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New trends or return to traditional methods in the production of grain spirits?

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ABSTRACT

This review article is based on scientific and popular science publications as well as articles from branch magazines that refer to the production of alcohol in Poland based on traditional grain raw materials. New trends in the production of broadly understood alcoholic beverages point to a return to traditional raw materials and production methods, preferably carried out in small, traditional distillery – crafted beers, local wines or spirits. Consumers desire a return to tradition, however, it is equally important to maintain the right quality and efficiency of production. The future of alcoholic beverages based on malted and unmalted cereals in Poland is associated with the search for specific varieties of cereals, their mixtures as well as fermentation and distillation processes that will allow the production of 'craft spirits'.

KEYWORDS: rye, barley, cereal malts, alcoholic fermentation, natural products, agricultural distillate, spirit beverages

Introduction

The history of alcoholic beverages manufacturing dates back to the beginnings of humanity – over 10,000 years BC. There was wine made of figs, dates and grapes in China, Egypt, Persia, Greece and Rome. In turn, the first records of beer production in Mesopotamia are from 4000 to 2000 BC. The history of the distillation process, which is the precursor to today's distilled alcoholic beverages, dates back to the 8th century AD, when Arab alchemists invented the process of 'smoking wine'. Mention of the first distillation apparatus (producing *Aqua vitae* or *Aqua ardens*) comes from the 13th century. Significant development and modifications of distillation technique and later purification of the so-called raw alcohol/spirit by using rectification apparatuses took place in the 18th and 19th centuries. At that time, raw material other than fruit started to be used for fermentation – potatoes, molasses and cereals – and there was a rapid development of spirit industry at a high-volume scale (Cieślak and Lasik 1979; Rogala 2004).

Polish spirits industry

Spirit beverages produced in Poland are well known and popular all over the world. Our country is the largest vodka producer in the European Union and the fourth largest in the world. Only Russia, Ukraine and the United States have a higher spirit volume produce then Poland. Export of spirits contributes significantly to the improvement of the country's trade balance, and the value of the exported vodka was 142.4 million EUR in 2016 (Związek Pracodawców Polski Przemysł Spirytusowy [ZP PPS] 2021). On average, 71% of exported spirit beverages go to the European Union countries - France is one of the largest importers - and 16% go to the United States. Polish vodkas are well known and recognised around the world.

According to the European Parliament and Council Regulation (EU) (2019/787), vodka is a spirit drink produced from ethyl alcohol of agricultural origin (i.e. rectified spirit) obtained following fermentation with yeast of either potatoes or cereals or both, or other agricultural raw materials, distilled so that the organoleptic characteristics of the raw materials used and by-products formed in fermentation are selectively reduced. This may be followed by additional distillation or treatment with appropriate processing aids, including treatment with activated charcoal, to give it special organoleptic characteristics. The mini-mum alcoholic strength of vodka shall be 37.5% vol. The regulation also set limits for the content of volatile by-products, with particular emphasis on methanol.

Polish Vodka is protected by a geographical indication that proves its quality and reputation due to the region of production. The Act of 18th October 2006 (as amended) on spirit drinks and

registration as well as protection of geographical indications for spirit drinks defines the raw material for ethyl alcohol of agricultural origin used in the production of Polish Vodka. Ethyl alcohol produced from rye, wheat, barley, oats, triticale or potatoes cultivated in the territory of the Republic of Poland may be used. Moreover, all stages of production should take place in the territory of the Republic of Poland. Products benefiting from this geographical indication may also be aged to give them special organoleptic properties. The geographical protection of Polish Vodka is to emphasise the tradition and heritage of Poland in the production of spirit beverages. and to draw attention to the traditional raw materials used in the production of vodka.

Cereal grains and malts as raw materials for the production of spirit drinks

Among the starchy raw materials used to produce spirits, the undisputed leader in the production of vodka is rye, which has been used in the production of spirit distillates since the Middle Ages. This vodka, formerly known as okowita (Latin: *aqua vitae*), was described by the Frenchman Sieur d'Hauteville – steward at the court of the Polish king Jan Kazimierz (17th century) – who wrote: 'Vodka is runned in Poland from grain. It is in no way inferior to either the strength or the goodness of wines made with wine yeast (i.e. winemakers)' (Jarociński and Jarosz 1980).

The superiority of rye over the other types of cereals is due to its minimal growth requirements. The low habitat requirements of this species enable it to be cultivated in poorer soils and allow it to survive the unfavourable conditions of winter, as well as periods of water scarcity. The soils in which rye grows do not require a strong support with fertilisers; this factor is reflected in its quality. Due to a moderate supply of natural nutrients, rye grains are devoid of ingredients that may deteriorate the quality of the ethyl alcohol obtained (Dzienis 2018).

The tradition of making rye vodka has survived to the present day, and rye distillates are valued in the production of super premium vodkas, such as Belvedere Vodka or Wyborowa. Appreciated for their highest quality and unique, characteristic for the raw material used, taste and aroma have found many consumers around the world (ZP PPS 2021).

Changing trends and customer expectations have forced the producers of alcoholic beverages to be more creative in producing unique drinks and moving their production towards eco-friendly products. In their new creations, the producers convert traditional raw materials, such as cereal malts that have been used as enzyme sources, in new roles of flavour, taste and small enhancement components. At the same time, they need to meet the strict quality regulations of different countries. look for process efficiency parameters and understand all fermentation and distillation processes to share the knowledge with the customers, who 'want to understand, not only consume'. For this reason, many scientists have undertaken research on alcoholic products using traditional raw materials, such as cereal grains and malts, to produce the so-called 'crafted vodkas'. which are most often made from unrectified/raw spirits. An example of such spirit beverages are drinks called in Polish 'okowita' (category 'spirits/ grain spirits' according to the Regulation EU 2019/787). These spirits are produced exclusively by the distillation of a fermented mash of whole grain cereals and have organoleptic characteristics derived from the raw materials used. The

addition of other alcohol or flavours is not allowed (EU Regulation 2019/787).

Cereal grains can be used in the spirit industry in two ways: as a basic raw material (the main source of carbohydrates, namely starch) or as a supportive raw material in the form of malt, as a source of natural amylolytic enzymes (Kaukovirta-Norja *et al.* 2004). These enzymes are represented by α -amylase – catalyses the hydrolysis of starch to dextrins and liquefying the medium, and β -amylase – a saccharifying, maltogenic enzyme. These enzymes are necessary for the hydrolysis of starch during the hydrolysis/mashing to fermentable sugars.

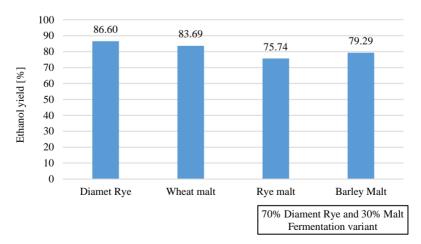
Traditionally, barley malt has been used as a source of enzymes in the production of okowita. The process is still used in the production of traditional whisky/whiskey, while the industrial scale producers more likely use comercial enzymes. Commonly used enzymes are bacterial α-amylases (Bacillus licheni-Bacillus stearothermo-philus) formis. and mould glucoamylases (Aspergillus niger, Aspergillus oryzae). The use of commercial enzyme preparations has many advantages, guaranteeing high efficiency and stability of industrial processes, but many of their features are a consequence of the use of genetically modified microorganisms (GMOs) for their production (Czupryński and Kotarska, 2011). The GMO approach is contrary to the assumptions of organic production. According to the Council Regulation (EC) 834/2007, the production of products from or using GMOs is prohibited in the production of organic products. The definition of 'ecoproduction' in the context of spirit production naturally guides the thoughts and actions of producers towards traditional production methods using endogenous amylolytic preparations, for example, barley malt or rye malt.

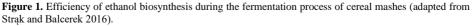
Strak and Balcerek (2016) studied the effectiveness of saccharification of cereal starch using malts as a source of amylolytic enzymes and the efficiency of alcoholic fermentation. Distillery mashes were prepared from unmalted rye of the Dańkowskie Diament cultivar with 30% (w/w) of wheat, rye and barley malts. For comparison, the unmalted-ryebased mashes were fermented using enzyme preparations of microbial origin. Figure 1 shows that the used malts, with particular emphasis on wheat malt, are suitable for enzymatic hydrolysis of starch. Mash with the addition of malts was characterised by different ethanol biosynthesis efficiencies. The highest efficiency (83.69% of the theoretical), similar to the rye fermentation with a commercial enzyme (86.60%), was observed in the sample with wheat malt. The lowest yield, despite the high enzymatic activity and the highest sugar utilisation, was achieved in mash sample with rye malt (75.74%). The authors explained this phenomenon by the possible presence of compounds inhibiting yeast fermentation activity in the mash. The mash with barley malt achieved results slightly higher than that

with rye malt. Rye grain contains a relatively high concentration of nonstarch polysaccharides (NSPs) that are predominantly of composed arabinoxylans (pentosans), β -glucans and cellulose. The detrimental influence of soluble NSPs is mainly associated with their viscosity and physiological effects on the digestive medium. Soluble NSPs increase medium viscosity, generally hampering the digestion process, whereas insoluble NSPs impede the access of endogenous enzymes to their substrates by physical entrapment (Hübner et al. 2010), which can result in reduced efficiency.

Regarding the chemical composition of the obtained distillates, the use of malts as a source of enzymes resulted in decreased concentrations of undesirable chemical compounds such as methanol and acetaldehyde. This reduction positively influenced the quality of distillates and their organoleptic values (Strąk and Balcerek 2016).

Balcerek *et al.* (2016) determined the efficiency of rye and barley starch hydrolysis in mashing processes using cereal malts as a source of amylolytic enzymes and starch; they also aimed to establish





the volatile profile of the obtained agricultural distillates. The raw material used were unmalted rve (Dańkowskie Diament variety) and rye and barley malts mixed 50%/50% with unmalted cereals. Two methods of pre-treatment of unmalted cereals were tested, namely pressureless starch liberation (PLS) and thermal-pressure starch liberation. All experiments were performed on a semitechnical scale and then verified under industrial conditions. The results showed that the efficiency of rye fermentation with rye malt in the PLS method was 77.2% (semi-industrial) and 76.2% (industrial test). The sample with barley malt had slightly lower results (76.5% and 75.5%, respectively). Compared with the findings from earlier studies, it can be deduced that increasing the malt content in the mash from 30% to 50% (w/w) did not significantly increase the ethanol production. The authors observed signifycant differences in the efficiency of ethanol biosynthesis depending on the starch liberation method. The pressurethermal starch liberation method contributed to higher efficiencies both on the semi-industrial (81.9%-87.0%) and industrial (84.8%-87.1%) scales compared with the PLS method (77.2% -80.0% on a semi-industrial scale and 75.5%-77.5% on an industrial scale) for all samples studied. The reasons for higher fermentation efficiency in mashes prepared with use of the pressure-thermal method might be due to the faster release of fermentable sugars during mashing, and their utilisation by yeast (Balcerek et al. 2016).

Volatile fermentation by-products and their effect on the quality of spirits

During the mashing, fermentation of grain raw materials and distillation processes, apart from ethyl alcohol, other volatile compounds are synthetised. These compounds include carbonyl compounds (e.g. acetaldehyde, isovaleric aldehyde, furfural), carboxylic compounds (e.g. acetic acid, propionic acid, valeric acids), esters (which usually occur at the highest concentration of ethyl acetate) and higher alcohols, commonly known as fusel oils (including 1-propanol, 3-methyl-1-butanol, 2-methyl-1-butanol, and phenylethyl alcohol), among others. The level of by-products is usually about 0.5% of the ethyl alcohol content in the distillate (Jarociński and Jarosz 1980). According the recommendations of the Polish Standard (PN-A-79523:2002). the maximum concentration of higher alcohols in agricultural distillate used for Starka production is 5 g/l absolute alcohol. Traditionally, some types of distillates are used without further purification for alcoholic beverages production. For example, agricultural rye distillate is used for the production of Starka, rum is obtained from sugar cane molasses and whisk(e)y is obtained from barley malt distillates (Jarociński and Jarosz 1980). In these spirits, it is crucial to maintain an appropriate balance between fermentation by-products and ethanol concentration to keep the desired organoleptic properties of the finished product. For this purpose, batches of produced distillates are aged for a specific time in oak barrels and then combined according to their best organoleptic and quality parameters to create a unique spirits (okowita).

The volatile compounds other than ethyl alcohol are undesirable compounds in the pure vodka. Therefore, the raw spirit/agricultural distillate is purified by a rectification process to reduce impurities selectively, and then diluted with water to a certain alcoholic strength.

The increased requirements regarding the quality and production of food and alcoholic beverages (especially on organic products) are factors indicating that technological innovations should be applied both to improve the quality of traditional spirits and to create new, original spirit drinks. An interesting group of agricultural distillates has revealed spirits produced from cereal grains mixed with cereal malts as a source of amylolytic enzymes and starch. Researchers have shown that when malts are used in alcoholic beverage production, they impact the level of fermentation byproducts in the distillates (Strąk and Balcerek 2016; Balcerek *et al.* 2016).

The most commonly analysed impurities of spirit distillates are methanol, acetaldehyde and higher alcohols (Biernacka and Wardecki 2012). Methanol is generated through hydrolysis of methylated pectins present in plants and fruit. While methanol does not directly affect the flavour of the distillate, it is subjected to restrictive controls owing to its high toxicity (Adam and Versini 1996). The content of methanol in alcohol of agricultural origin should not exceed 30 g/hl 100% alcohol. However, there are some differences allowed due to the fermentation ingredients used, for example, 10 g/hl for vodka, 1000 g/hl for grape marc spirit and 1500 g/hl for fruit marc spirit (Regulation EU 2019/787). The methanol concentration in the distillates produced from malted and unmalted cereal grains did not exceed 10 g/hl in the agricultural distillate, which is in accordance with the above-mentioned EU regulation for spirit (Strak and Balcerek 2016). Balcerek et al. (2016) presented a slightly higher result for methanol (less than approximately 20 g/hl 100% alcohol), but it was still within the limits for spirits of agricultural origin.

Conclusions

Although the malted ingredients use to produce alcoholic beverages and the technology by which they are converted have been known for a long time, the new approach for the malted cereals as a well-known flavouring component and process supportive ingredient need additional scientific investigation and deeper understanding. Based on our analysis of the literature, we conclude that the appropriate selection of malted and unmalted cereals, appropriate production technology and proper blending with rectified spirits can open the door to the production of a wide range of 'crafted vodkas', in which the most important factor will be the unique composition and organoleptic properties confirmed by the highest quality of this delicious drink. We believe that tradition can go handin-hand with innovative approaches to create new trends in alcoholic beverage production.

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