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THE EFFECTS OF PARTICULAR FACTORS CONNECTED WITH MARITIME TRANSPORT ON QUALITY AND SAFETY OF CEREAL AS A CARGO

Summary. The article discusses the effect of conditions during maritime transport on particular quality and safety parameters of cereal, in relation to quality management and logistics management. Therefore, transport requirements for cereal as a cargo were identified, and furthermore, threats resulting from improperly conducted logistic process of bulk material with strong sorption properties were described. The aim of this article was to compare the differences in sorption properties between four selected cereal species using the static desiccator method. This method is the standard reference method. As a result of the conducted research, the existence of significant variability in the sensitivity to the effect of maritime transport conditions among cereal as a product group was identified. The most resistant to water vapor was rye grain. The differences between each cereal species should be associated with variability in the physical structure and chemical composition of grains of each individual cereal species. Further works in this area should take into consideration not only the diversity but also the variability of cereal sensitivity owing to the combined effect of relative humidity of the atmosphere and ambient temperature with use of the in-depth thermodynamic analysis of sorption.

1. INTRODUCTION

Intensified production and technological development during recent years have created the demand for logistics services, which have become essential for optimizing the time and costs of production, supply, storage, and many other links in the logistics chain [15]. The essence of logistics is the synergy of its processes [37], which could be achieved owing to combination of the efficiency in their realization and the thorough knowledge of the specifics of the objects subjected to these processes. Progress in managing logistics processes has focused on intensifying and optimizing the flow of goods, increasing the role of quality in the TQM (total quality management) standards, improving the quality of customer service, accelerating the operation of particular branches of logistics, and minimizing the time when funds are frozen in the product, which could significantly reduce the popularity of water transport in comparison with other ways of transport [45]. According to that, it is reasonable to take actions leading to improvement in the indicated areas, as well as to take advantage of knowledge in the field of technical and natural sciences, for optimal proceeding with objects subjected to logistic processes in maritime transport. This approach will have a positive influence on reducing cargo losses, and thus will contribute to reducing the unjustified environmental burden connected with transport. It will also lead to decrease of insurance costs, resulting from the destruction or deterioration of quality of the cargo [3, 9].

Cereals in their nature are living organisms and display an extremely high hygroscopicity, owing to a low water content. To preserve storage durability during the process of their transport, the humidity level in the hold should remain in equilibrium with the water content characteristic of the grain type being transported, ensuring its stability. Cereal during transport should maintain the amount of water that supports life processes and, at the same time, lead to the lowest dynamics of these processes. If the humidity in the hold is too low, the desorption of free water from grains occurs and it causes the intensification of oxidative changes. On the contrary, if the humidity of the environment is excessive, it causes the intensification of adsorption processes, which causes intensification of hydrolytic changes and further also the development of microbes and the production of toxins by them [32]. According to that, the humidity of the environment should be considered to be the basic critical parameter in the process of transport and storage of cereal. Until now, cereals have been treated as a load with homogeneous properties, regardless of the existing physical and chemical differences, which is a gap in logistics knowledge. The results presented in this article are intended to show that even cereals from our climate zone differ in their susceptibility to exposure to water vapor. An innovative approach to the optimization of logistic processes involves the use of physicochemical methods to determine the sensitivity of cereals as cargo, primarily in sea transport.

Operation of Polish grain terminals shows a huge diversity in the quantities of international maritime trade in cereals. In 2018, Polish grain terminals conducted loading and unloading of approximately 4,944.7 thousand tons in total of agricultural products (cereals, soybeans, etc.). The Polish leader in international grain transport is undoubtedly the Baltic Grain Terminal in Gdynia, which in 2018 served 3,249.9 thousand tons of agricultural products. Next in order is the terminal in Szczecin, through which 672.2 thousand tons were reloaded, whereas the terminal in Gdansk served 574.9 thousand tons of cereals, and the rest 368.2 thousand tons were served in the terminal in Świnoujście. According to the Central Statistical Office of Poland, in 2019, these were the only grain terminals in Poland, although until 2015, inclusive cereal was also served in the terminal in Police [6, 7].

Maritime transport is one of the oldest ways of transporting goods, especially in international relations. This method of communication enables to move bulky loads, as well as those of significant weight, facilitating an access to major economic centers, thanks to almost unlimited reach of maritime fleet [43]. Maritime transport, as a single mode of transport, is not able to meet the needs of the consumer, because it is not capable of delivering goods directly from the producer to the recipient. Therefore, it is an example of combined transport [11, 14, 22], where specificity is determined the variability of external parameters during its realization. This therefore, contributes to destabilization of quality and, in an extreme situation, also to the occurrence of threats to the safety of transported cargo.

Maritime transport is also one of the important sources of smog, which is particularly evident in ports [36]. Annex VI to MARPOL 73/78 (The International Convention for the Prevention of Pollution from Ships) aims to reduce the emission of toxic compounds into the atmosphere, in particular, those derived from the process of fuel combustion in marine piston engines and other burning devices. It is extremely important that marine cargo ships, as well as their power stations, usually use compression-ignition piston engines. Two-stroke main engines of each individual vessel may have a power exceeding even 80 MW. The operation of such an engine without ecology-oriented optimization consumes from about 0.170 to 0.180 kg / kWh of residual fuel, while emitting more than 0.03 kg / kWh of harmful compounds. The exhaust gases include, for example, sulfur oxides, nitrogen oxides, carbon oxides, hydrocarbons, and solid particles [23], which not only pollute the environment but also can be adsorbed by products with developed specific surface area.

Transport susceptibility characterizes cargo resistance to conditions as well as to effects of transport. It consists of many partial susceptibilities resulting from the physico-chemical characteristics of the transported goods. In case of cereal transport, their high hygroscopicity and sorptivity are the critical parameters. These properties are associated with a quite diverse chemical composition, as well as with a physical structure, which determine the significant development of the specific surface area. Goods with a highly developed specific surface area are susceptible to changes related to the adsorption not only of vapors (including steam) but also of gases, and these changes are adverse to their safety and quality. Therefore, the results of the research on the sorption properties of all dry materials, especially cereal, may also be used in the assessment of the risk connected with the effect of pollution emitted by the ship [42].

Each product in its nature has specific physical, chemical, physico-chemical, and biological features. According to this, the knowledge of these characteristics is extremely important in the case of creating a logistics chain for their transport. The most important properties of cereal include physical structure, density, bulk density, compressive strength, hardness, water absorbability, microbiological stability, and sensitivity to temperature factors [8].

Grain cargo shows high sensitivity to the effect of water in the state of liquid, as well as vapor and gases, temperature changes, exposure to light, the presence of foreign odors, and the presence of pests and rodents. The longer is the duration of transport, the more important the effect of transport conditions. Each of the aforementioned risk factors may contribute to the occurrence of damage in transport and may adversely affect the quality and safety of cargo such as cereal. The quality but also the safety, of cereals and, as a consequence, of the products obtained from them, is undoubtedly related to the method and the conditions of their transport, especially when this process is long. The possibilities of improving the quality, which has been reduced as a result of the transport process carried out in an improper condition, are very limited, and sometimes these possibilities are completely non-existent. Therefore, when organizing the logistic process of maritime transport of cereals, especially factors that are known as critical to the quality of cereal should be taken into consideration. First of all, verification of critical factors will reduce the dynamics of adverse changes leading to a deterioration of quality and, consequently, a safety of cereal as a cargo and as a raw material for food production.

In reference to food, safety is a basic element of quality. If the raw material that is used to produce food is not safe, it would be harmful and must be qualitatively disqualified. Therefore, the matter of food safety is a case that interests producers as a fundamental requirement for further operations relating to conditions of processing, storage, and trade and even in determining the price, while transforming a product into a commodity. Liu and Guo [20] have defined food safety as a state in which the risk of threats (biological, physical, chemical, chronic, or immediate) has been completely eliminated or reduced to an acceptable level.

Nevertheless, there is undoubtedly no cause-effect relationship between the duration of the process and the quality changes of the cargo, because it is not the time that affects the changes but the specifics of the cargo and the factors determining the probability and energy of possible thermodynamic reactions. Time can only be considered as an indicator of the extent of such reactions, but in a relatively short range. It should be remembered that the accumulation of products of a particular reaction in time leads to the reversal of this reaction in accordance with the Chatelier's principle described by Le Chatelier i Braun [4, 18]. Undoubtedly, however, the long duration of transport, in conditions that are inappropriate for the requirements of a particular cargo, will negatively affect its quality and, in extreme situations, also safety. Notably susceptible to the quality changes are food cargo, particularly fresh products demonstrating features of living organisms. The quality of such cargo is determined by three basic biochemical processes to which fresh products, including cereal, are subjected- respiration, transpiration, and senescence. During the respiration process, primarily all carbohydrates undergo an oxidation process, which results in the release of carbon dioxide, water, and energy, and also in the form of heat. Therefore, cargos that need to respire in order to maintain proper quality require oxygen. In reliance to that, they cannot be tightly closed, but ventilation should be carried out regularly in the covered holds. On the contrary, the transpiration process, the essence of which is the release of water vapor into the environment in order to achieve a balance between evaporation and condensation, causes the accumulation of water vapor in the hold. The more dynamic the transpiration, the higher the water content of the cargo and the lower the humidity of the environment in which it is stored. When it comes to processes of maturation and senescence, they are closely related to the physiological state of the grain at the time of loading, the course of postharvest transpiration, and the intensity of respiration. Each of these processes is stimulated by the temperature in the cargo hold, and thus, this parameter should be considered to be critical in the process of transport and storage of cereal.

2. MATERIALS AND METHODS

The research material consisted of grains of four cereal species: wheat, rye, barley, and oat. The test material, in an amount of 2 kg from each species, was obtained directly from its producer. Before cereal grains were taken, they had been stored in the silos, and their condition had been analogous to the one which they have on market.

Cereals are characterized by significant variability of properties related to differences in both the physical structure of the caryopsis and the chemical composition. This determines their sorption properties. Taking the aforementioned into consideration, a comparison of these properties was made by determining the sorption isotherms. Moreover, the ratio of water content and water activity that is optimal for maintaining quality and safety during the transport for grains of each species was estimated. These were achieved by conducting the transformation of empirically determined sorption isotherms using three mathematical models (Brunauer, Emmett and Teller – BET [5], Guggenheim, Anderson and de Boer – GAB [2], and Peleg [31]). This enabled determination of the relative humidity of the air in equilibrium with the grain which has the optimal parameters and thus the optimum relative humidity that should be maintained in the ship's hold during transport of cereal.

Each analytical method included determination of water content, water activity, and sorption isotherms using the static desiccator method. The water content was determined by thermal drying process to constant mass at a temperature of 373-378 K (100-105°C) at normal pressure. Water activity was determined in the AquaLab apparatus, with an accuracy of ± 0.003 (Series 3 model TE, Decagon Devices Inc., Pullman, WA, USA) at a temperature of 293.15 K (20°C). Sorption isotherms were determined using the static desiccator method. The relative humidity was regulated with saturated solutions of appropriate substances. The scope of the study covered the water activity from 0.07 a_w to 0.98 a_w, and the temperature of the research was 293.15 K (20°C). The time when equilibration of the system was determined was 90 days after the samples had been placed in the desiccators. In reliance with the initial weight of samples of particular cereals and changes in the water content, the equilibrium water content was calculated and adsorption isotherms were plotted. Measurement of the water activity in the samples, 90 days after they had been placed in the desiccators, was conducted using the AquaLab apparatus [27].

The diversity of the course of sorption isotherms within the entire range of water activity was statistically analyzed using Student's t-test of differences between the means for paired samples, considering statistically significant differences at the significance level not exceeding P = 0.05.

Sorption properties were determined on the basis of empirical data, which were transformed using three mathematical models: BET, GAB, and Peleg.

The BET equation used in the study was as follows:

$$v = \frac{v_m C a_w}{(1-a_w)[1+(C-1)a_w]} \tag{1}$$

where a_w – water activity (–); v – equilibrium water content (g H_2O/100 g d.m.); v_m – water content in the monolayer (g H_2O/100 g d.m.), and C – energy constant [38].

The GAB equation used in the study was as follows:

$$v = \frac{v_m C K a_w}{(1-Ka_w)(1-Ka_w+CKa_w)} \tag{2}$$

where a_w – water activity (–); v – equilibrium water content (g H_2O/100 g d.m.); v_m – water content in the monolayer (g H_2O/100 g d.m.); C – Guggenheim energy constant, and K – constant correcting properties of multilayer molecules compared to the liquid phase [38].

The Peleg's equation used in the study was as follows:

$$v = Aa_w^B + Da_w^E \tag{3}$$

where *A, B, D* i *E* – constants; a_w – water activity (–), and v – equilibrium water content (g H_2O/100 g d.m.) [34].

The parameters of the equations were determined on the basis of empirical data using non-linear regression with a Monte Carlo algorithm, which prevented inhibition of the estimation process by a local minimum. Minimizing the sum of squared deviations (SSD) was assumed as a function of the objective. Standard errors of the determined parameters of the BET, GAB, and Peleg equations were estimated using the SolverAid macro command based on the Hessy's matrix. [28]. The usability of the models tested for the description of experimental data was evaluated based on the Root Mean Square (RMS) error expressed in %.

$$RMS = \sqrt{\frac{\sum (\frac{v_e - v_o}{v_e})^2}{N}} \cdot 100\%, \quad (4)$$

where N – number of data; v_e – experimental equilibrium water content (g H_2O/100 g d.m.); v_o – predicted equilibrium water content (g H_2O/100 g d.m.) [17].

3. RESULTS AND DISCUSSION

One of the essential ingredients of each raw material for food production is water, which not lonely determines the sensory properties of food but also forms the physical, chemical, and biochemical properties of it. The presence of water affects the microbiological stability of food and also determines its susceptibility to spoilage determined by physical processes (diffusion), chemical processes (hydrolysis), as well as biochemical processes, e.g., enzymatic hydrolysis [32]. According to that, water has a huge effect on the safety and stability of the quality characteristics of cereals during their storage and transport.

The most frequently mentioned factors that are important during storage of cereal grains are water activity and water content. They determine both the direction and the dynamics of the processes occurring at that time.

Cereal grains have limited sorption capacity. The research proved that initial water content in grains was relatively high and ranged from 14.69 to 16.49 g H_2O per 100 g dry matter.

Table 1

Summary of average water content and water activity in analyzed cereals

Product	Water content	SD	Water activity	SD
	(g H_2O/100 g d.m.)	(g H_2O/100 g d.m.)	(-)	(-)
Oat	14.6887	0.2992	0.372	0.003
Rye	15.7133	0.1755	0.362	0.003
Wheat	16.4937	0.4637	0.383	0.004
Barley	15.7417	0.0660	0.376	0.003

It was also indicated that each of the examined samples of cereals had a low (0.36-0.38) level of water activity, guaranteeing microbiological safety. Data collected from literature indicate that microorganisms have the ability to reproduce and thus to threaten the safety of grains' masses and, consequently, the health of the consumer, if the water activity in the grain is higher than 0.6. [32]. In the conducted research, it was proven that this a_w level, which is critical for cargo safety, was not exceeded. Therefore, during the storage of cereal, under conditions that allowed maintaining the equilibrium state, in which neither the increase nor the decrease of water content in the grain's mass occurred, each of investigated cereal species was characterized by microbiological stability, guaranteeing safety, and enzymatic stability, ensuring adequate quality.

Sorption properties have a significant role in the process of stationary cereal storage as well as in the storage during maritime transport. Knowledge of these features provides important information about water in the cargo. According to them, the characteristic relationship between water content and water activity at a constant temperature for a particular material could be defined. This relationship, featured by sorption isotherms, enables to determine the sensitivity of the investigated material to water vapor in the environment, and therefore allows to state the range of humidity in which the cargo could be considered stable and safe. Knowledge of the isotherm shape enables to identify the mechanism that determines the binding of water in the cargo and influences the prognosis of possible changes during the storage process [32]. Hence, the next stage of the research was to determine the sorption isotherms for grains of each particular cereal species and to make their graphic and statistical comparison. Figure 1 shows the course of sorption isotherms.

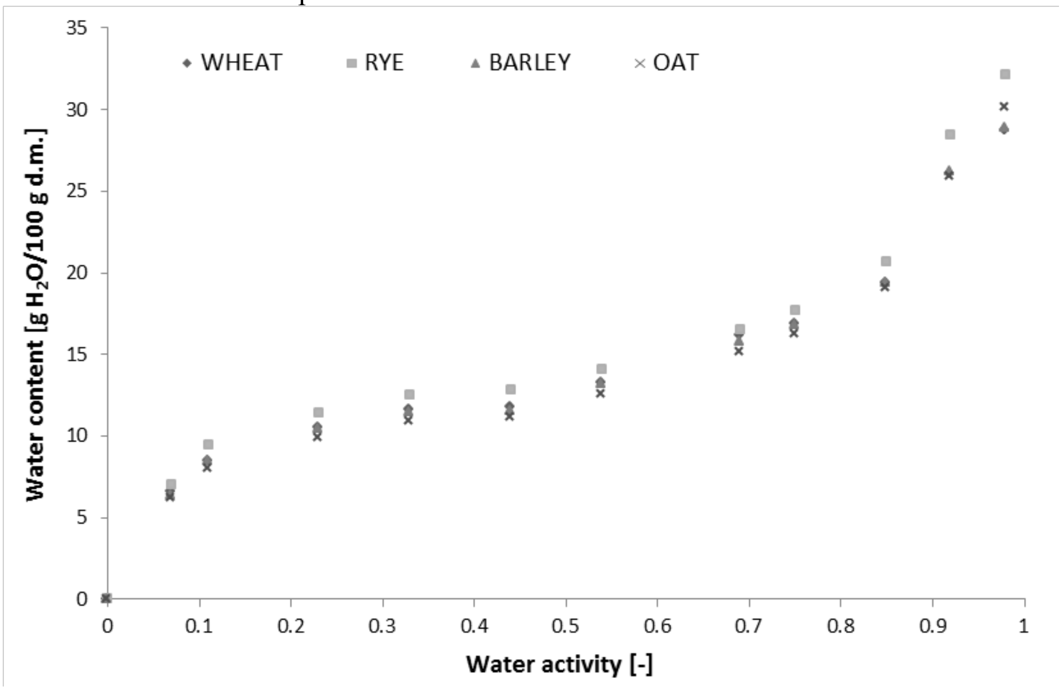

Fig. 1. Sorption isotherms of analyzed cereals determined at 20°C

The diversity of sorption properties of particular cereal species was determined by comparing results of Student's t-test for paired samples ($t_{0.05}$=2.228; $t_{wheat/rye}$=4.366; $t_{wheat/barley}$=1.969; $t_{wheat/oat}$=2.046; $t_{rye/barley}$=5.594; $t_{rye/oat}$=12.630; $t_{barley/oat}$=1.802). This led to the conclusion that cereal which was significantly different from all the others was rye.

The determined sorption isotherms were characterized by the continuity of the course in the whole range of a_w. This indicates that there was no change in the extent of organization of matrix structure as a result of the interaction of cereal masses of each examined cereal species with water molecules at 20°C [25, 28]. This, therefore, could be considered to be a prerequisite to the conclusion that examined cereal masses are quite physically resistant to water, if the ambient temperature is maintained relatively low. However, it should be emphasized that this conclusion is not synonymous with chemical, and what is more, biological stability. Furthermore, the physical stability of cereal masses is significantly connected with the ambient temperature [26].

In addition, it was found that sorption isotherms were characterized by a sigmoidal shape, which means that the process of interaction with water molecules takes place in three stages. In the first of them, water molecules occupy free hydrophilic groups. The first inflection point corresponds to the completion of unimolecular layer. Water contained in the cereal mass in an amount corresponding to this level is most strongly associated with the material, and thus does not cause hydrolytic changes and at the same time protects the material from oxidative changes. This amount of water is the most advantageous, in terms of safety and stability of the quality characteristics of cereals. The quantity of water forming the monolayer depends on the content of hydrophilic polymers such as proteins and polysaccharides. Exceeding this water content, as a result of storing grain masses in a humid space, leads to the initiation of phenomenon of multilayer adsorption. This is defined as the second stage of sorption. In this range, the mechanical properties of grain change, and the dynamics of chemical and biochemical reactions increase. Grain begins to respirate intensively, and this leads to the release and accumulation of metabolic water and energy, in the form of heat. The coexistence of these two factors (heat and water), which are considered critical for safety and quality of cereal masses, leads to a rapid deterioration of such cargo. The second stage continues until the accumulating water fills all the capillaries on the surface of the cereal grains. Thus, the third stage in the sorption process begins, which is described as the capillary condensation phenomenon. This stage is identified on the sorption isotherm as the second inflection point. Absorption by cereal the amount of water that leads to the initiation of capillary condensation phenomenon dramatically increases the dynamics of all biochemical processes typical of living organism and allows the growth of microbes and the production of toxins. [30, 32]. Safety and all changes determining the quality of cereal are so advanced that this product should be considered not suitable for further storage.

Described changes, typical for dry cargo with hygroscopic properties, under the influence of sorption of water molecules, demonstrate some predictability. Nevertheless, to preserve optimal transport conditions and to avoid losses associated with varied characteristics of different cereal species, it is necessary to know the ranges in which maintaining critical parameters will ensure the safety and quality of cereal as a cargo. Therefore, in the next stage of research, data describing sorption isotherms were transformed using two theoretical models (BET and GAB), which parameters a particular physical significance have been imputed. In addition, one empirical model was used (Peleg), which in the literature is indicated as the best model for comparing the differentiation of sorption properties. The use of theoretical mathematical models enables to determine water content with corresponding water activity, which should characterize each particular cereal species to provide grains as a cargo with optimal features. Thus, the knowledge of these parameters makes it possible to determine the level of relative humidity of air in holds, which would guarantee the maximization of stability and safety of cereal as a cargo.

The use of mathematical models, characterized by the theoretical interpretation of their parameters, such as GAB and BET, enables to define the optimal storage conditions for dry cargo [28].

The BET model, describing multilayer adsorption of vapor, has the greatest practical application in the description of sorption isotherms. This theory assumes that for each adsorption layer it is possible to apply the Langmuir adsorption model. The authors of the theory claimed that each particle of adsorbed water vapor, reaching the occupied site on the surface of the adsorbent, forms an adsorbed complex with it. This phenomenon was called multilayer adsorption. Each newly adsorbed particle transforms into the adsorption center of another adsorbed particle. The forces accompanying this transition are analogous to those that are present during the condensation of water vapor. This equation characterizes the course of sorption isotherms very well, unfortunately only in the range of water activity to 0.5 [33].

The BET equation is used to estimate the amount of water strongly bound through polar area of a dry matrix (v_m – monolayer value). Drying grain to such a level of water content before its transport and then keeping it during transport creates the possibility of protecting cereal masses against adverse changes connected with oxidative processes, which affect both the condition of the cereal ingredients and also the sensory quality of cereal masses. The water activity, which is typical of monolayer, describes the extent to which the water molecules are bound to the matrix [16]. The BET theory uses also the C parameter (heat of adsorption) [30]. This value expresses the difference between the heat of desorption from the monolayer and the heat of vaporization of the liquid adsorbent. In the process of physical adsorption, enthalpy is at the level of 20 $kJ\cdot mol^{-1}$. Such low energy level does not lead to changes in the state of adsorbed particles [1]. The results of parameter estimation using the BET model are presented in Table 2.

SSD values indicate that the BET model best described the process of adsorption of water vapor on the surface of oat, and the least rye. Parameters of model for each of the investigated cereal were calculated with similar accuracy. Taking into consideration the fact that models with RMS value, which is lower than 15%, are considered to be acceptable [38], it could be affirmed that the BET model was correctly used to identify the optimal water content in the investigated cereals to ensure their high quality during storage.

The largest monolayer was identified in rye grain (8.3), and the smallest in oat (7.7). This statement indicates that to preserve the safety and stability of cereals during transport, the highest water content can be left in the rye grain. The least resistant to water was oat grain. This difference was probably owing to the presence of hydrophilic pentosans in rye grains, which are capable of binding water, making it less active. Furthermore, the low water level, which is safe for oat grain, was probably caused by the presence of a fruit-seed coat, whose components weakly bind water, making it threaten the condition of the grain. Estimated a_w values, which correspond to the monolayer, indicate that the lowest relative humidity of the environment should be ensured in the case of transport of rye (9.20%), whereas the highest humidity may have a hold used for in the transport of barley (10.61%). At the same time, it can be stated that the phenomenon of water vapor adsorption by the investigated cereals at 20°C was of a physical nature, which is indicated by very low values of the energy constant.

Table 2

The BET model parameters of analyzed cereal species

WHEAT			RYE		
Parameter	Value	Error	Parameter	Value	Error
v_m	8.2595	±4.5187	v_m	8.3409	±4.6396
a_w	0.1051		a_w	0.0920	
C	0.9008	±0.3873	C	0.9466	±0.4103
SSD	4.6985	±1.5327	SSD	5.7807	±1.7001
RMS	11.35		RMS	11.72	
OAT			**BARLEY**		
Parameter	Value	Error	Parameter	Value	Error
v_m	7.6727	±4.0486	v_m	8.2560	±4.9261
a_w	0.0962		a_w	0.1061	
C	0.91118	±0.3771	C	0.8896	±0.4180
SSD	3.9099	±1.3910	SSD	5.3707	±1.6387
RMS	11.10		RMS	12.64	

The second model that was used was the GAB model, whose importance in the research on the sorption properties of dry products is growing, because it takes into account the modified adsorbent properties in the field of multilayer adsorption [40, 41]. This model enables to describe sorption isotherms in the greater range of a_w and to transfer the results obtained to other temperatures.

Lewicki [19] also pointed out that the value of the constant K should be in the range of $0.24 < K < 1$; therefore, keeping the error in calculation of the water content in the monolayer at the level of ± 15.5% entails that the parameter of constant C is higher than 5.67. These requirements have been met. The GAB model parameters are compared in Table 3.

The obtained results of the sum of squared deviations (SSD) and the values of errors in regard to them indicate that the GAB model described the water vapor sorption by the investigated cereal samples very precisely. This model best described the phenomenon of sorption on the surface of oat, and the worst rye. The empirically determined parameters were calculated with similar accuracy. In addition, RMS values indicate that the results obtained using the GAB model better describe the sorption properties of the analyzed cereals than those obtained using the BET model.

Determining the parameters of the GAB equation also enabled to estimate the monolayer. Knowledge of this dimension allows to take rational actions to optimize the costs of storage and transport processes [10]. The obtained results came in a similar way as in the case of estimation using the BET model. However, the monolayer values were higher. Rye was characterized by the largest monolayer (10.3) and the smallest concerned oat (8.8), which was most likely associated with differences in the chemical composition and physical structure of kernels [39]. At the same time, the estimated a_w values that correspond to the monolayer indicate that the lowest relative humidity of the environment should be ensured in the case of transport of oat (15.8%), whereas the highest humidity may have a hold used for transport of wheat (17.83%).

The energy constant C is the difference between the monolayer desorption enthalpy and the liquid adsorbent evaporation enthalpy [29]. The obtained results ($C \geq 2$) allow to state that the phenomenon examined at 20°C had the characteristics of physical sorption. Additionally, in accordance with Lewicki

[19] publication, in which it was indicated that the value of parameter C should be higher than 5.67, it can be stated that errors in the modeling the course of a multilayer sorption were lower than 15.5%. Thus, there is an evidence that the GAB model describes empirical data very well.

Table 3

The GAB model parameters of analyzed cereal species

WHEAT			**RYE**		
Parameter	Value	Error	Parameter	Value	Error
v_m	9.6638	±0.4612	v_m	10.3276	±0.5788
a_w	0.1783		a_w	0.1647	
C	53.3757	±13.1294	C	59.2395	±17.8932
K	0.5966	±0.0321	K	0.5839	±0.0387
SSD	1.5149	±0.5025	SSD	2.3697	±0.6284
RMS	9.15		RMS	11.24	
OAT			**BARLEY**		
Parameter	Value	Error	Parameter	Value	Error
v_m	8.7786	±0.2598	v_m	9.4702	±0.5024
a_w	0.1580		a_w	0.1707	
C	58.0637	±13.2356	C	53.0880	±14.7742
K	0.6355	±0.0138	K	0.6043	±0.0352
SSD	1.4313	±0.4223	SSD	1.8529	±0.5557
RMS	10.01		RMS	9.71	

Values of the constant K lower than 1 confirm the usability of the GAB model. The values of the constant K are close, which clearly indicates the similarity of the examined material (cereal). On this basis, it is assumed that the energy states of the water molecules forming the multilayer system were very similar [27].

To describe sorption isotherms also the semiempirical four-parameter Peleg equation was used [31]. This model best describes the sorption properties of dry food. Parameters of Peleg model are presented in Table 4.

Taking into consideration the assumption that the value of root-mean-square error (RMS) for the best models is lower than 10%, it was found that this model is the prime reflection of empirical data regarding the sorption properties of cereals, moreover in a wide range of a_w. At the same time, taking into account the empirical nature of this equation, it should be emphasized that it had an application only in comparing the investigated cereal species. Obtained values of particular parameters, especially B and E, indicate that rye grain significantly differs from the grains of other examined cereal species, in terms of sensitivity to water vapor in its environment.

Analysis of the obtained results indicates that cereal grains of different species differ in terms of sorption properties. During stationary storage and even more during maritime transport, grains of different cereal species will react in a different way to the same environmental conditions. Therefore, when the process of storage or transport is being organized, the grain should be dehydrated to a level of water content that will correspond to the monomolecular layer. Afterward, it is necessary to provide protection against water, not only in the form of liquid but also vapor. In addition, it should be taken into account that the possibility of occurrence and the dynamics of adverse changes are determined not by the water content but by its activity. This, however, can change under the influence of temperature, even when the water content remains constant.

The BET, GAB, and Peleg models proposed in the study described the experimental data very well. In relation to good and well-founded theoretical foundations of the GAB model [2], and due to recommendations from European Project COST 90 for its wide use in modeling sorption data [44], and regarding the fact that obtained results of optimal water content and relative humidity of the atmosphere correspond to practical experience in the field of maritime transport of cereals, this equation should be indicated as the most useful.

Table 4

Parameters of Peleg equation for analyzed cereal species

WHEAT			RYE		
Parameter	Value	Error	Parameter	Value	Error
A	16.6284	±1.3109	*A*	18.7689	±1.4921
B	0.2939	±0.0582	*B*	6.8066	±1.2707
D	15.5644	±1.4242	*D*	16.4594	±1.2813
E	6.0895	±1.2759	*E*	0.2780	±0.0554
SSD	5.3785	±0.9468	SSD	6.3787	±1.0310
RMS	4.47		RMS	5.04	
OAT			**BARLEY**		
Parameter	Value	Error	Parameter	Value	Error
A	14.8144	±0.9822	*A*	15.3479	±1.3764
B	0.2970	±0.0476	*B*	0.2924	±0.0622
D	18.1108	±1.1199	*D*	16.1151	±1.4966
E	6.7064	±0.9686	*E*	6.0910	±1.2959
SSD	3.4916	±0.7628	SSD	5.9545	±0.9962
RMS	3.99		RMS	5.11	

Very intensive respiration of cereals, especially at increased humidity and when there is lack of ventilation, will lead to a significant increase in temperature in the hold. This, instead, will result in self-heating, brewing, and decay and ultimately may lead to the auto-ignition of the cargo. Therefore, regular inspections of conditions prevailing in the cargo hold are extremely important, because finding any signs of the self-heating process is the first warning, thanks to which it is possible to resist the deterioration of the cargo. The easiest and at the same time the most effective preventive measure is regular active ventilation of cereal, using cooled air or at ambient temperature. The first one will only cool the grain, whereas the second one will additionally dry it gently [13].

It is also important to take the possibility of occurrence of pests in transported cereals into consideration, e.g., wheat weevil, mealworm, confused flour beetle, khapra beetle, saw-toothed grain beetle, flour mite, mill moth, and European grain worm. These pests directly damage the grains, deteriorating their quality. Furthermore, their excrements, moults, and dead specimens additionally contaminate the cargo. In addition, metabolic products favor dampness and heating of grains, and these directly increase the risk of mold and fungus growth, and what is more, under conditions of water stress, there is risk of production of mycotoxin. Microflora of cereals is very diverse in both quality and quantity. The differentiating factors are, among others: the type of grain, maturation during harvest, place of cultivation, and climatic conditions. The development of microflora during storage is closely related to the conditions in the hold. Maintaining proper conditions, i.e., temperature, oxygenation, and humidity in the hold, may lead to reduction of mold, yeast, and bacteria growth [12, 21]. The occurrence of each of the described phenomena, conditioned by a biotic factor, is equivalent to a significant deterioration of cereals and quantitative losses [34].

Regarding rodents existing in cereals on ships, currently if adequate cleanliness is maintained and proper quality management systems are introduced, this problem is not noticeable.

Care for quality and safety in food transport is extremely important; therefore, supply chain management principles have been developed. According to the literature [35], this aims to the following: 1) maximum reduction of the costs of trading goods and information while maintaining the expected level of customer service; 2) minimizing the time of order execution while maintaining a high level of reliability, frequency, and flexibility of deliveries; and 3) rationalizing the size of inventory throughout the entire supply chain while adapting to the needs of individual customers.

The supply chain for maritime transport is as follows: 1) production; 2) consolidation; 3) port of shipment; 4) port of arrival; 5) storage and distribution; and 6) final recipient. It should be noted that transport is carried out between each of the stages [46].

Within the supply chain, an important role is played by the risk management process based on analysis of the structure and activities inside the chain; determining the responsibility within its structure; identification of potential sources of threats of internal and external origin and estimation of the probability of their occurrence, and thus losses and dangers; and grading the risk importance by creating on this basis security plans and implementing them [24, 47].

To avoid risks and consequences associated with them, appropriate measures must be taken already at the stage of planning the maritime transport of dry cargo, such as follows:

- compliance with legal regulations, where in the case of grain transport, it is, e.g., IMO guidelines on bulk grain transport in the SOLAS Convention (Chapter VI, Part C, Regulation 8 and 9) or International Code for Safe Carriage of Grain in Bulk – IGC Code;
- development of appropriate procedures for loading, storage, supervision, together with systematic training for personnel, taking into account appropriate procedures during precipitation;
- regular preservation and technical control of used machines and devices;
- purchase of cargo insurance, including random events;
- requirement to check the quality and tightness of ship's cargo covers;
- storage of the cargo in a way to protect it from dampness and influence of high temperatures, and, in the event of errors in this field, the possibility to separate lumpy, damp, or damaged cargo quickly;
- defining and assigning responsibility for supervising particular works; and
- choosing the appropriate storage technique [46].

4. CONCLUSIONS

Cereal transport is a demanding and complicated process owing to the characteristics of the cargo, which is characterized by significant surface development and, consequently, susceptibility to gas adsorption and strong hygroscopicity, and also owing to the considerable variability of cereal properties, associated with relevant differences in the physical structure of their kernels and chemical composition. The existence of this type of differences has been proved in accordance with the results of studies on sorption properties, which are presented in this article. Comparing the size of the monolayer grain of individual types of cereals, it was shown that rye grain was the most resistant to the presence of water vapor in the environment, whereas oat grain was the most sensitive. The method proposed in this study for the assessment of the sensitivity of cereal grain to environmental conditions during long-term transport or storage can also be used to assess the storage stability of other cereals. In addition, the proposed method allows to determine the parameters at which the cereal grain will remain in the state of dynamic equilibrium, conducive to maintaining its high quality.

While managing supply chain, all sensibilities of transported cargo must be taken into consideration. These are duration of transport, exposure to water vapor or gases, temperature changes, exposure to light, presence of external odors, and presence of pests and rodents. Adaptation of modes of combined transport to conducting maritime transport is extremely important and a complicated undertaking. Therefore, logistic activity should include taking appropriate measures and procedures to avoid losses associated with the destruction of the cargo. A sign of rationalization of activities in this area is reaching for knowledge in the field of science of commodities, cargo science, warehouse science, and functioning of the HACCP (Hazard Analysis and Critical Control Points) system, which in practice will contribute to effective use of advantages and will allow to avoid threats. Building specialized cereal terminals is an activity within this scope. It also seems reasonable to search for new technical arrangements to improve the effectiveness of currently functioning solutions.

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