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Full Length Research Paper

Effect of varied quantities of zeolite on the reduction of polycyclic aromatic hydrocarbons in tobacco smoke

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This research was carried out to determine the possibility of total and selective reduction of polycyclic aromatic hydrocarbons (PAHs) content in cigarette smoke by applying different amounts of zeolite directly to the cigarette blend. Zeolite catalysts CuZSM-5 were applied in the form of suspension to the cut tobacco blend in the quantities of 1 and 3%. After the equalization of the blend, the cigarettes were rolled on the cigarette making machine type MOLINS–9. The cigarettes were smoked according to the standard of ISO 3308 procedure. The smoke condensate which was extracted from Cambridge filter with methanol was analyzed by gas chromatography-microscopy (GC-MS). The obtained results indicated that there is a possibility of effective and selective catalytic reduction of PAHs in tobacco cigarette smoke. The determined reduction degree for the PAHs was 35.78 to 40.88%. The decrease of PAHs was proportional to the quantity of the zeolite added. CuZSM-5 showed a certain selectivity, especially towards fluoranthene (reduction ratio was 55.25:77.96%) and acenaphthylene (reduction ratio was 42.39:71.15%). It is possible to apply zeolite in the form of suspension to factory-made cigarettes because it does not affect the operation of machinery, especially the work of a cigarette maker.

Key words: Tobacco smoke, polycyclic aromatic hydrocarbons (PAHs), zeolite catalyst, total reduction, selective reduction.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of several hundred diverse compounds usually containing two to seven fused benzene rings. They belong to a special group of ubiquitous contaminants known as persistent organic pollutants (POPs) (Liu et al., 2006; Sehili and Lammel, 2007; Menichini and Monfredini, 2003). The PAHs are formed during incomplete burning of organic matter in lack-of-oxygen conditions.Cigarette smoking and environmental tobacco smoke is an important source of air pollution (Hoffmann and Hoffmann, 1997).

The presence of PAHs in the main stream of cigarette smoke has been well explored and documented (Rodgman, 2001; Rodgman and Perfetti, 2006; Rouse, 2006; IARC, 1986; Snook et al., 1975, 1977, 1978). The mechanism of PAHs formation has two steps: the degradation of large complex molecules with the formation of free radicals and recombination of free radicals into different PAHs (new synthesis) (Rodgman and Perfetti, 2009). There is also the possibility of transformation of complex molecules, for example phytosteroles, to diverse aromatic forms of PAHs. The main PAHs precursors are solanesol, phytosteroles, terpenes, nicotine, lipids and cellulose (Rodgman, 2001; Severson et al., 1979). The most important and the earliest isolated PAH compound from tobacco smoke was benzo[a]pyrene (BaP) which is commonly used as an environmental indicator for PAHs. Studies on PAH levels in cigarette smoke often show only BaP (Dumont et al., 1993; Risner, 1988; Kayali and

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Rubiobarroso, 1995; Tomkins et al., 1985). A recent directive of the European Commission (EU, 2005), used BaP as an indicator of the carcinogenic risk of PAHs and sets a limit value for this toxicant, which is to be attained as much as possible (1 ng/m^3). The average quantity of BaP in smoke is 3.9 µg/100 cig (Snook et al., 1976).

The quantity of PAHs in cigarette smoke depends on pyrolitic conditions, predominantly on the temperature range in the burning zone and the quantity of reduction elements in the burning material (Sharma and Hajaligol, 2003). In both streams of tobacco smoke (main stream-MS and side stream-SS), about 4,863 components were identified, of which 755 are PAHs (Rodgman and Perfetti, 2006, 2009).

According to a recent report of the International Agency for Research on Cancer (IARC), 10 carcinogenic PAHs together with 53 other known carcinogens are present in cigarette smoke (Ding et al., 2007). The PAHs persist mostly in the solid phase and predominantly in the SS of tobacco smoke (Hoffmann and Wynder, 1961). The total amount of PAHs in side stream smoke exceeds the amount ascertained in the main stream: the ratio of SS to MS is 2:20 (Evans et al., 1993). This indicates that the reduction of PAHs by smoke filtration does not affect their concentration in side stream smoke (Lodovici et al., 2004), and this is why both groups of smokers, active and passive are equally exposed to the PAHs in tobacco smoke. The procedure of removing PAHs by adding zeolite catalysts directly to the mixture (Yong et al., 2006) represents a modern technology which can be one of the possible solutions for the production of the so-called potentially reduced exposure products (PREPs) which are the cigarettes with less health risk. This means that the production of smoke with low PAHs content is possible. In this way, it is possible to control the speed and temperature of combustion and the chemistry of the material that is burned, which results in modifying the composition of tobacco smoke during it's formation (Radojičić et al., 2009), thereby possibly reducing the amount of harmful components in the main and side stream of tobacco smoke.

Based on the previous research of Radojičić et al. (2009), it could be seen that zeolites show the highest activity between the temperature range of 450 and 600°C which is the temperature range of the period of the smoldering process in the pyrodestilation zone (Baker, 1975). In addition, the selectivity of the zeolite to PAHs was studied in hand-made cigarettes (Meier and Siegmann, 1999). This experiment was carried out in industrial cigarette making conditions. It is important to note that only industrially manufactured cigarettes can be analyzed on an analytical smoking machine according to the conditions prescribed by the ISO standards. The hypothesis of this study is that the addition of zeolites directly to the cigarette blend would make them active centers for catalytic cracking inside the burning cigarette. Presumably, this will cause the breaking of large long-chain PAHs molecules. In this way, the zeolites can be more efficient as catalysts than adsorbents in filters; smoke enters the filter at the average temperature of 36°C (Moric and Newton, 1977).

Previous studies have shown that different materials may be used for the reduction of PAHs (Pérez-Gregorio et al., 2010). In this research, zeolites were selected as catalysts for two main reasons. From the perspective of smokers, the most important reason is that the zeolites are silicates which remain after the cigarettes burn to ashes, so it has no direct contact with a smoker and there is no change of the sensory properties of the smoke. Another important reason is their accessibility, reasonable price, as well as the possibility of purposeful synthesis (Bhatia, 1990).

The application of zeolite CuZSM-5 has already been tested on hand-made cigarettes. This research proved that zeolite CuZSM-5 effectively reduces the content of NO and NOx in cigarette smoke (Cvetkovic et al., 2002).

Because of the fact that all the previous researches reported in this study were based on hand-made cigarettes, we thought it important to carry out an experiment using the industrial conditions involved in making cigarettes. In industrial conditions, it is possible to apply different amounts of zeolite in the form of a suspension which will be distributed in the same proportion in the cigarette blend.

MATERIALS AND METHODS

Preparation of CuZSM-5 catalyst

CuZSM-5 catalyst was obtained from NaZSM-5 zeolite ion exchange process under the following conditions (Cvetković et al., 2002): ion exchange solution was 0.01 M Cu $(NO_3)_2$; the ratio of the mass of ion exchange solution to mass of zeolite was 100:1; T = 333°K.

The degree of ion exchange (DIE) of Na^+ with Cu^{2+} cations was calculated by the equation (1):

$$DIE\ (\%) = 2\ [Cu] / [Al] \quad (1)$$

[Cu]- Cu content; [Al]- Al content in the altered form of ion CuZSM-5 zeolite was determined by standard analytical methods of chemical analysis of zeolites; the catalyst which was used had 100% DIE.

The catalyst was milled into fine powder (diameter of 0.2 mm) and activated. Before using the catalyst, CuZSM-5 was dried for 4 h at 623°K. The milled and activated catalyst was kept in a sealed glass jar.

Preparation of cigarette samples

An already prepared mixture of tobacco blend, the American type blend which is the product of a cigarette factory was used for the experiment. From a conveyor belt at the exit of blend silo in which mixing was carried out was measured 3 times per 1 kg of tobacco mixture. Zeolite catalysts were applied to the tobacco blend in the form of a suspension, using propylene glycol (additive, humidifier) and 96% ethanol.

Table 1. Characteristics of determined PAHs.

Parameter	Molecular weight	Number of ring
Naphthalene	128	2
Acenaphthylene	152.2	3
Acenaphthene	154.21	3
Fluorene	166.2	3
Phenanthrene	178.2	3
Anthracene	178.2	3
Fluoranthene	202.26	4
Pyrene	202.3	4
Benzo[a]anthracene	228.29	4
Chrysene	228.3	4
Benzo[b]fluoranthene	252.3	5
Benzo[k]fluoranthene	252.3	5
Benzo[a]pyrene	252.3	5

Preparation of control cigarettes

A solution containing 20 ml of propylene glycol (2%) and 10 ml ethanol (1%) was applied using a compressor on 1 kg of tobacco blend with constant mixing. After the equalization of the blend for three hours at room temperature in plastic bags, the tobacco blend was inserted directly into the basket of the cigarette making machine (type Molins-9).

The cigarettes were produced using the following materials: filter rod 120 mm long, made of acetone fiber 2, 1Y/42000 with unknown filter paper, stainless tipping paper and corrodible cigarette paper with the ventilation capacity of 40 ± 2.5 CU. The length of the cigarette filter was 20 mm, while the length of the tipping paper was 24 mm. The cigarette length was 84 mm. For the experiment, only cigarettes weighing 970 ± 0.5 mg were used.

Preparation of cigarettes with the CuZSM-5 (AB - Cu) catalyst

To 1 kg of tobacco mixture was added the suspension in the following composition:
Cigarette AB - Cu_1: 10 g of the catalyst CuZSM-5, 20 mL of propylene glycol and 10 ml of 96% technical ethanol; Cigarette AB – Cu_2: 30 g of the catalyst CuZSM-5, 20 ml propylene glycol and 10 ml of 96% technical ethanol.

Two samples of the "test" cigarette and the "control" cigarette (Ø) were prepared in the same manner and on the same machine from this mixture of processed tobacco after equalizing.

Method of testing cigarette physical parameters

Before analysis, the cigarettes were conditioned for 48 h in the Borgwaldt conditioning chamber (Heinr. Borgwaldt GmbH, Germany) at a temperature of 22 ± 2°C, and at the relative humidity of 60 ± 5% according to ISO 3402 (ISO, 1999). The determination of the weight of cigarettes, draw resistance, and caliber and weight of cigarettes was performed on the device SODIMAT (Sodim SAS, HAUNI, France).

Module for draw resistance measuring was done according to ISO 6565 method (ISO, 2002).Twenty cigarettes from each sample (control and test cigarettes) were analyzed. The values of different physical parameters were expressed as the mean value ± standard deviation (x ± S.D.).

Method of collecting smoke condensate (particulate matter of tobacco smoke – TPM)

For collecting particulate matter of tobacco smoke, the cigarettes were smoked on the BORGVALDTH RM 20/CSR following the standard conditions of ISO 3308 (ISO, 2000): puffing 2s, smoldering 58s, buff lent 23 mm, puffing volume 35 ml/s. Twenty cigarettes were used from each sample (3 x 20 = 60 cigarettes in total). Particulate matter of tobacco smoke was trapped on Cambridge filter in accordance with ISO standard 4387 (ISO, 2000) and further analyzed. The smoke condensate was extracted from Cambridge filter with methanol.

Method of testing for quantity of PAHs

In this study, the quantity of PAHs was determined in the particulate phase of the MS of tobacco smoke (Table 1). To determine the quantity of PAHs in tobacco smoke, the Gas Chromatograph 6890 Network GC System with mass detector 5973 Network Mass Selective Detector (Hewlett-Packard Company, USA) was used. The GC column was a J&W DB-17ms (J&W, 30 m × 0.25 mm ID × 0.25 μm film thicknesses). The MS detector was set in selected ion monitoring (SIM) mode and electron impact ionization (electron energy 70 eV) was used to generate the ions. The oven temperature program was as follows: initial temperature at 50°C for 1 min, to 195°C at 10°C min^{-1}, to 280°C at 5°C min^{-1}, hold 10 min, and to 310°C at 30°C min^{-1}, hold 15 min. The injector temperature was set at 320°C and the flow rate at 1.0 ml min^{-1}. MS quadrupole temperature was set at 106°C, MS source temperature at 230°C, and transfer line temperature at 300°C. Degrees of reduction of PAHs were calculated according to the formula (2):

$$DR = \frac{Co - Ci}{Co} \times 100 \qquad (2)$$

Where, DR is the degrees of reduction of PAHs; Co is the content of component in the smoke of non-modified cigarettes and Ci is the content of component in the smoke of test cigarettes.

Method of testing for quantity of ash

The percentage of ash content after the burning of cigarettes was measured gravimetrically and was calculated by the formula (3):

Table 2. Physical characteristics of cigarettes.

Cigarette	Weight (mg) x ±S.D.	Caliber (mm) x ±S.D.	Draw resistance (mmH_2O) x ±S.D.
Ø	970.00±0.0294	7.84±0.0124	106±1.0198
AB – Cu_1	970.25±0.0245	7.83±0.0113	108±1.1124
AB – Cu_2	970.45±0.0216	7.86±0.0142	107±1.0132
S.D.	0.1841	0.0125	0.8165

$$x = P \times \frac{100}{t} \quad (3)$$

Where, x is the percentage of ash content; P is the quantity of ash (g) and t is the tobacco dry weight (g).

RESULTS AND DISCUSSION

Analysis of the physical characteristics of cigarettes

The aim of this research was to determine whether the addition of zeolite to the mixture of tobacco causes changes in physical characteristics of cigarettes. Any change in the physical characteristics of cigarettes will cause changes in the total production of smoke as well as its composition (Hoffmann et al., 1995; O`Connor et al., 2008).

The three most important physical characteristics of cigarettes which were examined in this experiment are given in Table 2. They include weight of cigarettes, cigarette diameter, and draw resistance.

The weight quality of each group of cigarettes is the standard size, while an aberration in the norm caused a movement of raw materials used for making cigarettes, and charging uniformity and smoking characteristics. If the weight of cigarettes increases and all the design parameters of cigarettes remain constant, it will lead to the production of large quantities of smoke. Cigarettes have a certain diameter which is constant for a given cigarette. Increasing the diameter of cigarettes reduces the burning rate which in turn increases the production of smoke. The draw resistance of a cigarette is measured by the pressure difference in a 17.5 mL per second air flow before and after passing through the rod. Increased draw resistance causes the difficulty in the flow of gases through the cigarette, which significantly changes the conditions of burning and smoke production. The cigarettes used in this study were manufactured on a modern cigarette making machine that automatically adjusts the weight of cigarettes in the process of development, so there were no significant differences in the weight and caliber of cigarettes.

Given that cigarettes are selected according to weight, it is expected that there will be changes in the permeability of air. Zeolite particles are much smaller than tobacco fibers. Smaller particles cause an increase in the resistance of air movement. Therefore, the movement of air through the cigarette is slow. This influence is determined by measuring the draw resis-tance. However, since the zeolite added was in the form of suspension, there were no significant differences in the values of draw resistance of the cigarettes tested. Slight increase in draw resistance means that there is a slightly slower movement of air through the cigarette which enabled the realization of a number of reactions that were confirmed in further analysis.

The results of the analysis of the cigarettes' physical charasteristics are of great importance because they confirm the effect of the zeolite applied directly to the tobacco blend in the process of cigarette manufacturing.

Reduction of PAHs in cigarette tobacco smoke

The PAHs concentration in the particulate phase of the MS of tobacco smoke are presented in Table 3. The analysis of the tobacco smoke confirmed the presence of the following PAHs: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene and fluoranthene (Table 3). The amounts of detected PAHs are not correlated with their molecular weight. The presence of PAHs with two and three rings was detected; the only detected PAH with four rings was fluoranthene. Acenaphthylene, fluoranthene, phenanthrene and naphthalene were in the greatest concentration in the control cigarette. These results are in accordance with the previous research of Lu and Zhu (2007). They did not detect PAHs with a large number of rings which is not in accordance with the results of previous researches.

The degrees of the reduction of PAHs in the tested cigarettes resulting from the addition of zeolites are presented in Table 4. The addition of zeolite in each of the given concentrations resulted in PAHs reduction in the main stream of tobacco smoke. The total PAHs reduction was at the level of 35.78% with zeolite addition of 1%, and 40.88% with zoelite addition of 3%. The effect of the zeolite was proportional to the amount added. The assumption was, if the quantity of zeolite was higher, there were more active centers for cracking reactions and less PAHs were formed. Regarding the selectivity of added catalysts CuZSM-5 (Tables 3 and 4), it is obvious that 1% on zeolite in a given tobacco mass is very selective towards acenaphthylene (71.15%) and

Table 3. The content of PAHs in tobacco cigarette smoke.

PAH (μg/cig)	Ø	AB – Cu_1	AB – Cu_2
Naphthalene	0.1178	0.1115	0.0970
Acenaphthene	0.0305	0.0790	0.0348
Acenaphthylene	0.2305	0.0665	0.1328
Fluorene	0.0235	0.0138	0.0358
Phenanthrene	0.0968	0.0793	0.0626
Anthracene	0.0283	0.0238	0.0159
Fluoranthene	0.181	0.0810	0.0399
Pyrene	/	/	/
Benzo[a]anthracene	/	/	/
Chrysene	/	/	/
Benzo[b]fluoranthene	/	/	/
Benzo[k]fluoranthene	/	/	/
Benzo[a]pyrene	/	/	/
Total PAHs	0.7084	0.4549	0.4188

Table 4. Degrees of reduction of PAHs (%).

Parameter	AB – Cu_1	AB – Cu_2
Naphthalene	5.35	17.66
Acenaphthene	-159.02	-14.10
Acenaphthylene	71.15	42.39
Fluorene	41.28	-52.34
Phenanthrene	18.08	35.33
Anthracene	15.90	43.82
Fluoranthene	55.25	77.96
Total PAHs	35.78	40.88

fluoranthene (55.25%). Also, zeolite CuZSM-5 showed high selectivity towards fluorene (41.28%). We did not neglect the percentage reduction of all other PAHs except for acenaphthene.

The addition of 1% concentration of zeolite led to extreme increase of acenaphthene concentration (159.02%). The addition of 3% concentration of zeolite to tobacco blend also caused similar increase in the concentrations of PAH, although the percentage of individual PAHs observed varied.

Generally, it is possible to conclude that the percentage reduction of the observed PAHs was high, with the exception of acenaphtylene which had a decrease of 42.39% which is 1.68 times less than the increase observed when 1% concentration of zeolite was added. However, the percentage increase in acenaphthene when 3% concentration of zeolite is added to the tobacco blend is only 14.10%. In other words, this increase is 11.28 times smaller than the increase in the amount acenaphthene when 1% concentration of the zeolite is added (Table 4).

It should be noted that the addition of 3% concentration of zeolite caused an increase of 52.34% of fluorene, while the addition of 1% concentration of zeolite caused a decrease in the amount of fluorene by 41.28%. Further researches may be carried out to explain this phenomenon.

It is important to particularly emphasize that regardless of the increase in the amount of two PAHs (acenaphthene and fluorene), there was no new synthesis of PAHs in the cigarette smoke with the addition of zeolite (Table 3). It also important to note that there was no synthesis of benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene and benzo[k]fluoranthene. This is a very important fact because the IARC asserts that benz [a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene and benzo[k]fluoranthene are possibly carcinogenic to humans (IARC, 2004). Therefore, it can be concluded that zeolite CuZSM-5 manifested a certain selectivity (Table 4), especially towards fluoranthene (reduction ratio was 55.25 : 77.96%) and acenaphthylene (reduction ratio was 42.39 : 71.15 %).

Results of the investigation of ash content

The addition of zeolites directly to the tobacco blend caused changes in the ash content (Table 5). Based on the results shown in Table 5, it can be concluded that the amount of ash left after the burning of cigarettes AB – Cu_1 is 1.10%, while the amount of ash left after the burning of cigarettes AB – Cu_2 is 3.07 % which shows more amount of ash in comparison to the control cigarette Ø. The increase in the amount of ash is proportional to the amount of zeolites which were added, since they all turned to ash after the burning process.

Conclusions

In this study, the possibility of effective and selective

Table 5. Change in the ash content relative to the quantity of added zeolites.

Cigarette	Ø	AB – Cu_1	AB – Cu_2
Ash (%)	17.26	17.45	17.79

catalytic reduction of PAHs from the main stream of cigarette smoke was examined. Based on the results of the experiment, the following conclusions were drawn:

(1) The addition of zeolite catalysts to cigarette blend does not alter the physical characteristics of cigarettes. It is possible to add a zeolite in the form of suspension during the factory processing of cigarettes as this does not affect the operation of machinery, especially the work of a cigarette maker.

(2) The obtained results show the possibility of effective and selective catalytic reduction of PAHs in tobacco cigarette smoke by using zeolites as catalysts.

The decrease of PAHs was proportional to the quantity of the zeolites added. A better result was achieved with the addition of 3% concentration of zeolite (40.88 %).

(3) It was found that zeolite CuZSM-5 manifested a certain selectivity, especially towards fluoranthene (reduction ratio was 55.25 : 77.96%) and acenaphthilene (reduction ratio was 42.39 : 71.15 %).

(4) There was no synthesis of benzo[a]pyrene, benzo[a]anthracene which are classified as causative factors of human cancer, and benzo[b]fluoranthene, and benzo[k]fluoranthene which are classified as possible causes of cancer.

(5) Increase in the amount of ash is proportional to the amount of zeolites which were added since the zeolites are silicates which turned to ash after the burning process.

(6) Instead of the use of traditional adsorbents in filters, the use of zeolites can present a new possibility for obtaining PREPs of tobacco.

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