Original Research Article

Effect of draw resistance on Benz [a] Pyrene and its contribution degree of cigarette hazard index

Abstract：Effect of cigarette draw resistance between 860-1130Pa on deliveries of Benz [a] Pyrene in mainstream cigarette smoke（MCS）was investigated, and contribution degree of cigarette hazard index was proposed for the first time to study how the contribution degree could be affected by 7 harmful components. Effect of Benz [a] Pyrene with different draw resistance on contribution degree of cigarette hazard index was also investigated. The results showed that contribution degree of Benz [a] Pyrene is uniform, which is different from variation of crotonaldehyde, HCN, CO and NNK, meanwhile, 1000Pa could be viewed as critical draw resistance, and there is an obvious mainstream cigarette smoke variation below and above 1000Pa. Analysis of contribution degree of cigarette hazard index separately is a feasible tool to study variation of smoke harmful components, which lays foundation for further changing trend and roles of different harmful components while the cigarette hazard index changes.

Keywords: Benz [a] Pyrene; Draw resistance; Mainstream cigarette smoke; Harmful components; Cigarette hazard index

1 Introduction

In 1998, a modified Hoffmann list was widely recognized by the medical profession and the tobacco industry, causing a great impact in the world. Most countries concentrate more stringent restrictions on the release of Hoffmann in cigarette products, and consumers are increasingly concerned about the Hoffmann components. Now filtering function of the filter is mostly based on tar and nicotine, and there is little study on filtering efficiency on harmful ingredients such as tar and nicotine. At present, product design philosophy targeting on release amount of Hoffmann components (CO, NNK, NH_3, HCN, B[a]P, croton aldehyde and phenol) has been widely accepted. Hoffmann components (CO, NNK, AMMONIA, HCN, Benz [a] Pyrene, croton aldehyde and phenol) were applied by China's tobacco industry as a significant standard of the target products[1]. chemical formula: C20H12, is a ring of polycyclic aromatic hydrocarbons. Crystal is yellow solid. This substance is produced in an incomplete combustion state between 300 and 600 ℃. Benz [a] Pyrene existed in coal tar and coal tar can be found in the smoke produced by the burning of the motor vehicle exhaust (especially diesel engine), tobacco and wood, and grilled food. As a mutagen and benzopyrene carcinogen, and it was found to be associated with many cancers. The in vivo metabolite BPDE causes carcinogenic substances.

Xie Jianping provided a characterization method of harmful ingredients including CO, NNK, ammonia, HCN, Benz [a] Pyrene, croton aldehyde and phenol. This method is widely applied in the design and evaluation of cigarettes[2]. Wei Yuling[3], Christophe L M[4], Zheng Qin[5], Liu Jianfu[6], Zhai Yujun[7] et al. investigated the effect of cigarette paper, tipping paper and other materials on the release of cigarette smoke components, Liu Xianjun[8], Li Qianjin[9], Yu Hongxiao [10,11], Du Yongmei[12] and Fu Qiujuan[13] carried out research on the harmful components and its release of mainstream smoke. Cai Junlan[14], Li Yanqiang[15], Yang Hongyan[16], Yu Chuanfang[17, 18] et al. studied the effect of the design parameters of cigarette auxiliary materials such as the filter tip on harmful components of cigarette smoke. Pang Yongqiang[19], Chen Huan[20], Zhang Xia[21], Kong Haohui [22] et al. studied the effects of different pumping conditions on harmful gas emissions, and Qiu Ye[23] et al. studied the main harmful substances emission and hazard assessment. Peng Bin[24] proposed a cigarette hazard assessment system based on the multi objective decision making. Draw resistance affects the sensory quality of cigarette and harmful components in smoke, and Wu Zhiying [25], Sun Dongliang [26] et al researched on the relationship between the physical indicators of cigarettes and draw resistance. Although the influence of auxiliary materials parameters on the harmful components has been reported, the influence of the draw resistance on the harmful components of cigarette smoke has not been systematically studied and reported. The research provides the basis for the optimization of the design parameters to decrease harm cigarette process, which provides theoretical reference for follow-up study on variation of the harmful components and design of cigarette products while the H value changes.

2 Experimental

2.1 Test materials and instruments

Test raw materials and reagents.

Cigarette samples with different draw resistance were provided by China Tobacco Yunnan Industrial Co. Ltd. The products applied in the experiments are all standard products (purity > 99%) , including 9-phenyl, chrysene, Benz [a] Pyrene, 2, 4-dinitrophenylhydrazine formaldehyde, acetaldehyde, acetone, propylene aldehyde, propaldehyde, crotonaldehyde, 2-butanone, butyraldehyde, o-, p-, m-, hydroquinone, phenol, o-, p-, m- cresol, NNK, d-NNK, ammonia, HCN. Cyclohexane, acetonitrile, tetrahydrofuran and ISO alcohol are all chromatographic pure. The following reagents arise out of analytical grade, including perchloric acid, 2, 4-dinitrophenyl hydrazine, methyl sulfonic acid, hydrochloric acid, polyethylene ether, NaOH, chloramine T, potassium hydrogen phthalate, ISO nicotinic acid, KCN, potassium citrate, potassium molybdate and potassium sodium potassium sodium.

Main instruments. Cigarette ignition device, a cigarette by mouth suction collection system; RM20H smoking machine (Borgwaldt KC company, Germany); Research N1 infrared thermal imaging instrument (Alpha company, USA); Agilent 1200 HPLC, Agilent 7890A gas chromatograph, Agilent7890-5975 gas chromatography mass spectrometry combined with analyzer (Agilent); IC3000 ion chromatograph (Dionex Corporation, USA); AA3 continuous flow analyzer (Bran Luebbe company, Germany); Gas Trace2000 phase chromatography -TEA610 type thermal energy analyzer (Thermo Finigan company, USA).

2.2 collection, treatment and harmful components analysis of flue gas

According to national standard GB/T 23356-2009, GB/T21130-2007, YC/T253-2008, GB / T23228-2008, YC / T377-2010, YC / T255-2008, YC / T254-2008, harmful components of CO, Benz [a] Pyrene, HCN, NNK, ammonia, phenol and crotonaldehyde in the cigarette smoke were tested[27-33].

3 Results and discussion

3.1 Critical draw resistance and its effects on phenol

While the draw resistance varies, Benz [a] Pyrene varies obviously. Through analysis of draw resistance variation, the draw resistance between 860-1130Pa was selected to analyze the seven types of harmful smoke variations shown in Fig.1.

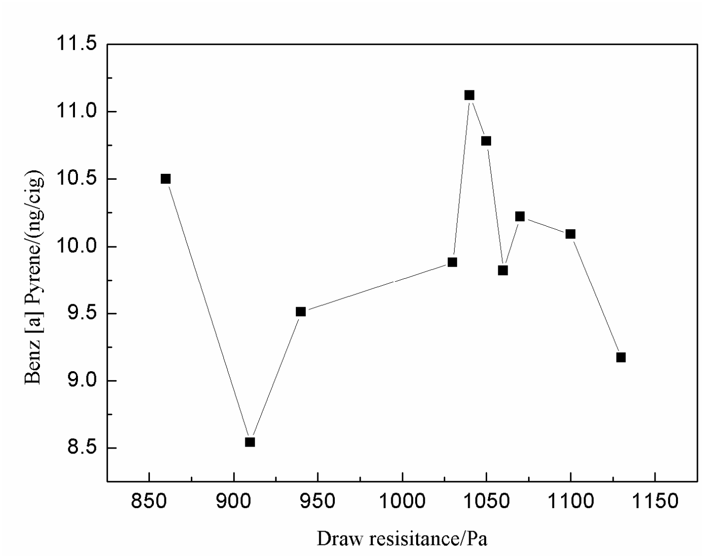

Fig.1 Variation of Benz [a] Pyrene with different draw resistance

As shown in Fig. 1, when the draw resistance is less than 1000Pa, Benz [a] Pyrene has obvious fluctuating value between 8.5-10.5 ng/cig, as the draw resistance continues to rise to above 1000Pa, variation of Benz [a] Pyrene tends to be stable and maintained between the 9.2-11.1ng/cig.

From the above discussion, draw resistance of 1000 Pa can be regarded as the critical draw resistance of Benz [a] Pyrene. It can be concluded that there is an obvious change of harmful components near the critical draw resistance, and the critical draw resistance has important effect on harmful smoke components, which also indicates that in the design process of cigarette parameters such as punching location and filter selection which are related to draw resistance, the effect of critical draw resistance should be considered in detail. To further analyze effect of draw resistance variation on phenol, authors proposed the concept of H value contribution of harmful smoke components, and the calculation and analysis are as follows.

3.2 Definition and calculation of H value contribution degree

In this paper, the determination of emission quantity of 7 harmful components in cigarette mainstream smoke and H index is used to calculate the corresponding national or industrial standards to determine the release amount of tar in cigarette mainstream smoke and 7 harmful ingredients, and according to the calculation formula which Xie Jianping put forward to calculate flue gas of H value index [2].

$$H=\left(\frac{X_{CO}}{C_{CO}}+\frac{X_{HCN}}{C_{HCN}}+\frac{X_{NNK}}{C_{NNK}}+\frac{X_{\text{ammonia}}}{C_{\text{ammonia}}}+\frac{X_{\text{Benz [a] Pyrene}}}{C_{\text{Benz [a] Pyrene}}}+\frac{X_{\text{crotonaldehyde}}}{C_{\text{crotonaldehyde}}}+\frac{X_{\text{phenol}}}{C_{\text{phenol}}}\right)\times\frac{10}{7}$$

(1)

Where H is the hazard value index, X_{CO}, X_{HCN}, X_{NNK}, X_{NH_3}, $X_{\text{Benz [a] Pyrene}}$, $X_{\text{crotonaldehyde}}$ and X_{phenol} are the harmful components emission quality respectively, C_{CO}, C_{HCN}, C_{NNK}, C_{ammonia}, $C_{\text{Benz [a] Pyrene}}$, $C_{\text{crotonaldehyde}}$ and C_{phenol} are responding the calculation reference value from the national standard，and their value are C1 = 14.8，C2 =126.7，C3 = 4.7，C4 = 7.8，C5 = 8.2，C6 = 22.1，C7 = 19.4 respectively.

To further study different harmful components, authors proposed H value contribution degree, and the definition is as follows[],

$$\gamma_i = \frac{X_i}{H \cdot C_i} \times \frac{10}{7} \times 100\% \quad (2)$$

where γ_i is the H value contribution degree of harmful component type ***i*.**

$$\gamma_{\text{Benz [a] Pyrene}} = \frac{X_{\text{Benz [a] Pyrene}}}{H \cdot C_{\text{Benz [a] Pyrene}}} \times \frac{10}{7} \times 100\%$$

(3)

where $\gamma_{\text{Benz [a] Pyrene}}$ is the H value contribution degree of ammonia.

H value contribution degree reflects the contribution of each harmful smoke to the total H value. H value is influenced by 7 harmful smoke components, the greater the value, the greater effect of the harmful smoke on H value index is proved. Through the preliminary research and statistical work, 7 types of harmful smoke components can be divided into two groups according to the similar change trend of the seven kinds of harmful gas. Among them, resistance to suction effect on Benz [a] Pyrene, ammonia and phenol values are similar, and the statistics of the suction resistance of various factors and H value contribution were calculated according to formula (2) for statistical analysis.

Comprehensive comparison of the three types of smoke harmful components' contribution degree to the H value and the other four types of harmful components are as shown in Fig. 2[34].

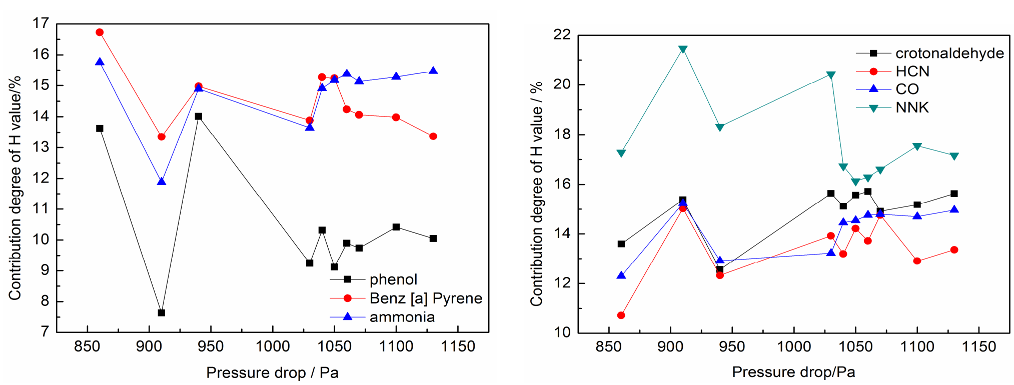

Fig. 2 Variation of H value contribution of 7 types of harmful flue gas components under different pressure drops[34]

As can be seen from the analysis on H value contribution degree of several types of harmful smoke components, H value contribution degree fluctuations of three harmful components of Benz [a] Pyrene, ammonia and phenol is basically similar. When the draw resistance is less than 1000Pa there is an obvious fluctuation of three kinds of harmful smoke components. When the draw resistance is no less than 1000Pa, H value contribution degree of Benz [a] Pyrene maintained at 13.3% - 16.7%. At the same time, in contrast to H value contribution degrees of the other four harmful ingredients of CO, crotonaldehyde, HCN and NNK, it can be found that H value contribution degrees of Benz [a] Pyrene, ammonia and phenol are consistent, which is significantly lower than that of the NNK. Although H value contribution degree of NNK is consistent with three harmful components of croton aldehyde, HCN and CO, it occupies greater proportion and plays an more important contributing role. Classifying other four harmful ingredients according to the similar variation as another group is a reasonable division[34].

3.3 Linear relationship among H value contributions of Benz [a] Pyrene, ammonia and phenol

In order to test the analysis above of H value contribution of Benz [a] Pyrene, ammonia and phenol, the linear relation and fitting degree were verified by Origin8.0 software, which can be seen in Fig. 3.

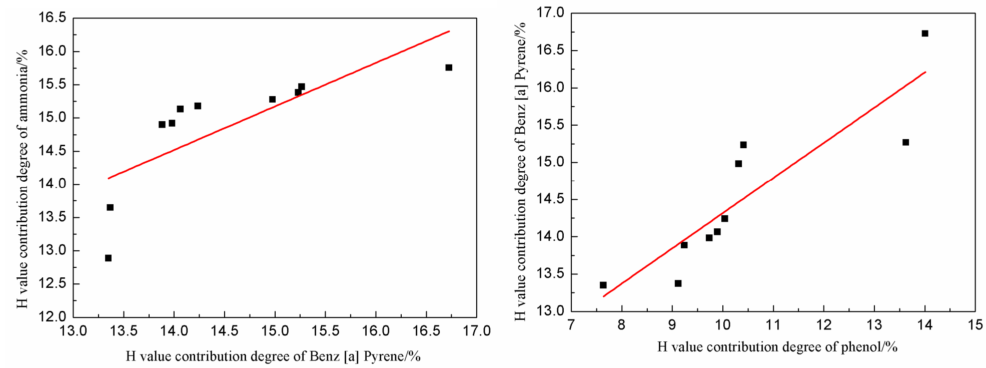

Fig. 3 Relationship among H value contributions of Benz [a] Pyrene, ammonia and phenol

Linear relationship exists among H value contribution degree of Benz [a] Pyrene, ammonia and phenol. Data points were collected from different changes in horizontal and vertical coordinates of draw resistance, equal distribution of the collecting data points could not be ensured. However, most of the data still satisfy linear distribution and fitting degree is greater than 0.65, which also proves that linear relationship among Benz [a] Pyrene, ammonia and phenol H value contribution exists, as discussed in Section 3.2. Meanwhile authors also analyzed the linearity between H value contribution degrees of these three types of harmful components and contribution degree of another group of HCN CO, NNK and crotonaldehyde, and the analysis showed that the method of classifying Benz [a] Pyrene, ammonia and phenol according to the variation of H value contribution degree from another group is sound, and H value contribution is effective and feasible when used as a tool to analyze different harmful smoke components.

4 Conclusions

1. The concept of H value contribution degree was defined, which reflects the contribution of the main harmful smoke components to the H value, which is also an effective tool to measure and calculate the variation of the harmful smoke components.

2. 1000Pa can be regarded as the critical draw resistance of phenola, and draw resistance is an important standard definition of corresponding smoke and its H value variation. When the draw resistance is less than the critical draw resistance, fluctuation of three types of harmful components and its H value is greater, while the draw resistance is more than the critical draw resistance, the fluctuation tends to be gentle.

3. Variation trend of relative H value contribution of three harmful smoke components is consistent, and there is a linear relationship. Analysis on H value contribution of the harmful smoke is a feasible method to study smoke variation, which also provides a theoretical basis for the changes of the harmful components for further study of H value.

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