.5% (v/v) alcohol content is used, with higher alcohol content up to 2 g/l of 100% (v/v) ethanol. The distillate is matured in small oak barrels (up to 300 litres) for at least 5 years. The Szczecińska Fabryka Wódek 'STARKA' states that currently the oldest barrel still sealed and maturing is dated to be from 1947, while the oldest Starka for purchase is 50 years old (Polish Vodka Association n.d.).

Microflora of the cereal grains

One of main concerns in the ethanol production industry is the presence of accompanying microflora in raw materials, which can cause further contamination of the mash during the fermentation process. Microorganisms can grow on the above-the-ground parts of plants, the so-called phyllosphere, which is a perfect environment for supporting growth of such microbiota, due to the easy access to a food supply and optimal growth conditions. The development of the accompanying microflora is also supported by a warm and humid climate (Dix and Webster 1995).

The accompanying microflora in cereal can be divided into two groups. The first group, epiphytic microflora, comprises microorganisms growing on the surface of the plant on the field during the growth process. The second group comprises deep microflora, which get inside the grain during growth and thus develop during the storage process (Broda and Grajek 2009).

Epiphytic microflora include both fungi and bacteria. The main bacterial genera are Bacillus, Flavobacterium, Pseudomonas and Agrobacterium. Moreover, there can be pathogenic bacteria also such as *Mycobacterium* spp., Escherichia coli. Clostridium botulinum. and Listeria monocytogenes (Bakken 1997, Maciorowski et al. 2007). The fungal genera include moulds such as Alternaria, Cladosporium and Rhizopus, which are safe, but also species generally considered as dangerous for humans and animals, such as Fusarium spp. and Helminthosporium spp. (Barney et al. 1995, Bakken 1997). The moulds belonging to the second group are especially undesirable in the ethanol production industry because they produce mycotoxins, such as zearalenone; deoxynivalenol; and fumonisin B1, B2 and B3. Because mycotoxins are resistant to degradation in the conditions used during ethanol production, mycotoxins are present in the waste material/distil-lery stillage, which is used as animal feed. Moreover. mycotoxins in mashes have a direct impact on the acetaldehyde content in the finished agricultural distillate (Kłosowski et al. 2011).

The deep microflora that develops during storage of the grain mostly comprises fungi: the quantity of bacteria during the storage process falls below 1000 cells/g of grain (Broda and Grajek 2009). The fungal genera include *Chaetomium*, *Hansenula*, *Aspergillus*, *Candida* and *Penicillium* (Maciorowski *et al.* 2007).

Buckwheat – a new raw material for agricultural distillate production

Buckwheat has gained popularity around the world due to its low soil requirements and the comparable starch content relative to widely used cereal grains; these factors make it a potential new raw material for spirit beverage production. In some countries, buckwheat is used for the production of alcoholic beverages: French and U.S. distillers use this raw material in whisky production, while in Japan buckwheat grain is processed to make an alcoholic beverage called soba shōchū (Haros and Sanz-Penella 2017).

Buckwheat does not belong to the grass family (Poaceae), as cereals do, and it is therefore referred to as a pseudocereal. There are fifteen species of buckwheat, nine of which are used in agriculture, but only two are grown for food purposes: Fagopyrum esculentum and Fagopyrum tataricum (Dziadek et al. 2016). Buckwheat has a similar chemical composition to cereals (Figure 2). The average starch content in buckwheat grain is about 50%. The content of other macromolecules is 12% proteins. 4% lipids, 2% soluble saccharides, 7% dietary fiber, 2% ash and 18% other substances (Im et al. 2003).

Buckwheat is often used in the manufacture of products intended for consumers with coeliac disease. A buckwheat malt is used in the production of gluten-free beer (Deželak *et al.* 2014). In the case of distilled alcohols, the absence of gluten proteins in buckwheat grains is of little interest because all spirits are gluten-free. The distillation process makes it unlikely that allergenic



Figure 2. Average chemical composition of buckwheat (adapted from Im et al. 2003).

proteins will be carried over into the distillate during this process (European Food Safety Authority 2004). Many researchers have reported on the use of buckwheat for the production of various food products, including alcoholic bever-ages (Starowicz et al. 2018). Moreover, the direct interest of Polish producers of spirit drinks to produce new, original beverages prompted us to undertake research on the use of buckwheat grain for the production of spirit drinks. In our study (Ługowoj et al. 2020), we assessed the suitability of two cultivars of buckwheat grains, Panda and Kora, for agricultural distillate production. Both cultivars had a similar starch content. Fermentation of the Kora-cultivar-based mashes resulted in a higher fermentation efficiency (up to approximately 85% of the theoretical yield) compared with the Panda-cultivar-based mashes (up to approximately 75%). The obtained distillates contained relatively low concentrations of unde-sirable compounds, such as acetaldehyde and methanol, and revealed pleasant organoleptic features. The results of this study confirm the possibility of using this pseudo-cereal in the production of original distillates with a specific aroma, flavour and raw material identity.

Conclusions

The ethanol and spirits production industry is an important branch of the economy in many developed countries, including Poland. This is due to the fact that ethanol is used in many industries, including chemical, pharmaceutical, food and beverage production, among others. Hence, research in this field is crucial to provide further development. Moreover, there is increasing interest in niche craft products from both micro-distilleries and large spirit plants, which are considering the use of new raw materials while taking into account social attachments and tradition.

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