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Review

Rye Flour and Rye Bran: New Perspectives for Use

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Abstract: Rye (*Secale cereale* L.) is abundantly cultivated in countries like Europe and North America, particularly in regions where soil and climate conditions are unfavorable for the growth of other cereals. Among all the cereals generally consumed by human beings, rye grains are characterized by the presence of the highest content of fiber. They are also a rich source of many phytochemical compounds, which are mainly distributed in the outer parts of the grain. This review focuses on the current knowledge regarding the characteristics of rye bran and wholemeal rye flour, as well as their applications in the production of both food and nonfood products. Previous studies have shown that the physicochemical properties of ground rye products are determined by the type of milling technique used to grind the grains. In addition, the essential biologically active compounds found in rye grains were isolated and characterized. Subsequently, the possibility of incorporating wholemeal rye flour, rye bran, and other compounds extracted from rye bran into different industrial products is discussed.

Keywords: rye; milling; ultrafine grinding; wholemeal flour; bran; phenolic compounds; biofuel; food additive; feed

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Citation: Dziki, D. Rye Flour and Rye Bran: New Perspectives for Use. *Processes* **2022**, *10*, 293. https://doi.org/10.3390/pr10020293

Academic Editor: Bernd Hitzmann

Received: 16 December 2021
Accepted: 29 January 2022
Published: 1 February 2022

1. Introduction

Rye (*Secale cereale* L.) is the second most important cereal, next to wheat, used for the preparation of bread. European countries contribute to about 90% of the world's rye production [1]. The main countries that produce this cereal are Russia, Poland, Germany, Finland, Ukraine, and Denmark [2,3]. This crop is characterized by minimal nutritional requirements and is more productive than other cereals when cultivated in poorly prepared lands containing infertile and sandy soil [4]. Importantly, rye is a valuable crop that can grow efficiently in sandy or peaty soils. Moreover, this cereal exhibits climate-resilient properties and hence can be cultivated in low-temperature and high-altitude zones [5]. The main constituents of rye grain are starch (57.1%–65.6%), dietary fiber (14.7%–20.9%), protein (9.0%–15.4%), and ash (1.8%–2.2%) [6]. The shape and size of rye starch granules are similar to wheat starch granules [7]. The dominant proteins in rye grain are albumins and prolamins (34% and 19%, respectively) followed by globulins (11%) and glutenins (9%). About 21% of rye protein is unextractable [8]. The chemical composition of rye is mainly determined by genetic factors, soil quality, and climatic and cultivation conditions [9].

Rye is mainly processed into white flour or wholemeal flour using roller mills. Hansen et al. [6] studied the properties of 19 rye cultivars. The authors found that variations in grain milling procedures and baking properties are strongly influenced by the year of the harvest rather than by the genotype. Rye flour contains a relatively lesser amount of starch and proteins but is richer in fiber content than wheat flour [9]. Rye proteins are rich in lysine but cannot form a continuous gluten network like wheat proteins [10]. Moreover, wholemeal rye flour has been found to exhibit several beneficial effects on health, owing to the presence of a high content of dietary fiber [11] and many bioactive compounds, such as phenolic acids (PA), lignans, benzoxazinoids, and fructans, in the rye grains [12–15]. Rye is also a rich source of arabinoxylans (AX), β-glucans, and resistant starch [16,17]. In addition, wholemeal rye flour and wheat flour are rich in alkylresorcinols and minerals such as Fe, Mn, Zn, and Cu when compared to other cereals [18]. In particular, alkylresorcinols are major phenolic compounds found in wheat and rye grains [19] and are used as biomarkers for the estimation of whole grain content in various cereal products [20].

Rye flour is mainly used as an ingredient for the preparation of sourdough bread. However, rye bread can also be prepared by using a single-phase method and yeast [21]. When compared to wheat bread, which has a similar amount of available carbohydrates, rye bread reduces the demand for insulin production more effectively [22], thus exhibiting a positive effect on the glucose levels in the human body [23]. Moreover, rye bread shows higher antioxidative activity in comparison to wheat bread [11]. The wholemeal rye bread can be used for the production of kvass [24], which is a rich source of vitamins like B1 (thiamine), PP (niacin), B2 (riboflavin), and B6 (pyridoxine). This product is also a rich source of folate and shows a positive influence on metabolism and thus is used for the treatment of many digestive disorders [24]. Rye grains can also be used as a substitute for coffee grains in the production of coffee. However, this raw material is known to contain high amounts of acrylamide after processing at higher temperatures. Recently, Pitsh et al. [25] revealed that long-term storage of coffee prepared by roasting rye grains (minimum of 6 months at room temperature) reduces the acrylamide content in the final product. Additionally, rye bread exerts positive effects on insulin metabolism and reduces the demand for insulin when compared to wheat bread [23]. This effect is especially observed immediately after the consumption of whole grain rye bread and during subsequent meals [16]. Rye grains can also be used for the production of other food products, such as flakes [9], snacks [26], biscuits [27], crispbread [28], and animal feed [29,30]. Food products prepared by the processing of rye grains show many positive effects on human health. The consumption of rye food products increases satisfaction levels and also plays a role in controlling blood lipid concentration and inflammation. Moreover, in recent years, many innovative approaches have been investigated to produce novel food and nonfood rye products. Several studies are being conducted worldwide to obtain more detailed information about the nutritional benefits of rye grains. Among the publications selected from the Web of Science Core Collection from the year 2010 up to 11 December 2021, 6218 articles published information regarding rye and rye products. Most of them were published in journals such as Food Science and Technology (19.9%), Agronomy (17.3%), and Plant Sciences (16.1%) (Figure 1).

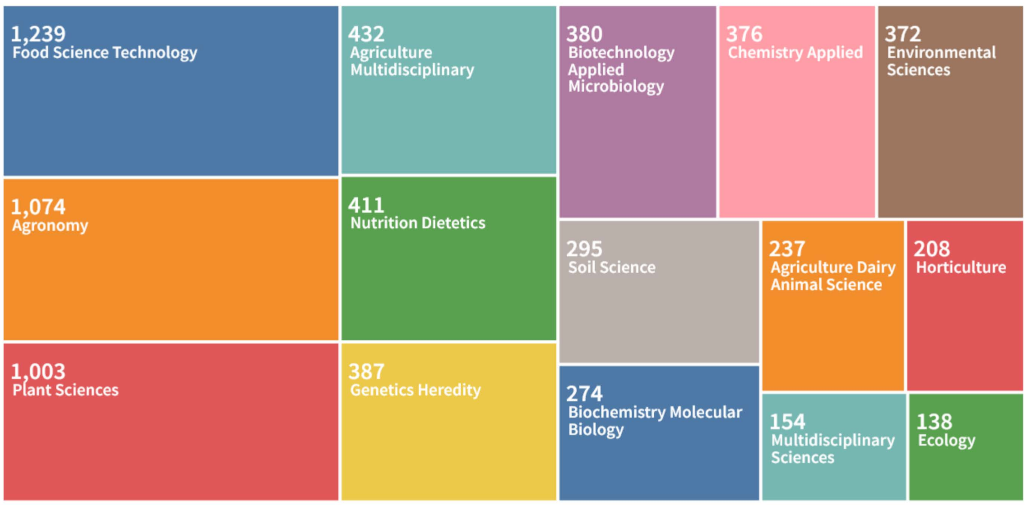

Figure 1. Tree-map chart showing the number of articles that focused on rye and rye products in different Web of Science scientific categories (chart presents the data obtained from Web of Science Core Collection base for 15 categories from 2010 to 11 December 2021).

This review aims to present the current knowledge regarding the characteristics of rye grains and recent trends in using rye flour and rye by-products for food and nonfood applications.

2. Rye Flour Milling

Roller mills are generally used for the production of white rye flour [30]. Milling of rye grains to produce refined rye flour is a relatively less complicated process when compared to the wheat flour milling process, and therefore only a few types of rye flour are produced. However, during this process, several flour fractions are also obtained from different milling streams. These fractions are characterized by the presence of different amounts of phytochemicals [31]. Before the milling process, the grain is tempered to strengthen the bran layer and germ and to facilitate the extraction of the endosperm. The outer layers of rye kernels are strongly attached to the endosperm, and therefore the milling of rye grains involves a more aggressive procedure and includes a lower number of stages when compared to the wheat flour milling process [9]. The flour obtained from different streams shows different chemical compositions due to the irregular distribution of chemical compounds inside the grain [32]. Different streams of ground rye flour are mixed to obtain different types of flours with desirable characteristics. Importantly, starch granules of rye flour are more susceptible to mechanical injury during the milling process when compared to starch granules of wheat [7]. The extent of damage to starch granules has a significant impact on the fermentation process and determines the properties of rye crumbs [9]. The extraction ratio also governs the chemical composition of milled flour. It was observed that with an increase in the flour yield, the starch content decreased, but the content of ash, protein, and β-glucan increased. These differences in flour composition can be attributed predominantly to the contamination of flour with the bran [33]. In particular, the presence of ash in the flour is an indicator of bran contamination, which occurs due to the presence of increased amounts of mineral compounds in the outer parts of the grain. The production of whole grain flour is less complicated when compared to the production of refined rye flour. However, the granulation of flour streams and bran significantly influences the properties of wholemeal flour. Therefore, different grinding techniques are used to increase the degree of fineness of the outer layers of grain [34–36]. Wholemeal rye flour contains about 2% ash and 15%–21% fiber [9]. Michalska et al. [11] found that total phenolic content is about twofold higher in wholemeal rye flour when compared to that found in white rye flour (70% flour yield). Kołodziejczyk et al. [31] proposed a dry fractionation method for the production of rye flour rich in fiber content from wholegrain rye flour. The authors used both a roller mill and ball mill for grinding purposes and obtained two different fractions: coarse flour and fine flour, with an average particle size of 427 and 102 μm, respectively. The flour fractions were characterized by the presence of a high content of dietary fiber (50% and 36.6%, respectively). Additionally, fine flour was characterized by the presence of increased amounts of soluble fiber when compared to the coarse fraction. The chemical composition and consequently the baking properties of rye flour significantly depend on the milling process and the flour yield [32]. The type of mill used for milling operation, grinding conditions, and separation parameters have a significant impact on the chemical composition and properties of rye flour [30–37]. Bread obtained from wholemeal flour is characterized by a lower volume and a denser and dark crumb compared to bread produced from refined flour. Moreover, bioactive compounds such as PA, minerals, and lignans are located in the outer layers of the rye kernels and exhibit a strong positive influence on human health [32].

Ultrafine grinding (UFG) is a quick and efficient technology to reduce the size of cereal grains [38,39] and other foods [40–42]. Such a reduction in size, also called superfine grinding or micronization, particularly impacts the functional properties of the particles and flour processing methods [43]. The adequate particle size of flour can be adjusted through the correct choice of mill and mill settings [44–46]. Methods to produce ultrafine flour employ two types of grinding techniques: dry milling and wet milling. To process cereal grains or by-products obtained from the processing of cereals, dry grinding is the most frequently used method. The UFG methods that have been extensively used for the processing of cereals are jet milling (high-speed airflow pulverization) [47], ball milling [48], and different kinds of impact milling techniques [49,50]. Kołodziejczyk et al. [31] developed a technology for the milling of high-fiber rye flour using a ball mill followed by a roller mill and the fractionation of wholemeal flour by sieving. They obtained fine and coarse rye flour fractions with 36% and 50% dietary fiber, respectively. The coarse flour was characterized by a higher yield (25.6%) and higher content of insoluble dietary fiber, whereas the yield of fine flour was lower (16.8%), and the flour had a larger amount of soluble fiber. Some authors [30] have studied the efficiency of the jet milling process in the grinding of rye grains. In the jet mill, the speed of the particles in the material to be ground is accelerated by pressurized gas, and a reduction in the grain size is achieved by the collision of particles against a solid surface [10]. This method of grinding increased damage to starch granules in the rye flour, but the degree of fineness showed no significant influence on the extraction of total phenolic compounds from the pulverized rye flour [30]. Darkos et al. [10] used the jet milling technique for the processing of rye flour to facilitate protein isolation. Silventoinenet et al. [8] adopted a different methodology for the milling of rye bran, where air classification of rye bran was followed by UFG. The authors used a pin disc mill and fine impact mill to reduce the size of bran particles. Their study revealed that pin disc and air classification processes resulted in the production of twofold higher protein-rich fractions when compared to the protein content found in rye bran before the grinding process. In addition, they noticed a positive correlation between the size of bran particles and the colloidal stability of emulsions (10% rapeseed oil to 10% (w/w) dispersions of rye flour). The amount of soluble dietary fiber increased about threefold in the protein-enriched fractions.

The particle size and particle size distribution have a strong influence on flour properties [51]. However, the higher degree of fragmentation causes an increase in grinding energy requirements [52]. Moreover, grinding energy depends on the used grinding technique, parameters of the process, and strength properties of the grain. The strength properties of cereal grains are mainly determined by moisture content [53]. Grain with higher moisture content is less brittle and more plastic, decreasing the grinding efficiency of such material [54]. Therefore, the grinding energy increases as a the moisture of the grain increases [55]. On the other hand, grain tempering (adding water to grain and allowing the grain to rest) is commonly used before milling and allows for separation of the bran from the endosperm [56]. Werechowska et al. [57] found that the specific milling energy of rye ranged, depending on cultivar and genotype, from 84.8 to 123.1 $kJ \cdot kg^{-1}$. Similar values of this parameter were found for wheat [58]. Hassoon and Dziki showed [59] showed that hammer mill grinding of rye is more energy consuming than roller milling. Additionally, they found that the preliminary grinding of rye using a roller mill significantly reduced specific grinding energy requirements for hammer mill size reduction. In addition, an increase in the speed of working parameters of the mill increases the grinding energy [60]. The above-mentioned facts and the currently available information suggest that an adequate grinding technique for rye grains or rye bran, combined with separation techniques like sieving or air classification, facilitates the production of final products with different chemical compositions and for different applications (Figure 2 and Table 1). These products can be used in the food and pharmaceutical industries to prepare a concentrate of bioactive compounds. It is also possible to extract phytochemicals from rye flour or bran fraction using different techniques [61–63]. Moreover, the grain or bran tempering to adequate moisture levels and proper selection of the grinding technology makes it possible to decrease the energy requirements for size reduction [55,59].

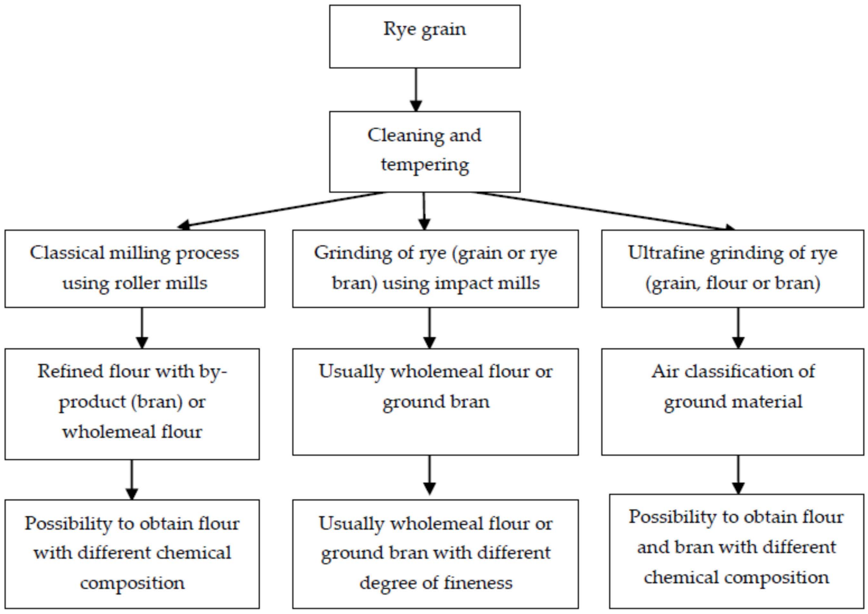

Figure 2. Modification of rye flour properties using different milling techniques.

Table 1. Advantages and disadvantages of different rye milling techniques.

Milling Technique	Advantages	Disadvantages	Ref.
Classical milling—this process involves several grinding stages (passages). Roller mills are commonly used.	Possible to obtain different types of white flour and wholemeal flour and efficient separation of endosperm from the bran. Minimal dust and minimal heat generation during grinding.	Complicated and expensive technology. Different types of machines are involved. Limited possibility of bran disintegration into fine particles.	[64,65]
Impact milling—usually performed by different types of mills, such as hammer mills or pin mills.	Especially preferred for wholemeal flour production. Relatively simple technology and easy to mill. Fine particles of bran and flour may be produced.	Much heat can be generated during grinding, which can have a negative influence on flour properties. Difficulty with the separation of endosperm from the bran. A wide range of particles sizes is produced.	[65,66]
Ultrafine grinding—different kinds of mill can be used, such as superfine impact mills, jet mills, ball mills, impact classifier mills, and colloidal mills.	Very fine particles are obtained (usually from 1 to 50 µm). Increases bioavailability of bioactive compounds. Modifies dissolution rates and solubility of flour particles. Allows for easy reduction of bran particles.	Very high energy input is required. Fast wearing of working elements. Low capacity. High temperature is often generated. Contamination of product with metal might occur due to wear and tear.	[42,44]

3. Rye Phenolic Compounds

The phenolic compounds in plants are constituted by many subgroups of aromatic compounds, such as PA, flavonoids, coumarins, lignans, stilbenes, and condensed tannins [19,67]. These compounds are responsible for antioxidant activity and show health-protective effects as food ingredients [68]. They effectively scavenge free radicals and reduce the risk of many diseases [69]. Rye grain is an important source of many phytochemicals. These compounds are irregularly distributed in the rye bran particles.

3.1. Phenolic Acids

The most important phenolic compounds in rye are PA. They are mainly located in the aleurone layer and bran [70] and include two groups: *p*-hydroxybenzoic acid and its derivatives (especially vanillic and syringic acid) and *p*-coumaric acid and its derivatives (such as ferulic and caffeic acid) [71]. In the cereal grains, the majority of the PA are present in an insoluble bond form [72]. Though free PA constitute less than 3% of the total phenolic content in rye [71], they contribute significantly to the antioxidant activity of rye flour [73]. In addition, bound phenolic compounds are released from food materials in the colon during the fermentation process of gut microbiota, resulting in many health benefits [74]. The content of PA in rye grain has been found to be between 65 and 300 mg/100 g of grains [19]. Compared to other cereal grains, rye is richer in gallic, *p*-hydroxybenzoic, and caffeic acid (Table 2). The ferulic (85%–90%), sinapic (9%–10%), and *p*-coumaric (3%–5%) acids are the predominant phenolics found in rye grains [19]. In addition, small amounts of caffeic, gallic, protocatechuic, vanillic, and syringic acids were observed in rye grains [61,73]. Ferulic acid (4-hydroxy-3-methoxycinnamic acid) is a common ingredient in different plant foods. This compound shows strong antioxidant and anti-inflammatory properties, with well-documented protective action against many diseases, such as cardiovascular diseases, certain types of cancers, and diabetes [75]. Sinapic acid (3,5-dimethoxy-4-hydroxycinnamic acid) shows many documented health benefits, such as anticancer, anti-inflammatory, antiglycemic, antimutagenic, neuroprotective, and antioxidant properties. This compound is widely distributed in spices, fruits, vegetables, and cereals [76]. Para-cumaric acid (4-hydroxycinnamic acid) is also widely distributed in the plant kingdom and is associated with many pharmacological activities, especially anti-inflammatory, antineoplastic, and antimicrobial activities [77].

Table 2. Average values of phenolic acid content in different cereal grains (µg/g) [78].

Phenolic Acid	Wheat	Rye	Oat	Barley	Rice	Corn
Galic	6.49	7.74	1.71	6.53	5.54	0.49
Protocatechuic	nd *	4.74	1.15	5.47	4.74	nd
p-hydroxybenzoic	4.89	17.14	8.07	6.41	5.158	4.87
Vanillic	4.18	12.93	20.55	5.92	4.38	5.35
Caffeic	0.53	12.33	9.17	5.61	0.99	5.65
Syringic	0.53	6.29	19.71	6.22	4.45	4.29
p-coumaric	14.45	29.88	607.25	74.93	22.83	96.78
Ferulic	254.62	218.68	1035.94	323.82	68.24	954.52
Synapic	46.53	51.68	107.12	43.52	24.19	79.27
Salycilic	nd	nd	4.56	9.75	nd	nd

* nd—not detected.

3.2. Rye Flavonoids

Flavonoids are natural polyphenolic compounds that are commonly found in fruits, vegetables, seeds, and other plant products [79]. Flavonoids are divided into six main subclasses: anthocyanins, flavonols, flavones, flavanols, flavanones, and flavans [80]. These show beneficial effects on human health, which can be attributed to their anti-inflammatory and anticarcinogenic properties [81]. Relatively few studies have been conducted on rye flavonoids. Pihlava et al. [15] estimated the amount of flavonoids in refined rye flour, wholemeal flour, and rye bran. The authors expressed the measured amount of total flavonoid aglycones as quercetin equivalents. The results of the study demonstrated that the content of these compounds varied from 46 mg/kg in wholemeal flour to 168 mg/kg in the bran fraction, whereas the content of flavonoids in the refined flour was found to be below 5 mg/kg. Comparing rye flavonoids with those of other cereals is challenging because little has been published on these compounds in other cereals, and different methods of extraction and determination have been used. Zengin et al. [82] found the total content of flavonoids in wheat grain ranged from 21.6–126.1 mg rutin equivalent/kg. Other authors [83] have used high-performance liquid chromatography to determine the concentrations of flavonoids versus four species. The level of flavonoids ranged from 123.2 to 700.4 mg/kg. A higher level of these compounds was found in oat (3816 mg rutin equivalents/kg) and in different cereal pigmented-grain [84]. Some authors have studied the structural profile of flavones [85]. This group of flavonoids is particularly important because it shows enhanced anti-inflammatory properties [86] and improved insulin sensitivity [87]. The authors found that the content of flavones ranged from 57 to 137 µg/g, depending on the rye variety, and the dominant flavones were found to be O-glycosides (50%–68%), which occurred as derivatives of apigenin, chrysoeriol, and tricin. Compared to other cereal grains, rye contains a similar level of flavones to wheat [88] but a higher content of these compounds than barley (from 5.5 to 29 µg/g) [89] and rice (<20 µg/g) [90]. Pihlava et al. [15] also reported the presence of flavonoid C-glycosides and anthocyanidins in rye bran and wholemeal rye flour. The content of anthocyanidins was the highest in rye bran (15 mg/kg), while it was only 1.8 mg/kg in wholemeal rye flour.

3.3. Rye Lignans

Lignans are phytoestrogens present in vegetables, fruits, and seeds. Several hundred structures of the lignan compound were observed in the grains of different cereals. These compounds occurred as sugar-decorated free aglycones and were also found to be esterified to the cereal matrix [91]. Many researchers have suggested that a diet rich in lignans may have a positive effect on human health, as well as a protective effect against many lifestyle-related diseases [92–94]. Plant lignans are converted by gut bacteria into enterolignans, enterodiol, and enterolactone. These compounds are absorbed in the small intestine and exert a beneficial effect on human health. In particular, enterolignans play a major role in decreasing the risk of cardiovascular diseases and cancer [95]. Among the cereal grains, rye has the highest content of lignans [96]. However, the amount of these compounds in rye grains ranges from 11.4 to 67.0 mg/kg [73,91,96]. Similar to the distribution of other bioactive compounds in rye grain, lignans are mainly concentrated in the bran. The average content of these compounds in the bran fraction of different cereals is shown in Figure 3. In addition, wheat grain, compared to other cereals, is a rich source of lignans [97], whereas the lowest content of lignans is found in barley [96].

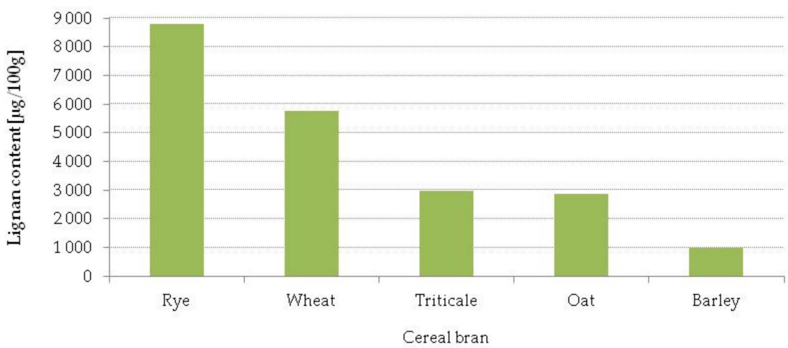

Figure 3. Lignan content in cereal bran [92,96].

In rye grains, seven dietary lignans were identified. The predominant rye lignin was secoisolariciresinol, which constitutes about 80% of the total lignan content in rye. Medioresinol and pinoresinol account for about 10% each, and small amounts of secoisolariciresinol, matairesinol, and 7-hydroxymatairesinol were also found in rye grains [98]. Secoisolariciresinol diglucoside, a potent multifarious bioactive phytoestrogen with high antioxidant activity, shows protective effects against cancer, cardiovascular diseases, mental stress, and diabetes [99–102].

3.4. Arabinoxylans

AX are hemicelluloses that are commonly found in the cell walls of bran and husk of cereals and seeds. They are dimers of arabinose and xylose [103]. These polysaccharides are the major components (85%–90%) of pentosans and comprise the dietary fiber fraction [104]. In general, the structure of these compounds consists of a linear backbone of β-(1→4)-linked D-xylopyranosyl units with arabinose side chains [105]. AX occur in two forms: water-extractable and water-unextractable fractions. The water-unextractable fraction of these compounds can account for up to 60% (w/w) of the total AX. Both these fractions are structurally heterogeneous and show significant variations in molecular weight [106]. Water-extractable AX are characterized by a high capacity to absorb water and the ability to produce high-viscosity solutions [107]. In food products, AX act as soluble dietary fiber. The soluble AX have potential health benefits. They reduce the rate of glucose diffusion and alleviate glycemic response [14,108]. In addition, AX stimulate prebiotic bacteria, which further show a protective effect against many diseases, such as cancer, diabetes, and hypercholesterolemia [105]. The insoluble AX have the ability to swell and hold water, whereas soluble AX increase the viscosity of the liquid phase [14,109]. AX exhibit strong antioxidant properties, which are evident by their ability to reduce metal chelating activities and their capacity to scavenge free radicals [110]. Among the cereal grains, the highest content of these compounds is found in rye (6%–8%), where it corresponds to about 60% of the total polysaccharides [14]. The water-soluble AX present in rye grains show a positive effect on the bread quality and hence can be used to improve the baking properties of gluten-free bread [63]. In addition, the results of a study showed that water-extracted AX improved the quality of gluten-free bread to a greater extent when compared to the bread obtained from alkaline-extracted AX [111]. The incorporation of water-extractable rye AX into wheat flour prevented the occurrence of the staling process, increased the water absorption capacity of flour, and reduced the crumb hardness [112]. The enrichment of white rye flour (type 720) with this compound leads to an increase in the water absorption capacity of flour and bread volume and a decrease in crumb hardness [113]. Stępniewska et al. [114] revealed that rye flour volume is highly dependent on the proportion of water-extractable compounds to the total pentosans. The studies indicated that water-soluble pentosans have a positive influence on bread volume. Li et al. [103] investigated the influence of AX that were extracted from the bran of different cereal grains (wheat, corn, rice, and rye) on the oxidative stability of oil-in-water emulsions. The authors found that the addition of 0.5% rye AX significantly improved the oxidative stability of different emulsions.

The chemical structure of rye flour has been found to be similar to that of wheat flour. However, rye flour contains a greater amount of soluble pentosans [104,115]. Rye flour is mainly used for the preparation of bread and biscuits. In addition, rye flour is often used as a substitute for wheat flour in many cereal products. In particular, wholemeal rye flour could be utilized in the production of antioxidant-rich food products [116]. Nasabi et al. replaced 20% wheat flour with wholemeal rye flour during the production of wafer batter [117]. The authors observed that rye flour improved the texture of the final product. The hardness of wafers decreased by about 20%, and an approximate twofold increase in the fracturability characteristic was observed in these products when compared to that observed in the control product. This phenomenon can be attributed to the decreased protein content and increased porosity in wafers enriched with wholemeal rye flour. A previous study by Tiefenbacher et al. [118] confirmed that rye flour increases the porosity of the wafer, resulting in the synthesis of a more fragile product. Some authors [119] used wholemeal rye flour for the production of food products rich in dietary fiber and protein snacks using an extrusion-based three-dimensional printing technique. The authors mixed different proportions of milk powder and wholemeal rye flour to obtain different formulations. The studies found that the obtained products showed good printability and shape stability after printing and baking at 150 °C. However, snacks produced using only rye flour tended to shrink during the baking process, resulting in the bending of the product. The most homogeneous structure was obtained by substituting 25% of milk powder with wholemeal rye flour. Rye flour can also be used as an ingredient of starch biocomposite films that are used for food packaging purposes. Beigmohammadi et al. [104] demonstrated that replacing corn flour with rye flour (10%) and cellulose (10%) improved the properties of extruded biocomposite. The authors suggested that hydroxyl and carboxyl groups in rye flour can reduce the diffusion of water molecules into the biocomposite, which further decreases the water permeability of enriched biocomposite. In addition, the incorporation of rye flour increased the stiffness of the product.

Rye bran is a by-product that is obtained during the production of refined rye flour and is an ingredient of wholemeal rye flour. The worldwide production of rye bran ranged between approximately 17 and 36 million tons over the last decade [120]. According to Juhnevica-Radenkova et al., rye bran [121] is mainly composed of dietary fiber (33.4% cellulose, 5.3% hemicellulose, and 3.3% lignin), starch (18.6%), protein (17.0%), and lipids (2.5%). Rye bran is a valuable source of many bioactive compounds. Notably, rye bran is one of the richest sources of ferulic acid [122], which is commonly used in the food, pharmaceutical, and cosmetics industries. It is characterized by low toxicity and shows antioxidant, anti-inflammatory, and anticancer properties [123]. Rye bran finds application in various industries (Figure 4).

Figure 4. Recent trends in the use of rye bran.

Juhnevica-Radenkova et al. [121] proposed a method for the production of ferulic acid from pretreated rye bran using nonstarch polysaccharide-degrading enzymes (multienzyme complex Viscozyme® L, which is a mixture of endo-1,4-β-xylanase, α-L-arabinofuranosidase, and 1,4-β-D-endoglucanase). The yield of ferulic acid was found to be 11.3 g/kg when enzymatic hydrolysis was performed for 24 h. One of the techniques to improve the nutritional and technological value of bran is the fermentation process. Interestingly, the fermentation of rye bran is an efficient approach to increase the content of many bioactive compounds, such as folates, ferulic acids, and soluble pentosans [124]. Katina et al. [124] confirmed that the optimum fermentation time for rye bran to obtain enhanced bioactivity and increased content of soluble pentosans with limited microbial contamination is from 12 to 14 h at 21 °C. The authors found that the fermentation of rye bran increased the levels of phenolic compounds, pentosans, and folates. In particular, the level of free ferulic acid increased by about 50%. The maximum concentration of this acid was observed at pH 6.0–6.5 under fermentation conditions that included a time period of 20 h at 20 °C or 6 h at 35 °C. Iftikar et al. [61] used an ultrasonic-assisted method for the extraction of bioactive compounds from ground rye bran. This technique produced extracts that were characterized by an increased content of bioactive compounds and antioxidant activity when compared to those obtained by conventional extraction techniques. The results showed that the content of total phenolic compounds and flavonoids increased from 175.5 to 245.7 mg GAE (gallic acid)/100 g and from 127.5 to 169.1 mg RE (rutin equivalent)/100 g, respectively. In addition, the DPPH (2,2-diphenyl-1-picrylhydrazyl) assay, ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) assay, and ferric reducing antioxidant power (FRAP) assay showed that the antioxidant activities were about 30% higher in the extracts obtained from the ultrasonic-assisted method when compared to extracts obtained by conventional methods.

4. Current Trends in the Use of Rye Flour and Rye Bran

Many articles have been published in recent years on the possible use of rye bran as a functional food additive. Rye bran can be a valuable additive to increase the nutritional and health properties of food. Levent et al. [125] replaced 20% of wheat flour with dephytated rye bran during pasta and noodle production. Phytic acid, a natural component in rye bran, is capable of binding to different minerals, thus impairing mineral absorption [126]. This enrichment resulted in a several-fold increase in the content of minerals (Ca, P, K, Fe, Mn, Mg, Zn) and total fiber when compared to that observed in the control sample. In addition, the use of rye bran led to about a threefold increase in the content of total phenolic compounds and antioxidant activity (determined by DPPH assay) of enriched pasta when compared to the control product. Some authors [120] have used rye bran as a raw material for the production of fermentable sugars, which are subsequently used for ethanol production. The authors optimized the conditions for dilute sulfuric acid hydrolysis of rye bran and obtained hydrolysates that contained 0.72 g of reducing sugars per gram of bran, with glucose as the main reducing sugar (0.25 g glucose/g of bran). However, acidic hydrolysis of wheat bran resulted in the formation of inhibitors such as phenolics, 5-hydroxymethylfurfural, acetic acid, and formic acid. Koistinen et al. [127] used a combination of hydrolytic enzymes (xylanase and ferulic acid esterase) and fermented yeast for the bioprocessing of rye bran. Then, the bran was used to enrich wheat bread. The authors replaced 35% of wheat flour with dry and fermented bran fraction, and the proportion of rye bran was adjusted such that bread with similar total fiber content (10%–13%) was obtained. They found that the bioprocessing of rye bran leads to partial degradation of the cell wall of bran particles, resulting in the release of phenolic compounds and an increase in the level of free PA in the bread. This is most probably due to the activity of ferulic acid esterase enzymes, which releases ferulic acid from the bran matrix and increases the bioaccessibility of bread. Although bran is a rich source of fiber and many bioactive compounds, it has a negative influence on bread properties, due to the weakening of the starch–gluten matrix, decrease in gluten hydration capacity, and disruption of the gluten network [128]. An interesting study was performed by Nikinma et al. [129]. The authors used fermented and acidified rye bran containing high fiber extrudates as an additive. Acidification and fermentation of rye bran improved the structure and texture of the final product, while fermentation alone produced a less significant effect. They revealed that pH plays a crucial role in the extrusion process during the fermentation of rye bran in the presence of lactic acid bacteria. As a result, the water-binding capacity of starch increased, and better quality extrudates were obtained. Other authors [130] replaced corn grits, by 20% and 40%, with rye bran during the production of corn snacks. The final product showed an increased level of dietary fiber (average 9.04%) and desirable sensory properties when the substitution was restricted to 20%. Rye bran can also be used as a source of dietary fiber and for partial replacement of fat in meat products [131–133]. Hjelm et al. [133] incorporated rye bran (6%) and a mixture containing rye bran (3%–5%) and collagen (1%–3%) into Frankfurter-like sausages. The addition of bran alone resulted in undesirable stale flavor in both cooked and fried sausages. A positive effect on meat flavor was observed when a combination of rye bran and collagen was used. Recently, Kowalska et al. [134] used a water-extractable AX fraction isolated from rye bran for the microencapsulation of honey. Microencapsulation has become a very popular technique in recent years, as it enhances the stability and bioavailability of phytochemicals during digestion [135]. Kowalska et al. [134] found that the encapsulation of honey significantly increased the antioxidant activity of microcapsules (from 147% to 471%) compared to the antioxidant activity of honey. The maximum increase was observed when the antioxidant activity was estimated by FRAP assay (increase of 471%) and the lowest when the antioxidant activity was expressed by ABTS assay (average increase of 147%). The authors explained this increase by the presence of a high content of PA in rye bran and the fact that encapsulation increases the content of free PA in microcapsules.

Apart from being used as a food additive, rye bran may also have other applications. Recently, Mihajlovski et al. [136] investigated the potential use of different substrates (wheat bran, barley bran, rye bran, sunflower meal, and soybean meal) in the production of microbial enzymes such as cellulase, amylase, xylanase, and pectinase. The authors found that rye bran is a very useful substrate for the growth of selected strains of microorganisms (Streptomyces fulvissimus CKS7) and for the production of various enzymes that can be used for the hydrolysis of different types of waste materials to obtain bioethanol. Rye bran was particularly suitable for the production of xylanase, owing to the presence of high content of AX in rye bran when compared to other substrates. In addition, the proposed approach to obtain industrially important enzymes was found to be more economical and feasible when compared to the commercial methods of enzyme production. Although hydrolysis of lignocellulosic waste materials is a very slow process, it is more economical because additional chemicals are not needed [136].

Tahir et al. [137] extracted alkylresorcinols from rye bran and used it to protect apples against fungal diseases during their storage in an organic orchard. The authors found that spraying the trees with an alkylresorcinol emulsion reduced fungal infections in apples. This kind of protection was observed in apples both at the time of harvest and after storage. The preventive effect was proportional to the concentration of alkylresorcinols in the emulsion. Such treatment showed no negative effect on the quality of fruits, but a slight decrease in the yield of apples was noticed, which may be due to the nature of the solvents (i.e., salts) used in the preparation of the emulsion [137]. Wang et al. [138] proved that water-extractable AX extracted from rye bran can be used to improve the quality of frozen steamed bread dough. The study results revealed that AX could inhibit ice formation, thus preserving the yeast viability and activity during frozen storage and elevating the glutenin macropolymer content. Consequently, AX addition increased the volume of bread and contributed to the softer texture of bread. Some authors [139] used a mixture of sawdust and rye bran to produce pellets for fuel purposes. The findings showed that rye bran can be used as an excellent binding material and produces better quality granules when compared to the granules obtained from sawdust. The authors also found that granules prepared using rye bran contributed to the high calorific value of pellets, which resulted in little ash content after the combustion process. An increase in the proportion of rye bran enhanced the binding capacity and decreased the granulator demand for power consumption during the pelleting process. Nska et al. [140] used a mixture of ground plum stones and rye bran for pellet production. The study showed that biofuels can be used as substitutes for wood pellets. The authors found that plum stone pellets with 20% rye bran meet the emission standards for air pollutants proposed by the European Union Ecodesign Directive. Similar results were found by Dołożyńska et al. [141] when wheat bran was used as an additive for fuel preparation from cherry stones.

In summary, wholemeal rye flour, and in particular rye bran, has many industrial applications (Table 3), which facilitate the production of final products with unique properties. In addition, the use of bran effectively reduces the production of by-products during the milling of rye grains.

Table 3. Recent trends in the use of rye bran and wholemeal rye flour.

Kind of Raw Material	Method of Use	Effect	Ref.
Wholemeal rye flour	Addition into wheat wafer batter	Increased porosity and fracturability and decreased hardness of wheat wafers enriched with wholemeal rye flour.	[117]
Wholemeal rye flour	Mixture of wholemeal milk powder and snack production used extrusion-based 3D printing technique	Wholemeal rye flour improved snack shape stability and enriched snacks with fiber.	[119]

Table 3. *Cont.*

Kind of Raw Material	Method of Use	Effect	Ref.
Rye flour	Ingredient of biocomposite (10%) for packaging purposes	Decreased water permeability and stiffness of biocomposite.	[104]
Dephytated rye bran	Replaced 20% of wheat flour in pasta production	Increased content of minerals, fiber and total phenolics in pasta.	[125]
Dry rye bran and rye bran treated by hydrolytic enzymes and fermented with baker's yeast	Partial replacement of wheat flour during wheat bread production	Increased content of free phenolic acids (with over 100-fold increase for ferulic) with bread enriched with bioprocessed and unprocessed bran.	[127]
Rye bran	Fermented and acidified rye bran as an additive to rye flour extrudates	Improved texture (decreased hardness and increased crispness) and structure of extrudates. Increased level of soluble dietary fiber.	[129]
Rye bran	Partially replaced (20% and 40%) corn grits in snack production	Obtained the final product with increased level of dietary fiber (average 9.04%) and acceptable sensory properties when 20% of corn grits was replaced by rye bran.	[130]
Rye bran and mixture of rye bran with collagen	Partial replacement of fat in Frankfurter-like sausage	Undesired stored stale flavor in sausage when rye bran was added alone and positive effect on sausage flavor when combining rye bran with collagen.	[133]
Rye bran	Production of fermentable sugars	Hydrolyzates with 0.72 g reducing sugars per gram of bran were obtained with glucose as main reducing sugar (0.25 g glucose/g of bran).	[120]
Water extractable arabinoxylans extracted from rye bran	Frozen steamed bread	Increased volume of bread and decreased crumb hardness.	[138]
Rye bran	Production of various enzymes useful for hydrolysis of many wastes	Obtained enzymes could hydrolyze different lignocellulosic substrates to obtain reducing sugars for the production of ethanol.	[136]
Alkylresorcinols isolated from rye bran	Protection against fungal storage diseases of apples	Decreasing fungal attacks on apples at harvest and after storage.	[137]
Water extractable arabinoxylan from rye bran	Microencapsulation of honey	Increased antioxidant activity, biostability and bioavailability of bioactive compounds; reduction of the carrier for microcapsulations.	[134]
Dephytinized rye bran	Pasta enrichment	Increased wheat pasta with ash, protein, fat, total phenolic content, and antioxidant activity.	[125]
Rye bran	Pellets (sawdust with rye bran) for fuel purposes	Increased kinetic strength of pellets; excellent binding properties of rye bran with little ash content after pellet combustion.	[140]
Rye bran	Additive of plum fuel pellet	Increased the kinetic durability of plum-stone pellets, but slightly decreased heating value. Reduction in emission of carbon monoxide sulfur dioxide, nitric oxide, and hydrogen chloride in comparison to whole plum stones.	[140]
Rye bran	Ingredient of fuel pellets from cherry stones	Increased the kinetic durability of pellets but slightly reduced heating value; 20% rye bran in cherry stones gives the highest values.	[141]
Rye bran	Substrate of various enzyme production for hydrolysis of wastes for bioethanol production.	Rye bran was especially suitable for production of xylanase.	[136]
Alkylresorcinols extracted from rye bran	Plant protection product	Spraying apple trees with an alkylresorcinols emulsion decreased fungal infestations of fruits and had no negative effect on fruit quality.	[137]

5. Conclusions

The products obtained during the milling of rye grains, in particular whole grain flour and bran, are a source of many valuable bioactive compounds, and their addition to food products increases their health-promoting characteristics. However, the synthesis of products enriched with a high proportion of bran and with desirable consumer acceptability properties is a constant challenge. The adoption of appropriate methods for grinding and sorting of the mill products facilitates the modification of their chemical composition and functional properties. Rye bran deserves special attention, as it is used as a food additive and also has several industrial applications. Compared to other cereal grains, it is a rich source of fiber, phenolic acids, and especially lignans. Moreover, among the cereal grains, the highest content of arabinoxylans was found in rye. In addition, fermentation and enzymatic hydrolysis of rye grains result in the production of many biologically active compounds, as well as an increase the content and bioavailability of phytochemicals. These variations enable the use of rye bran in food, cosmetics, pharmaceuticals, and feed, as well as for protecting plants from harmful organisms. Rye bran can also be a valuable raw material for the production of biofuels. However, extensive studies are required to explore other applications that involve the use of rye by-products for the production of food and nonfood products and to develop new and innovative technologies for the efficient processing of rye products.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The author declare no conflict of interest.

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