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THE INFLUENCE OF ZEOLITE TYPE ADDED TO CIGARETTE BLEND ON THE CHANGES OF PYROLITIC TEMPERATURES*

Reduction of harmful tobacco smoke compounds, such as nitrosamines and polycyclic aromatic hydrocarbons (PAHs) could be particularly controlled by adjusting the cigarette pyrolitic conditions. One possible way to do that is by adding zeolite materials directly to the cigarette. In this work two types of zeolites, namely, pentasil type (ZSM-5) and Y type were used, both in the quantity of 3% in respect to the tobacco mass. The results of the experiment have shown that both zeolite types influenced the changes in pyrolitic temperatures, as well as that both zeolites were catalytically active and that as the outcome of that activity there were changes in conditions of the burning process. It was concluded that the type of zeolite had more influence on the temperatures of the gas phase than on the temperatures of the solid phase. Actually, adding the two zeolite types resulted in a decrease of temperatures in both the solid and gas phase, while the decrease was higher when the zeolite of pentasil type was added.

The presumption of the experiment was that the processes of catalytic cracking will develop without any difficulties on the zeolite's active centers in the zones of pyrolisis and pyrodistillation. These processes are endothermic and that fact had a direct influence on the changes during pyrolisis.

The conditions under which the pyrolitic changes have been happening in the cigarette have so far been analyzed in detail [1–5]. The first step in the research of any kind is to measure the temperature of burning during the puffing and smoldering processes, having in mind that the burning process and the smoke formation process depend mostly on the temperature distribution inside the cigarette [6,7]. Inside the burning cigarette, the tobacco blend is subjected to temperatures from the ambient one to 950 °C, with the addition of a small and variable quantity of oxygen. The material does not burn completely and many damaging components of the tobacco smoke are formed. These issues were particularly studied by Baker [8–11], who gave fundamental information and directions about the pyrolysis during the puffing and smoldering of cigarette. Together with his associates Baker established that the temperatures of the solid phase change from 790 to 950 °C in the puffing process, and in the gas phase they change from 790 °C in the smoldering process to 860 °C in the puffing process.

Many researches have shown that the mechanisms of sublimation, thermic decomposition, synthesis and transfer of the smoke compounds depend exactly on the temperatures developed during the pyrolysis of the material in cigarette [12]. The function of control of the burning conditions inside the cigarette is achievement of complete burning, or at least burning which will produce less damaging substances like PAHs, nitrosamines and CO. The latest approach to this problem is the attempt of direction or blockage of the pyrolitic processes or upgrading synthetic processes of certain compounds. One of the possibilities to achieve this is the application of catalytically active substances directly to the tobacco blend.

In this paper, the changes of the temperatures of pyrolisis during every single puffing have been followed and observed. The main hypothesis was that the conditions of the burning process can be regulated by accelerator's action. Based on the data found in scientific papers zeolites are the ones which have the maximum activity in the temperatures between 450 and 600 °C [13], which are the temperatures in the period of smoldering process in the pyrodistillation zone. Consequently we supposed that the process of catalytic cracking will develop on the zeolite's centers without any difficulties. In that way, the processes of formation of certain components, especially damaging ones could be controlled.

EXPERIMENTAL

In this research, two types of zeolites were used: pentasil (ZSM-5) and Y type. Zeolites were chosen regarding to the pore-size and thermal stability on the high temperatures [14,15]. These zeolites were synthesized and chemically characterized at the Faculty of Physical Chemistry in Belgrade.

Zeolites, in the quantity of 3% regarding to the tobacco mass, were added to prepared tobacco blend from the product line of the tobacco factory by the scheme shown in the Table 1.

Table 1. Tabular display of making of test cigarettes

Zeolite	Percent of zeolite added	Cigarette mark
Zeolite type Y	3	L_1
Zeolite type pentasil	3	C_1

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The zeolites were added in the form of powder, and with constant mixing. After the equalization was finished we made cigarettes type "Modified American blend" and it was done on the cigarette machine MOLINS-9. In this way, we got two samples of the "test" cigarette and the "control" cigarette (Ø), altogether three samples. The control cigarette was made of the same tobacco blend, but with no addition of zeolites.

For the making of all cigarettes the same material was used: 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 40±2,5 CU. The length of the cigarette filter is 20 mm, and the length of the tipping paper is 24 mm. Cigarette length is 84 mm.

The cigarettes were smoked according to the standard procedure ISO 3308. For the determination of the temperature zones in the smoldering and puffing processes, 10 cigarettes were used from each sample (altogether 3×10 = 30 cigarettes) and then the average temperature in smoldering and puffing process was calculated for each sample. The experiment was repeated 5 times, and the results were statistically analyzed. The state of temperature was measured 1 s after the beginning of the puffing process, and 2 s after the beginning of the smoldering process – in the equilibrium moment (in the transition between smoldering and puffing process). Twelve puffing processes were done for each cigarette. In order to organize results, we show the values of maximum temperatures in smoldering and burning processes.

In this experiment, an infrared system was used to measure the temperatures of the solid phase in the smoldering process. The system consists of:

1. one-channel smoking machine (Borgwaldt),
2. digital infrared camera (FLIR-therma CAM 675) and
3. computer for picture display and analysis.

The basic experimental equipment was connected in a way such that the infrared camera was moving in parallel with the cinder of cigarette (Figure 1), and to move by fixed, determined itinerary [6].

The temperatures of the gas phase in the puffing process were measured with a thermo couple Fluke 52/K-type (Chromel–Alumel).

RESULTS AND DISCUSSION

In the previous experiments we have established that the temperature of the gas phase reaches its maximum at the center of the cinder, while in the solid phase it reaches its maximum on the cinder's surface, approximately 1 mm in front of the burning line. Both temperatures of the solid and gas phase change during the puffing process while in the end of the puffing process they are balanced (temperature equilibrium). This balanced state ends during the smoldering process. Therefore, the temperatures of the solid phase at the end of every particular puffing were measured by an infrared camera and were displayed as the temperatures of smoldering of the cigarette.

The influence of the zeolite type to the temperatures of the solid phase during pyrolisis

Values of the temperature in the solid phase of the examined cigarettes are displayed in the Figure 2.

Based on the results here shown (Figure 2), it is obvious that the adding of both zeolite types has caused the temperatures to lower in the solid phase during the smoldering process. The changes in temperature values differ due to the type of zeolite added. In the control cigarette the temperatures in process of smoldering in the solid phase change in the interval from 598.8 to 637.2 °C.

The most extreme decrease of temperatures and the lowest values of the temperatures in the solid phase during the smoldering process are noticed in the cigarette

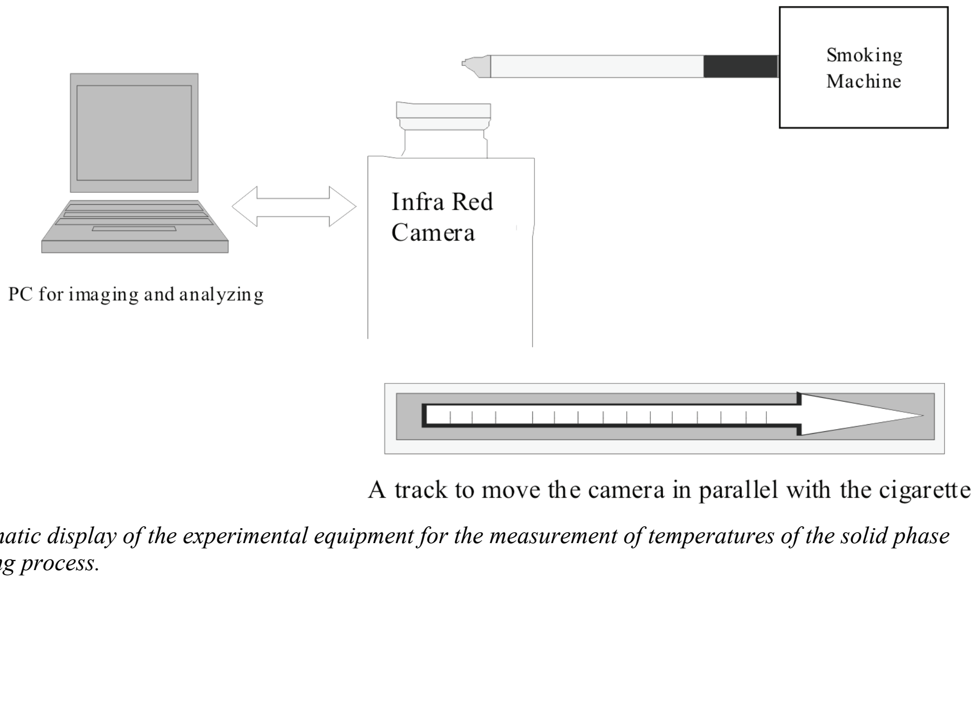

Figure 1. Schematic display of the experimental equipment for the measurement of temperatures of the solid phase in the smoldering process.

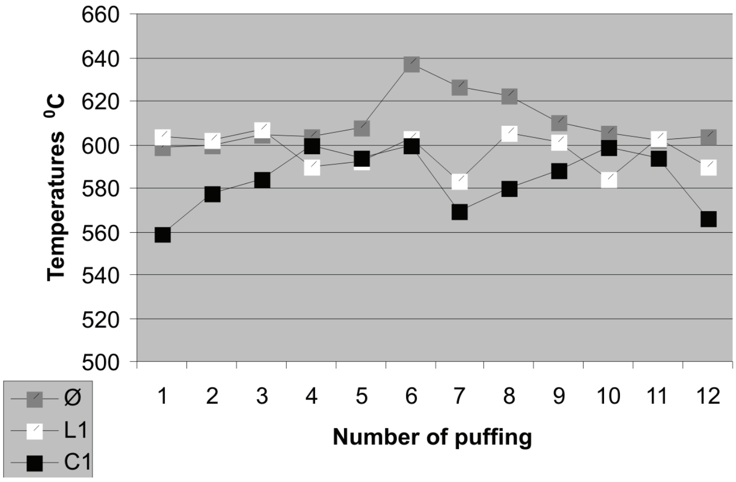

Figure 2. Values of the temperature in the solid phase while adding 3% of zeolites.

C_1, with the addition of zeolite type pentasil and they change in the interval from 558.6 to 599.8 °C. Therefore, zeolite type pentasil has shown extreme acceleratory activity, which due to the endothermic character of the process developing on the active centers, caused a significant decrease of the temperatures in the solid phase, compared to the control cigarette. The difference between the highest and the lowest temperature value in the solid phase for all the twelve puffing of the cigarette C_1 is 41.2 °C, which is an inconsiderable declination from the value of the control cigarette.

The decrease in the value of temperature was also noticed with the cigarette L_1, but compared to the control cigarette it was less intense. This kind of result can be explained with less intensive catalytic activity of zeolite type Y. The temperatures in the solid phase change in the interval from 583.6 to 607.2 °C. The difference between the temperatures at the end of each puffing is 23.6 °C, which is less than with the control cigarette, so the conclusion can be that the L_1 cigarette burns the most consistently.

Differences in the temperatures of pyrolisis during the particular puffings for each cigarette can be a consequence of the way of the application of the zeolite material. There is a presumption that silicate zeolite which was added in the form of powder, manually, was not equally transported onto the whole length of the cigarette, and therefore results varied.

Temperature zones for all of the three cigarettes in the end of the sixth puffing are shown in Figure 3.

When we compare these three images showing the cinder at the end of sixth puffing, we can see that the zone of high temperatures of the brightest colour is the biggest (on the largest part of cinder surface) on the control cigarette, therefore the temperature is the highest in that area (637.2 °C). At the end of the sixth puffing the high temeperature zone of cigarette C_1 is compact, closer to the paper burning line and takes up a larger part of the cinder. The cigarette has the smallest surface of high temperatures near the edge of the paper.

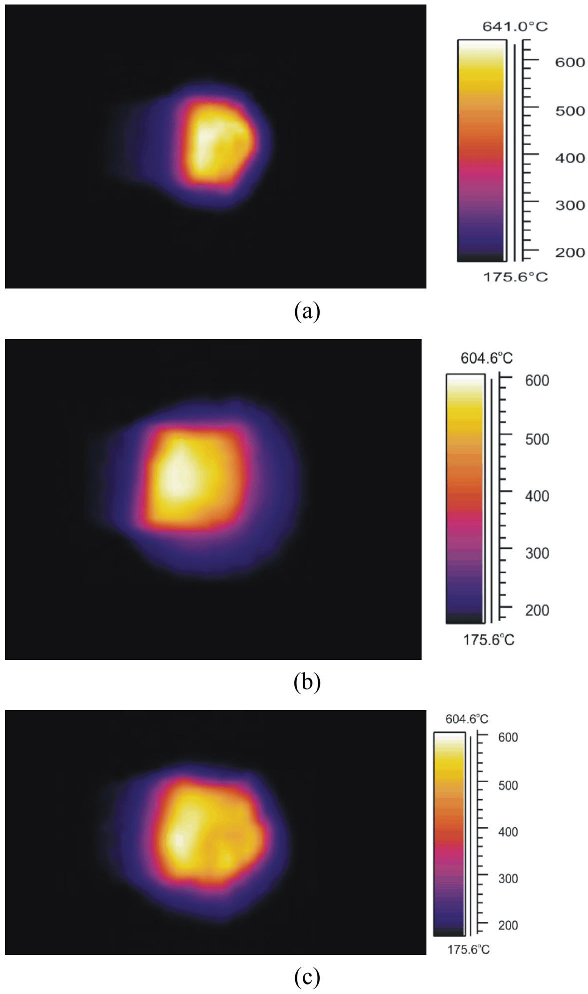

Figure 3. The end of the puff: a) control cigarette (maximum temperature is 637,2 °C); b) cigarette C_1 (maximum temperature is 599,6 °C); c) cigarette L_1 (maximum temperature is 602,5 °C).

To make the changes in the temperature values easily notable, in Table 2 only the values of the maximal temperatures in the solid phase are displayed, so is the extent of change compared to the control cigarette.

Table 2. Maximum temperature values in the solid phase and the changes in temperature compared to the control cigarette while adding 3% of zeolites

Sample	Temperature in the solid phase, °C	The change in temperature (% of decrease)
Ø	637.2	–
L_1	607.2	4.71
C_1	599.8	5.87

Based on the results shown in Table 2, it is clearly visible that the type of zeolite had influence on the values of maximal temperatures in the solid phase during the smoldering of the tested cigarettes. In comparison to the control cigarette, the addition of the zeolite type pentasil (cigarette C_1) has caused a decrease in the maximum temperature in the solid phase in the amount of 5.87%. When zeolite type Y is added, the decrease in the maximum temperature in the solid phase is lower and it is 4.71%.

The influence of the zeolite type to the temperatures of the gas phase during pyrolisis

In this experiment, the temperatures of the gas phase were measured during the puffing process of cigarette smoke. Based on the data from scientific papers (that the temperature profile of puffing process can be divided into three levels) in this experiment the temperature of the gas phase was measured in the middle level of the puffing. Therefore, we presumed that at the end of the first second of puffing the temperature will reach its maximum. For each cigarette, 12 puffings were done but only maximum temperatures are displayed in Table 3.

Table 3. Maximum temperature values of the gas phase and the change compared to the control cigarette while adding 3% of zeolites

Sample	Temperature of the gas phase, °C	The change in temperature (% of decrease)
Ø	961	–
L_1	912	5.10
C_1	902	6.14

The addition of the zeolite type pentasil in the amount of 3% there was a decrease in the maximum temperature of the gas phase in the value of 6.14% in comparison to the control cigarette. And the addition of the zeolite type Y (cigarette L_1) the decrease in the temperature was 5.10%. These results show that the method of changing the temperatures in the gas phase is the same as the one used on the temperatures of the solid phase.

Based on the results displayed in Tables 2 and 3, we can conclude that the type of zeolite which was added had stronger influence on the decrease in the temperatures of the gas phase of smoke.

CONCLUSION

Both types of zeolites which were added directly to the tobacco blend had influenced the changes in the temperature values of pyrolisis, both in the gas and solid phase. It was noticed that the influence of the zeolite type on the temperature changes was stronger in the gas phase.

Addition of both types of zeolites has caused the decrease in temperatures of the solid phase, and larger decrease was noticed when using zeolite type pentasil.

Addition of both types of zeolites has caused the decrease in the maximum temperatures of the gas phase, and larger decrease was noticed while using zeolite type pentasil.

Regarding the fact that the reactions which lead to the decrease of harmful components of the tobacco smoke such as primarily reactions of catalytic cracking are endothermic, we can conclude that by adding both zeolite types we can lower the production of PAHs in tobacco smoke.

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IZVOD

UTICAJ TIPA ZEOLITA DODATOG MEŠAVINI ZA CIGARETE NA IZMENE TEMPERATURA U PIROLIZI

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(Naučni rad)

Redukcija štetnih komponenata duvanskog dima, kao što su nitrozamini i policiklični aromatični ugljovodonici (PAHs), može se kontrolisati podešavanjem pirolitičkih uslova u cigareti. Jedna od mogućnosti je dodavanje zeolita direktno u duvansku mešavinu. U radu su korišćena dva tipa zeolita: pentasil tip (ZSM-5) i Y tip, oba u količini od 3% na duvansku masu. Rezultati eksperimenta pokazali su da su oba tipa zeolita katalitički aktivna i da su imala uticaj na promene u vrednostima temperatura pirolize. Dodavanje oba tipa zeolita uzrokovalo je sniženje temperatura i čvrste i gasovite faze, pri čemu je smanjenje izraženije pri dodatku zeolita tipa pentasila. Konstatovan je veći uticaj tipa dodatog zeolita na izmenu temperatura gasne faze.

Ključne reči: Tip zeolita • Temperature pirolize • Gasna faza duvanskog dima • Čvrsta faza duvanskog dima
Key words: Zeolite type • Pyrolitic temperatures • Gas phase of tobacco smoke • Solid phase of tobacco smoke