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Rye – nutritional and technological evaluation in Czech cereal technology – A review: Sourdoughs and bread

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Abstract: Rye is a nutritionally and healthy valuable cereal. It is a significant substrate for biotechnological processing. This review presents the basic procedures for rye sourdough refreshing, the characteristics of used LAB and yeast, the types of sourdough use in the Czech Republic and in global perspective. The fermentation process leads to the activation and accessibility of a number of healthy bioactive components of rye flour. Compounds with antifungal activity formed during fermentation can effectively enhance the microbial stability of bread. Rye sourdoughs as a part of the bread recipe cause not only the leavening of dough but also desired texture and sensory properties of bread.

Keywords: rye flours; fermentation; rye sourdough bread; antifungal compounds

Sourdough fermentation and its impact on rye flour components

It is to note that in Central Europe and in the Czech Republic rye has traditionally been a raw material for the manufacture of rye sourdough, rye-wheat and wheat-rye bread (Příhoda et al. 2003; Banu et al. 2011; Šedivý and Albrecht 2014; Siepmann et al. 2018). Bread rye flour is used for sourdough preparation in the production of traditional Czech bread. In the Czech baking technology, the flour before sourdough preparation is not treated anyhow. Thus, rye sourdough plays a key role in this case.

In a traditional recipe, rye sourdough is a mix of rye flour and water spontaneously fermented by the composite naturally present community of lactic acid bacteria (LAB) (homo- and heterofermentative ones) and yeasts (Příhoda et al. 2003; Ercolini et al. 2013; Šedivý and Albrecht 2014). In the manufacture of traditional bread active sourdough is added that is refreshed in such a way that leavened bread is made without yeast addition (Šedivý and Albrecht 2014). It means that a sufficient amount of sourdough is necessary; at the same time, besides lactic fermentation a sufficient rate of alcoholic fermentation should be evolved so that a sufficient amount of fermentation gas (carbon dioxide, CO_2) would be evolved. In typical Czech bread where the rye proportion is 40–50%, the entire amount of rye flour is undergoing the fermentation process. To make the addition of such a volume of sourdough to dough possible, its titratable acidity (TTA) should be relatively low (usually 100–130 mmol kg^{-1}) (Šedivý and Albrecht 2014). Such a sourdough is rather unstable and the continuity of the process is expected without frequent and long-time interruption or the sourdough should be refreshed every time again. Sourdough refreshing to the resultant repeatable degree is relatively complicated. To ensure the optimum multiplication of all populations of microorganisms (LAB and yeasts), it is necessary to adjust conditions during refreshing several times (temperature, sourdough consistency, aeration rate) and therefore sourdough is refreshed at several (usually three) steps (Příhoda et al. 2003). In the Czech terminology,

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it is spoken about active sourdough refreshed for the production of acids and fermentation gas. Another simpler and in modern bread making frequently used method is the use of "starter" – a starter culture whose microbial composition is designed by the producer and that contains selected cultures of LAB and sometimes of yeasts (Chavan and Chavan 2011; Kavitake et al. 2018; Brandt 2019). The principle of sourdough preparation or refreshing is easier in this case and an emphasis is laid on the production of a sufficient amount of acids (lactic acid and acetic acid). The sourdough prepared in this way is more acidic (TTA > 200 mmol kg^{-1}) and this is the reason why its addition cannot be as high as in the former case. In addition, the sourdough does not contain a sufficient amount of yeasts for the evolution of fermentation gas (alcoholic fermentation is a minor process or it does not take place at all). Therefore, the leaven addition to bread dough is necessary in both cases to create optimum conditions (temperature, consistency that is given by the flour to water ratio, and ripening time) (Chavan and Chavan 2011). In the Czech terminology, it is spoken about active sourdough refreshed for the production of acids (Příhoda et al. 2003; Šedivý and Albrecht 2014).

Final sourdough always becomes a direct ingredient of dough recipe to which another amount of flour and/or other recipe ingredients (particularly salt) are added. Besides flour, sourdough, salt and caraway the recipe of traditional Czech bread does not usually contain any other recipe ingredient (Příhoda et al. 2003).

According to the type of bread, only wheat flour is added to rye sourdough (in the former type of above-mentioned sourdough) or also rye flour in the latter case (Šedivý and Albrecht 2014).

In general, based on the applied inoculum three different methods of sourdough refreshing can be defined in the following way: original spontaneous fermentation by the present natural cultures (type 1), fermentation initiated by starter cultures (type 2) and fermentation initiated by final sourdough from the preceding cycle (type 3) (De Vuyst et al. 2017; Van Kerrebroeck et al. 2017; Weckx et al. 2019).

In our opinion, it is not quite a good classification because both above-mentioned types of active sourdough used in the Czech Republic can be refreshed for a certain time. Therefore, we suggest distinguishing originally spontaneous sourdough refreshed for the production of organic acids and CO_2 and starter-initiated sourdough refreshed mainly for the production of acids while both sourdoughs can be replicated for a certain time (Skřivan et al. 2020).

Nevertheless, a complex microbial ecosystem is typical of sourdough that is mostly represented by lactic acid bacteria and yeasts whose fermentation imparts to resultant bread its characteristic features such as palatability and high sensory quality (Hammes et al. 2005; Corsetti and Settanni 2007).

There are about 50 species of lactic acid bacteria and more than 25 yeast species that are involved in fermentation processes during refreshing of rye (and other cereal) sourdoughs (Sadeghi 2008; Banu et al. 2011; De Vuyst et al. 2017; Van Kerrebroeck et al. 2017; Brandt 2019). Typical representatives of lactic acid bacteria are the members of the genus *Lactobacillus*, *Leuconoctoc*, *Pediococcus* or *Weissella*. The majority genus is *Lactobacillus* (homofermentative: *L. plantarum*, *L. debrueckii*, *L. leichmannii*; heterofermentative: *L. brevis*, *L. sanfranciscensis*, *L. fermentum*, *L. buchneri*). The yeast species typical of sourdough are yeasts of the genus *Saccharomyces*: *S. cerevisiae*, *S. minor*, *S. panis fermentati* and *Candida*: *C. milleri*, *C. humilis*. The population of lactic acid bacteria becomes dominant over yeasts with increasing fermentation time (Rosenquist and Hansen 2000). The count of lactic acid bacteria is gradually increasing and the yeast count is decreasing with increasing fermentation time. The ratio of yeasts to lactic acid bacteria is approximately 1 : 100 in relation to flour type and, of course, mainly in line with the method of regulation of fermentation process parameters (Hammes et al. 2005; Gänzle 2014; De Vuyst et al. 2016).

Besides ethanol and carbon dioxide, the yeasts can produce metabolites specifically influencing the taste such as aldehydes, ketones, diacetyl, higher alcohols of branched-chain amino acids and esters derived from them (De Vuyst et al. 2016; Pétel et al. 2017).

From technological and sensory aspects, the most important products are lactic acid and acetic acid as the main products of lactic fermentation (Rehman et al. 2006). These acids underlie specific flavour and taste characteristics of rye bread and thanks to their antifungal activity. They are a certain alternative to preservatives used to prolong the bread shelf life (Corsetti et al. 1998; Arendt et al. 2007; Gänzle and Ripari 2016).

All the above-mentioned compounds and many others that will be mentioned below impart the rye sourdough its specific physicochemical and sensory properties. The main constituents of rye flour like starch, proteins and soluble arabinoxylans are subjected to hydration during sourdough ripening and subsequent dough ripening (Katina et al. 2005). Therefore rye dough has its typical appearance and rheological properties (Arendt et al. 2007; Šedivý and Albrecht 2014).

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Specifics of rye bread

Rye bread has a specific crumb structure, is less porous and more consistent than wheat bread (Hansen et al. 1989; Příhoda et al. 2003). The rye bread structure is not supple; it is rather gel-like. Besides the breadcrumb appearance, volume and structure, the fermentation products and the activity of amylases, proteases and xylanases influence the rate of starch retrogradation, which can contribute to slowing down of bread staling (Mihhalevski et al. 2012). Pétel et al. (2017) published a complete overview of volatile compounds in sourdough and bread: important substances contributing to bread aroma are aldehydes, ketones, alcohols, heterocyclic compounds, esters, acids, furans, pyrazines, lactones and various alkanes. The aldehyde furfural is one of the markers of typical aroma from rye bread (Rehman et al. 2006). Significant intensities of the flavour of sourdough samples were reached due to the following compounds: 3-methylbutanol, hexanol, 3-pentanone, acetaldehyde and ethyl ester of hexanoic acid, isoamyl ester of acetic acid, furan-2-pentyl, and hexanoic acid (Hansen et al. 1989; Pétel et al. 2017).

Properties of rye sourdoughs and/or their importance have traditionally been a reason for the use of sourdough in bread making (sensory properties, leavening and modification of breadcrumb structure and stabilisation) (Šedivý and Albrecht 2014). However, nowadays another essential sphere is discussed where sourdoughs, fermentation processes and their products are applied. Such a sphere is nutrition and/or nutritional benefits provided by sourdoughs.

Fermentation processes are an important procedure of increasing nutritive values, biological activity and generally beneficial effects of products from cereals on human health (Poutanen et al. 2009; Koistinen et al. 2016). During fermentation, there occur many changes and modifications of structure, properties, content and biological availability of rye grain constituents. Besides the production of organic acids, ethanol and carbon dioxide and a decrease in pH the fermentation of rye grain, flour and/or brans can involve particularly the following changes: slowing down of starch digestibility (Gänzle 2014), enzyme activation (Gobbetti et al. 2014), formation of wide spectra of volatile and non-volatile compounds (Kaseleht et al. 2011), release and increased biological availability of dietary fibre (Boskov Hansen et al. 2002) and phenolic compounds (Koistinen et al. 2016), production of some vitamins (Kamal-Eldin et al. 2007), inhibition of mould growth (Banu et al. 2010), and dephosphorylation of phytic acid (Karaman et al. 2018).

In the course of fermentation, new bioactive compounds like prebiotic indigestible oligo- and polysaccharides (e.g. dextrans and levans), amino acids (glutamate, ornithine) and their esters, peptides acting as antifungal compounds can be produced (Gänzle et al. 2007). Dominant heterofermentative lactic acid bacteria in rye sourdough preferably metabolise maltose and sucrose (Kumar and Mody 2009). Sugars are present in rye flour while maltose is released from starch by amylases. The presence of sucrose promotes the production of acetic acid by heterofermentative lactic acid bacteria and the production of selected exopolysaccharides (EPS) (Kumar and Mody 2009; Coda et al. 2018). In general, concentrations of EPS are relatively stable unlike rye β-glucan and arabinoxylan in the bread making process.

The enzyme activity induces the hydrolysis and solubilisation of rye proteins and dietary fibre constituents (Rosenquist and Hansen 2000). The physical properties of these cereal biopolymers like molecular weight, viscosity, absorption and solubility are changed. In general, these alterations can influence the bioavailability of nutrients, their resorption and physiological effects. Rye arabinoxylans have optimum solubility and swelling properties at low pH (Poutanen et al. 2009). The phytase activity of yeasts and lactic acid bacteria may decrease phytate content and increase biological availability of minerals (Karaman et al. 2018). The peptidase activity of lactic acid bacteria under acidic conditions determines the accumulation of bioactive peptides, amino acids and their metabolites (Gänzle 2014).

Sourdough can slow down starch resorption indirectly by the release of fibre constituents, which leads to a decrease in the bread glycaemic index while the activation of intestinal microbiome occurs at the same time (Katina et al. 2005). During rye sourdough ripening the ratio of soluble to insoluble fractions of dietary fibre increased and the nicotinamide content rose (by the microbial activity during fermentation) (Mihhalevski et al. 2013). Some lactic acid bacteria (mainly *Lactobacillus plantarum*) contributed to a decrease in the acrylamide content of rye-wheat bread (Bartkiene et al. 2017).

Rye bread is known to induce a lower postprandial physiological response of insulin than wheat bread. Differences in the initial rate of starch hydrolysis were revealed between rye and wheat bread during chewing (Pentikäinen et al. 2014).

The exopolysaccharides produced by specific strains of lactic acid bacteria, which can exert the abovementioned prebiotic effect, act as food hydrocolloids in the technological process. They can influence

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technological parameters, rheological characteristics of sourdough and dough and the quality of final baked bread (volume, crumb firmness) and its shelf life (Mihalevski et al. 2012; Torrieri et al. 2014). Moreover, exopolysaccharides can replace some improvers and contribute to a possibility of labelling the bread as a clean label product (Gänzle and Ripari 2016). Similarly, the substitution of naturally produced organic acids for additives used as preservatives is possible.

All the above-mentioned facts have recently been the object of deep interest and profound investigation. Possibilities of *in vivo* testing of bioavailability and bioactivity have been enlarged and it is to expect that the importance of the use of rye (and not only rye) sourdoughs in cereal technology will increase and they will be seen in a new light.

Traditional processes of sourdough refreshing have been adapted and modified in such a way that they meet the requirements of large-scale and automated bread production. A combination of sourdoughs and yeast prepared in different ways is often used while taking advantage of both cultures. Based on modified and optimised traditional fermentation processes dried, pasty and liquid sourdoughs were also developed (Gänzle et al. 2007; Brandt 2019). Dried or pasteurised sourdough is used as a recipe ingredient improving the properties of breads when active sourdoughs are not used as leavening agents.

These products are used for the industrial production of bread in the Czech Republic because due to leaving out sourdough refreshing quite often the whole production process is substantially simplified. However, we are convinced that considering both the sensory properties of bread and the above-mentioned nutritional reasons the use of active sourdoughs either in their traditional spontaneous form or as sourdoughs inoculated by starter cultures is desirable.

CONCLUSION

Rye is a nutritionally and technologically interesting cereal with long tradition of use in technology and nutrition in Northern, Central and Eastern Europe. The specific composition of rye grain and different properties of rye flour compared to wheat have an impact on the ability to form characteristic sourdough spontaneously, which is the object of research in terms of both nutritional and technological aspects. It is now appropriate to use the controlled fermentation process instead of spontaneous sourdough refreshing and often unstable for greater and more efficient use of rye for baking purposes. Optimised fermentation processes lead to the formation of rye sourdough with the rich profile of volatile and flavour compounds which (after the addition of sourdough to bread) increase the sensory quality of sourdough bread. During fermentation, some nutritionally beneficial components are activated and new compounds with significant functional properties are formed. The longer rye sourdough fermentation has a favourable effect on the structure of the breadcrumb and on characteristic more acidic taste and more pronounced aroma of bread. The more acidic environment in the dough also promotes the formation of some of the typical distinctive substances of bread aroma, compounds based on the aldehyde furfural. Traditional rye products are characterised by a stronger aroma, darker colour and stiffer structure compared to wheat products. Products of fermentation, especially lactic acid, also show significant antifungal activity and thus a stabilising effect.

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