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THE CONTENTS OF CARCINOGENIC PAHs ON CORN SEEDS AND THE ENERGY EFFICIENCY OF DRYING BY DIFFERENT ENERGY SOURCES

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Original scientific paper

A modern and intensive cattle breeding involves the use of good quality food, which has to be in accordance with the basic nutritional requirements and health standards to protect human health. Corn is one of the most important components of fodder mixtures and it is subjected to drying in kilns of different designs. The kilns use various energy sources and it is possible to contaminate corn grain with carcinogenic PAHs generated by fuel combustion. The aim of this study is to determine the presence of carcinogenic PAHs on the grain after drying in a direct-fired kiln plant in case when light oil and ground gas were used. The research results point to a regular presence of carcinogenic PAHs in case when both types of fuel were used, but their values are not significant in terms of the adsorbed amount and therefore they cause no significant risk. Ground gas has a considerably more favourable energy efficiency level compared to light oil.

Keywords: *combustion gases, direct drying, polycyclic aromatic hydrocarbons*

Sadržaj karcinogenih PAU na zrnima kukuruza i energetska učinkovitost sušenja različitim izvorima energije

Izvorni znanstveni članak

Suvremenø i intenzivnø støčarstvø uključuje kørištenje kvalitetne hrane, køja møra biti u skladu sa øsnøvnim hranidbenim pøtrebama i zdravstvenim standardima zaštite ljudskøg zdravlja. Kukuruz je jednaød najvažnijih kømpønenti u krmnim smjesama, a pødvrgnut je sušenju u pećima različitih kønstrukcija. Sušare køristite različite izvøre energije pa je møguće zagađenje kukuruza s kancerøgenim PAU (pølicikličkim arømatskim ugljikøvødikøm) generiranim kød izgaranja gøriva. Cilj øvøg rada je utvrditi prisutnøst kancerøgenih PAU na zrnu nakøn sušenja u pøstrøjenjima s izravnim izgaranjem u slučaju kada se køristi lakø ulje i zemni plina. Rezultati istraživanja ukazuju na redøvitu prisutnøst kancerøgenih PAU u slučaju kada su kørištene øbje vrste gøriva, ali njihøva vrijednøst nije značajna u smislu adsørbirane køličine i zatø ne uzrøkuju značajan rizik. Zemni je plin znatnø pøvøljnije razine energetske učinkøvitøsti u ødnøsu na lakø ulje.

Ključne riječi: *izravno sušenje, plinovi izgaranja, policiklički aromatski ugljikovodik*

1 Introduction
Uvod

Corn is the most important plant subjected to drying both in the Republic of Croatia and in the whole world. There are over 90 large industrial kilns and about the same number of smaller kilns in Croatia, where app. 1 million tons of corn is dried annually. When corn is dried in direct fired kilns it is directly exposed to combustion gases. The contents of combustion gases in a kiln are the result of the fuel kind and the way of combustion. When rating the quality of corn grain you have to assess the future purposes of the grain use. Light oil is the most often used liquid fuel. Ground gas, butane, propane and their mixtures are the most often used gaseous fuels. The choice of fuels and the way of air heating should be in accordance with the future use of the dried corn.

Carcinogenic and harmful substances (benzopyrene, anthracene, CO, CO_2, SO_2, NOx, soot, etc.) appear as the product of combustion and thus the improvement of the combustion process causes the reduction of harmful ingredients in warmth carriers in direct-fired kilns. Many studies point to the fact that structural factors have an unequal influence upon the contents of carcinogenic and toxic substances [1]. Many countries prohibit the use of mixtures of fuel gases and air in case when grain is exposed to longer drying but on the other side it easily absorbs combustion fuels. The usual concentration of CO is 0,0009 % or 9 ppm, and the maximum permitted concentration of CO in the United States is 30 ppm [2]. Combustion efficiency is shown as the ratio of CO and CO_2 and it should be 0,0004 % or less. British experience showed that combustion plants are out of use if this ratio is higher than 0,0009 %. CO_2 is twice as heavy as air, so detectors should be installed at the floor level with the maximum concentration of LTEL exposure of 5,000 ppm and the STEL value of 15,000 ppm [2]. Sulfur dioxide is an irritating gas which affects the throat and lungs, and its maximum concentration is 2 ppm. NOx is a term used for all forms of nitrogen oxides, the maximum annual concentration being 0,03 ppm.

Polycyclic aromatic hydrocarbons PAHs constitute a large group of compounds (over 200). According to their chemical structure they are aromatic hydrocarbons with condensed benzene nuclei. They have the chemical properties between benzene and olefins. The 1960's and 1970's experiments proved their carcinogenecity [1-3], mutagenity and teratogenicity [4-6]. This is explained by the terms of intercalation (implementation) into the DNA structure of cells as a consequence of their planar structure. The test results of the World Health Organization (WHO) on the occurrence of carcinogenic compounds show that PAHs are among the most researched environmental contaminants (found in water, air and soil). It was also determined that the most PAHs found in the environment result from an incomplete combustion of organic material at relatively high temperatures and at a certain ratio of carbon and oxygen. Combustion can result in two types of reactions: pyrolysis followed by formation of unstable PAH molecules structures as well as pyrosynthesis followed by the formation of more complex PAH structures.

Physical and chemical properties of PAHs are mainly determined through conjugation by alpha-electronic systems. At room temperature all the PAHs are in solid condition. Their common characteristics are the same: high melting and evaporation temperature, low vapor solubility, low water solubility, good solubility in organic solvents and high binding capacity of fat [3-4]. PAHs are decomposed by

photodegradation, biodegradation by microorganisms and metabolism in higher biotas. Since they are chemically stable and free of reactive groups, hydrolysis plays no role in their degradation [5].

Previous studies have shown that the release of total PAHs in 1985 was estimated at about 630 tons per year in the USA, 18 tons per year in Sweden, 1,5 tons per year in Norway [1]. In 1990 the emission in Canada was 13 t [6].

The best known carcinogenic, 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.

2
Materials and methods
Materijal i metode

The research was done on two corn kilns STABIL 3000, produced by Seting Delnice. STABIL 3000 kiln is a vertical continuous direct-fired kiln. Both kilns have the same design regardless of fuel, which is either ground gas or light oil. The drying tower is made of a supporting steel structure with fillings (canopy, semi-canopy and tin sheets) of aluzinc sheets, which are treated against corrosion in the areas exposed to major condensation. Canopies are placed in the drying column in parallel rows. Above them there are the sheets which convey grain and prevent grain delays. The flow regulation through the kiln is managed by adjusting the time relay which governs the working operations and manages the pausing of the feeder. This ensures a great flexibility of regulation capacities (1:40). The kiln ventilation system consists of a series of axial fans located at the outlet air channel. The input capacity of kiln drying in case of corn is 3,000 kg/h with the humidity reduction from 32 % to 14 %. The installed capacity of electricity is 14 kW and the installed capacity of thermal power is 780 kW.

According to the US EPA recommendations, either 14 or 16 components, which are signs that the samples are polluted with PAHs, were investigated in order to get insight into the risks as well as to assess them. A modified EPA 550.1 method was used for detection of PAHs presence on the surface of the sample corn grain (ultrasound extraction, the use of liquid chromatography with phosphorescent detection method HPLC-FLD). The limit of the method detection was 0,001 g/kg. When necessary a combined method of gas chromatography and mass spectrometry, which records the selected ions, was used (GC - EI - MS - SIM U.S. EPA Method 625). The temperature of drying media ranged from 102 °C to 117 °C. The time the seeds spent in the kilns (exposure length to combustion gases) was 3 hours in the kiln with ground gas and 4 hours in the kiln with light fuel oil. A total of 24 pairs of samples (at the entrance raw grain and at the exit dried corn) were examined for both kilns (gas and light oil). Grain moisture at the entrance of the dryer ranged from 25-30 %, and at the end of drying it was between 10-15 %. Energy efficiency was determined by the Mollier chart.

3
Results and discussion
Rezultati i rasprava

The test results prior to corn drying showed that they did not contain any compounds from the group of PAHs, ie. that these compounds were not detected in raw samples (less than detection limits of the method, < 0,001 g/kg.

Certain amounts of carcinogenic PAH-s were found in all samples, regardless of the energy source used for drying (Tab. 1).

The total amount of the adsorbed PAHs compounds in the kiln burning ground gas was lower and it ranged from 1,688 to 6,696 g/kg (the average of 5,756 g/kg). The kiln burning light oil produced higher amounts ranging from 1,097 to 8,239 g/kg (the average of 5,492 g/kg).

Dibenzo [a, h] anthracene is the component which was both very rarely detected and found in all the samples dried in both ways. It was detected only once in 24 test samples dried in the kiln burning ground gas, whereas it was detected 8 times in the samples dried in the kiln burning light oil. The most present component from the PAH group were acenapthene (the average for the kiln burning natural gas was 1,539 g/kg; the value for the kiln burning light oil was 1,47 g/kg) and pyrene (average for the kiln burning natural gas was 1,394 g/kg and the average value for the kiln burning light oil was 1,067 g/kg. The comparison of the adsorbed amounts of the ingredients which are significant in toxicological terms showed that the values for benzo [k] fluoranthene and indeno [1, 2, 3-c, d] pyrene were approximately the same in the case of both drying methods (the average for B [k] F for ground gas kiln was 0,024 g/kg), and for the light oil kiln the average was 0,021. The average value for [1, 2, 3-c, d] P the average amount for natural gas kiln and light oil kiln were 0,034 g/kg and 0,036 g/kg, respectively. Benz [a] pyrene is the most important ingredient from the toxicological point of view and it showed a significant difference in adsorbed amounts: the ground gas kiln showed an average value of 0,058 g/kg, whereas the light oil kiln showed the value of 0,168 g/kg.

It can be explained in the way that the relatively bigger amounts of B(a)P resulted from light oil combustion. This speaks in favor of ground gas. Lesser amounts of B(a)P can also be explained by shorter exposure time of corn grain to drying. The PAHs amounts in combustion gases may be related to the shorter contact time. Considering that in combustion gases the amounts of PAH contents were not determined, it is not possible to verify the above statements. The research should be carried on in order to learn more about the above mentioned.

Tab. 2 shows energy efficiency of drying of corn grain with different fuels.

4
Conclusion
Zaključak

We can make the following conclusions based on the research:

1. The corn samples did not contain PAH compounds previous to the exposure to any kind of drying, i.e. the compounds were not detected in raw samples before drying.
2. Regardless of energy sources used during the drying process certain PAH amounts were always found.

Table 1 *The content of carcinogenic PAHs in the grain after drying*
Tablica1. *Sadržaj kancerogenih PAU u zrnu nakon sušenja*

Parameter	Parameter	Driers 1 Natural gas	Driers 2 Light oil	P value
Acenafthene (ppm)	Average	1,543a±0,141	1,247b±0,315	***
	Min	1.250	0,364	
	Max	1.839	1,869	
Flourene (ppm)	Average	0,0152±0,006	0,0202±0,014	NS
	Min	0,006	0,003	
	Max	0,034	0,074	
Flourathene (ppm)	Average	0,531±0,043	0,487±0,137	NS
	Min	0,452	0,077	
	Max	0,612	0,860	
Anthracene (ppm)	Average	1,008±0,022	1,087±0,261	NS
	Min	0,956	0,154	
	Max	1,063	1,294	
Pyrene (ppm)	Average	1,450a±0,068	1,118b±0,263	***
	Min	1,315	0,229	
	Max	1,566	1,467	
Benz[a]anthracene (ppm)	Average	0,117±0,054	0,218±0,290	NS
	Min	0,039	0,022	
	Max	0,230	1,227	
Benzo[b]flouranthene (ppm)	Average	0,057±0,037	0,058±0,039	NS
	Min	0,016	0,005	
	Max	0,111	0,133	
Benzo[k]flouranthene (ppm)	Average	0,024±0,018	0,022±0,017	NS
	Min	0,004	0,003	
	Max	0,051	0,054	
Benzo[a]pyrene (ppm)	Average	0,058b±0,026	0,169a±0,117	***
	Min	0,029	0,005	
	Max	0,099	0,382	
Dibenz[a.h]anthracene (ppm)	Average	0,00a±0,00	0,171b±0,178	***
	Min	0,00	0,009	
	Max	0,00	0,925	

Table 2 *Energy efficiency of the drying of corn grain with different fuel*
Tablica 2. *Energetska efikasnost sušenja zrna kukuruza s različitim gorivom*

Parameter	Driers 1 Natural gas	Driers 2 Light oil
Energy efficiency ($kJ/kg_{misspelled\ water}$)	4198	4150
Drying cost ($€/kg_{misspelled\ water}$)	0,0305	0,0677

3. There is a significant difference in adsorbed amounts concerning the toxicologically most important ingredient called benz [a] pyrene as well as acenaphtene, pyrene and dibenzo [ah] anthracene. On the other hand, generally speaking, there are no significant differences in adsorbed amounts of the PAH ingredients on corn grain surfaces. This speaks in favor of ground gas, especially when the cost of energy source is taken into consideration.
4. Individual ingredients and the total amount of the tested PAH compounds from the group which were found to have adsorbed onto the surface of the grain, were not significant and therefore they do not pose any health risks.

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