A Comparative Analysis of Corn Drying in Stabil 3000 Dry Kiln Using Different Energy Sources

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Summary

Agricultural entrepreneurship has been boosted by land concentration, organization of farms, and the establishment of new small centers for admission, processing, and storage. At the same time former large organizations failed, which diverted the process of handling agricultural products. The trend of small dry kilns and storage facilities from 1 to 5 t/h is growing. New customers, who do not have proper knowledge and criteria when choosing proper equipment, are usually offered dry kilns of foreign production. Trade representatives who sell dry kilns also lack the necessary specialist knowledge as it is the case with their customers. The research project considered STABIL 3000 dry kilns produced by "Seting", Delnice and used for seed drying. The dry-kilns used natural gas and fuel oil. We determined incombustible carbohydrons as well as the presence of harmful substances belonging to polycyclic aromatic carbohydrons (PAHs) on the seeds after the drying process. For this purpose we used a device known as employed the EPA 550.1 and EPA 625 method.

Key words

direct drying, combustion gases, polycyclic aromatic hydrocarbons (PAH)

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Introduction

Corn is the most important agricultural plant exposed to drying in the Republic of Croatia. Approximately one million tons of corn is dried annually in 90 big industrial dry kilns and there are also about 90 smaller dry kilns in Croatia. In order to determine a level of corn quality you have to determine its future use. The way of combustion and a fuel kind determine the composition of combustion gases. Light fuel is the most widely used fuel among liquid fuels. Among gaseous fuels the most widely used are natural gas, butane, propane, or a mixture of the before mentioned fuels. A future use of dried corn determines both fuel choice and the way of air heating. Carcinogen and harmful substances (benzopyrene, anthracin, CO, CO_2, SO_2, NO_x, grit, etc.) appear in the process of fuel combustion. A reduction of harmful substances, which are present within the heat carrier in direct-fired dry-kilns, can be achieved by improving the combustion process. Many researches point to constructive and system factors not having the same influence upon carcinogen and toxic components (Treherne, 2003). Many countries do not allow a lengthy exposure of those kinds of corn that are prone to a major absorption of combustion gases to a gas mixture and air. A common concentration of CO is 0.0009% or 9 ppm, and the maximum allowed concentration in the USA is 30 ppm (Treherne, 2003). The efficiency of combustion is presented as a ratio of CO and CO_2 and it is allowed to reach the value of 0.0004% or less. Based on the British experience it has been shown that combustion machines are not used in case when this ratio exceeded 0.0009%. CO_2 is a gas twice as heavy as air, which requires detectors to be installed at a floor level with a maximum LTEL (Long-Term-Exposure-Limit) being 5,000 ppm and the value of STEL (Short-Term-Exposure-Limit) being 15,000 ppm (IARC, 1983). Polycyclic aromatic hydrocarbons PAH form a large group of compounds (over 200). Their carcinogenicity as well as mutagenicity and teratogenicity were proven by experiments as far back as the 1960ies and 1970ies, which was explained by the terms of intercalation (implementation) into the DNA cell structure due to their planar structure. WHO (World Health Organization) presented the research results on the appearance of carcinogen compounds, which point to PAHs as the most researched environmental pollutants (found in air, water, etc.). Combustion can cause two different reactions: pyrolysis followed by a production of instable PAH molecules; and pyrosynthesis followed by a production of more complex PAH structures. The general characteristics of the above mentioned are the following: high melting and evaporating temperature points, a low steam pressure, very low water solubility, good solubility in organic solvents, and a great ability to link to fats (IARC, 1983; Lide, 1991). PAHs are dissolved in the process of photosynthesis, the biological dissolution, and the metabolism in higher biotas. Since they are stable from the chemical point of view and there are no reactive groups, hydrolysis takes no part in the process of their dissolution (Howard et al., 1991). The reasearch so far has shown that the emission of total PAHs in 1985 was estimated to be about 630 tons in USA on an annual basis, 18 tons in Sweden, and 1.5 tons in Norway (Bjorseth and Ramdahl, 1985). The emission in Canada in 1990 was 13 tons (ATSDR, 1990). Some of the best known carcinogen, mutagenic, and teratogenic PAHs are: Benz[a]anthracene, Benzo[b]flouranthene, Benzo[k]flouranthene, Benzo[ghi]perylene, Chrysene $C_{18}H_{12}$, Benzo[j]flouranthene, Dibenz[a,h]anthracene, Benzo[a]pyrene, Coronene, Indeno[1,2,3 cd]pyrene, and Ovalene.

Materials and methods

The research was done on two dry corn dry-kilns "STABIL 3000", produced by Seting, Delnice. "Stabil 3000" dry kiln is a vertical continuous direct-fired dry kiln. Both dry-kilns were the same from the constructional point of view regardless of fuel, which could be either natural gas or light oil. In order to get a better insight and estimation of the risks the presence of 14 or 16 compounds was examined according to the recommendations issued by US EPA. These compounds were the indicators of a sample contamination by PAH. PAH presence on the surface of the sample corn seeds was examined. Modified EPA 550.1 method (ultrasound extraction, liquid chromatography using a phosphorescent way of detection HPLC-F1D) was employed in which case the limit of 0.001 µg/kg of the detection method was reached. A combined method of gas chromatography and mass spectrometry was used. It recorded characteristic ions (GC - EI – MS – SIM US EPA method 625) in order to prove the presence of certain components in the samples. The temperature of the drying medium was between 102 °C and 117 °C. The time seeds spent in the dry-kilns (exposure length to combustion gases) was three hours in the dry-kiln combusting natural gas and four hours in the dry-kiln combusting light oil. Altogether 24 pairs of samples (raw seeds at the entrance, dried seeds at the exit) were examined for both dry-kilns (natural gas and light oil). Seed humidity at the entrance varied between 25% and 30%, and at the end of the process it was between 10% and15%.

Results and discussion

The results of corn seed raw samples examination prior to drying showed no presence of PAH compounds (values were lower than the limit of the detection method, <0.001 µg/kg). Table 1 shows the content of PAH compounds on a corn seed after drying in the dry-kiln using natural gas and in the dry-kiln using light oil as an energy source.

The range of totally adsorbed PAH compounds on seed surface after drying is narrower and varies between 1.688 do 6.696 µg/kg (5.756 µg/kg on average). In case of the light oil dry-kiln this range is wider – between 1.097 and 8.239 µg/kg (5.492 µg/kg on average). Dibenz[a,h]anthracene is a compound belonging to the PAH group and it was rarely detected or determined on the samples dried both ways and exposed to both energy sources. In 24 examined samples dried in the natural gas dry-kiln it was detected only once, whereas in the samples from the light oil dry-kiln it was detected and determined eight times. The most often PAH compounds found in both dry-kilns were acenphthene (1.593 µg/kg on average in

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Table 1. The contents of PAHs' compounds on corn seeds after drying

Parameter	Parameter	Dry-kiln 1 Natural gas	Dry-kiln 2 Light oil	P value
AC	Average	1.543a±0.141	1.247b±0.315	***
	Min	1.250	0.364	
	Max	1.839	1.869	
FLR	Average	0.531±0.043	0.487±0.137	NS
	Min	0.452	0.077	
	Max	0.612	0.860	
ANT	Average	1.008±0.022	1.087±0.261	NS
	Min	0.956	0.154	
	Max	1.063	1.294	
PIR	Average	1.450a±0.068	1.118b±0.263	***
	Min	1.315	0.229	
	Max	1.566	1.467	
B(A)NT	Average	0.117±0.054	0.218±0.290	NS
	Min	0.039	0.022	
	Max	0.230	1.227	
B(K)FLR	Average	0.024±0.018	0.022±0.017	NS
	Min	0.004	0.003	
	Max	0.051	0.054	
B(A)PIR	Average	0.058b±0.026	0.169a±0.117	***
	Min	0.029	0.005	
	Max	0.099	0.382	
DIB(AH)	Average	0.00a±0.00	0.171b±0.178	***
	Min	0.00	0.009	
	Max	0.00	0.925	
IN(123)	Average	0.050±0.058	0.037±0.024	NS
	Min	0.014	0.006	
	Max	0.309	0.100	

the natural gas dry-kiln, and 1.24 µg/kg in the light oil dry-kiln) and pyrene (1.45 µg/kg on average in the natural gas dry-kiln and 1.118 µg/kg).

This may be partly due to relatively higher quantities of B[a]P produced by light oil combustion compared to natural gas combustion. A comparison of both certainly favors the former. Further, lower B[a]P quantities on corn seed samples dried by light oil combustion gases may be due to shorter exposure time. The amount of PAH components in combustion gases, which were used in raw seed drying, was not determined so it was difficult to relate these facts to each other. Further researche on this subject should be done. After a comparison of adsorbed amounts which were the most important from the toxicological point of view it was obvious that both the benzo[k]fluoranthene and indeno[1,2,3-c,d]pyrene values were approximately the same for both drying ways (average values for B[k]F were 0.024 µg/kg and 0.022 µg/kg for the natural gas dry-kiln and light oil dry-kiln, respectively). An average value of adsorbed amounts of I[1,2,3-c,d]P in the natural gas dry-kiln was 0.05 µg/kg ,whereas this value was 0.037 µg/kg for the light oil dry-kiln. As far as benz[a]

pyrene is concerned, which is the most important component from the toxicological point of view, there was a significant difference in adsorbed quantities. The values were 0.058 µg/kg and 0,169 µg/kg for the natural gas dry-kiln and light oil dry-kiln, respectively.

Conclusions

The following conclusions can be drawn based on our research:

1. No PAH compounds were detected on corn seed samples (raw samples) prior to drying.

2. Certain amounts of components belonging to the PAH group were detected in each examined sample regardless of the energy source.

3. Benz[a]pyrene is toxicologically the most important component. It showed a significant difference in adsorbed quantities. But generally speaking, there were no big or important differences of the adsorbed quantities on corn seed surface as far as other components of the PAH group were concerned. This speaks in favour of natural gas, especially when it comes to energy cost.

4. Individual components as well as the total amount of examined components of the PAH group adsorbed on seed surface due to either drying way, were not significant in relation with detected level of their adsorption and in this way they pose no health threat.

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