



## Effect of Draw Resistance on Phenol and Its Contribution Degree of Cigarette Hazard Index

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### Authors' contributions

This work was carried out in collaboration between all authors. Authors WH, ZJ and YZ designed the study, wrote the protocol and wrote the first draft of the manuscript. Authors YY, CL, YJ, YB, ZY, LM, JY, HD, CS and WL managed the literature searches, analyses of the study results and authors FR, ZN, PD, YT, XJ, ZH, ZJ, WT, DW, GW, GY and DH managed the experimental process and authors LL, LT, LX and YJ identified the species of materials. All authors read and approved the final manuscript.

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## ABSTRACT

Effect of cigarette draw resistance between 860-1130Pa on deliveries of phenol 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 phenol with different draw resistance on contribution degree of cigarette hazard index was also studied. The results showed that contribution degree of phenol 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:** Phenol; cigarette; critical draw resistance; mainstream cigarette smoke; harmful components; cigarette hazard index.

## 1. INTRODUCTION

With the developing research and study on reducing cigarette tar and harmful components in China tobacco industry in recent years, smoke analysis on the harmful components in cigarettes has been one of the significant research directions of tobacco research. Hoffmann components (CO, NNK, ammonia, HCN, Benz [a] Pyrene, croton aldehyde and phenol) were applied by China's tobacco industry as an important design and processing standard of the target products [1]. Xie Jianping proposed a characterization method of cigarette harm, applying 7 types of harmful ingredients including CO, NNK, ammonia, HCN, Benz [a] Pyrene, croton aldehyde and phenol. This method is scientific and feasible, which has been widely used in the design and evaluation of cigarettes [2]. Wei Yuling [3], Christophe L M [4], Zheng Qin [5], Liu Jianfu [6], Zhai Yujun et al. [7] studied the influence 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] conducted in-depth 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 influence 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 et al. [22] studied the effects of different pumping conditions on harmful gas emissions, and Qiu Ye et al. [23] studied the main harmful substances emission and hazard assessment during domestic and broad papermaking process. Peng

Bin [24] presented 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 et al. [26] made research 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. Through the study of different draw resistance on mainstream cigarette smoke of phenol, in-depth study contribution degree of phenol in mainstream smoke was studied in this paper. 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

#### 2.1.1 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 (homemade equipment which the laboratory of Yanshan University and Taiyuan University of Technology participated in the design); 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].

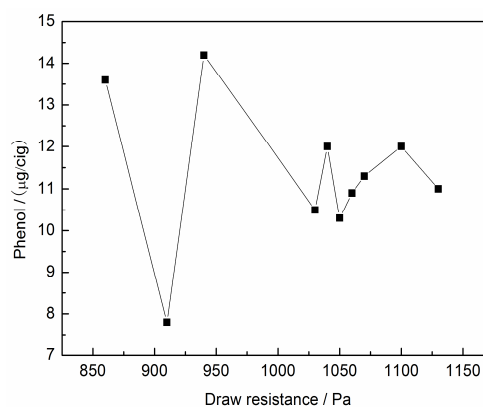
## 3. RESULTS AND DISCUSSION

### 3.1 Critical Draw Resistance and its Effects on Phenol

While the draw resistance varies, phenol changes obviously. Through analysis of draw resistance variation, the draw resistance between 860-1130Pa was selected to analyze the seven types of harmful smoke variation, and phenol was selected to analyze the effect of different draw resistance, as shown in Fig. 1.

As shown in Fig. 1, when the draw resistance is less than 1000Pa, the phenol has obvious

fluctuating value between 7.8-14.2 mg/cig, as the draw resistance continues to rise to above 1000Pa, the phenol variation tends to be stable and maintained between the 10.3-12.0 mg/cig.



**Fig. 1. Variation of phenol with different draw resistance**

From the above discussion, draw resistance of 1000 Pa can be regarded as the critical draw resistance of three types of harmful smoke components including phenol, Benz [a] Pyrene and ammonia. It can be concluded that there is an obvious change of harmful components near the critical draw resistance, and the critical draw resistance has significant 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 applying 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].

$$H = \left( \frac{X_{CO}}{C_{CO}} + \frac{X_{HCN}}{C_{HCN}} + \frac{X_{NNK}}{C_{NNK}} + \frac{X_{ammonia}}{C_{ammonia}} + \frac{X_{B[\alpha]P}}{C_{B[\alpha]P}} + \frac{X_{crotonaldehyde}}{C_{crotonaldehyde}} + \frac{X_{phenol}}{C_{phenol}} \right) \times \frac{10}{7} \quad (1)$$

Where H is the hazard value index, H value.  $X_{CO}$ ,  $X_{HCN}$ ,  $X_{NNK}$ ,  $X_{NH_3}$ ,  $X_{B[\alpha]P}$ ,  $X_{crotonaldehyde}$  and  $X_{phenol}$  are the harmful components emission quality respectively,  $C_{CO}$ ,  $C_{HCN}$ ,  $C_{NNK}$ ,  $C_{ammonia}$ ,  $C_{B[\alpha]P}$ ,  $C_{crotonaldehyde}$  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,

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

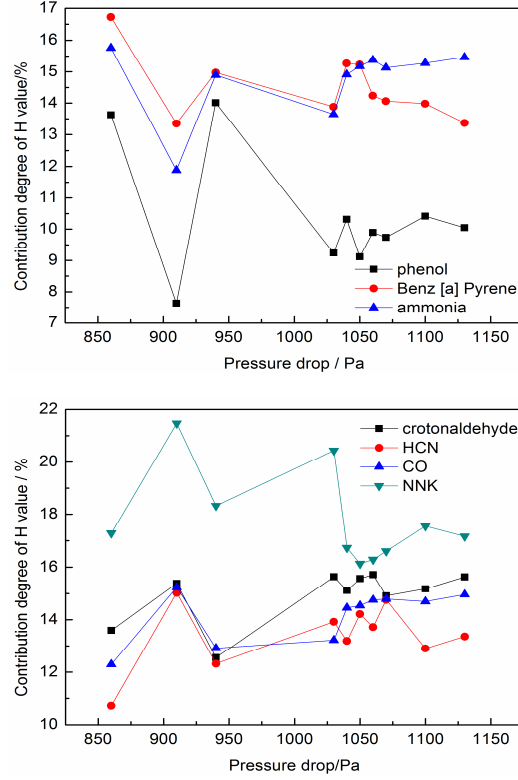
where  $\gamma_i$  is the H value contribution degree of harmful component type  $i$ .

$$\gamma_{phenol} = \frac{X_{phenol}}{H \cdot C_{phenol}} \times \frac{10}{7} \times 100\% \quad (3)$$

where  $\gamma_{phenol}$  is the H value contribution degree of phenol.

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 phenol, Benz [a] Pyrene and ammonia 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.



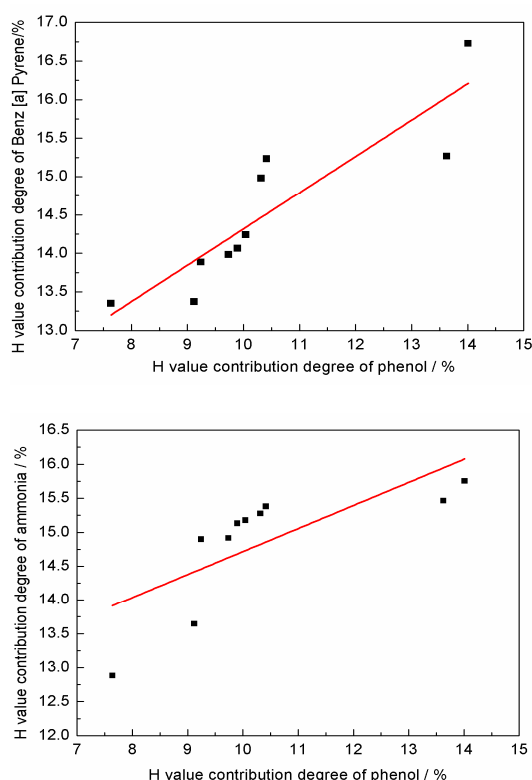
**Fig. 2. Variation of H value contribution of 7 types of harmful flue gas components under different pressure drops**

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 phenol, Benz [a] Pyrene and ammonia 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 phenol maintained at 9.1% - 10.4%. At the same time, in contrast to H value contribution degrees of the other four harmful ingredients of crotonaldehyde, HCN and CO, NNK, it can be found that H value contribution degrees of phenol, Benz [a] Pyrene and ammonia are in the same varying trend. Although H value contribution degree of NNK is in the same changing trend as three harmful components of croton aldehyde, HCN and CO, it occupies greater proportion and plays a more important contributing role. Classifying other four

harmful ingredients according to the similar variation as another group is a reasonable division, and the experiment results show that distinction of different harmful smoke components has theoretical and practical significance in the H value contribution theory and calculation.

### 3.3 Linear Relationship among H Value Contributions of Three Types of Harmful Smoke Components

In order to verify the similar change among H value contribution of phenol, Benz [a] Pyrene and ammonia, the linear relation and fitting degree of the three kinds of harmful gases were verified by Origin 8.0 software, which are as shown in Fig. 3.



**Fig. 3. Relationship among H value contributions of three types of harmful smoke components**

As can be seen from Fig. 3, there is a basic linear relationship among H value contribution degree of phenol, Benz [a] Pyrene and ammonia. As the data collection points are collected from different suction changes in horizontal and vertical coordinates of varying draw resistance,

equal distribution of the collecting data points could not be ensured. However, it can still be found that except for the individual data points, most of the data satisfy linear distribution and linearity were greater than 0.65, which proves that there is linear relationship among three types of harmful ingredients' H value contribution, and such linearity also proves that the three kinds of harmful components in the phenol, Benz [a] Pyrene and ammonia has the similar affecting trend of H value, 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 crotonaldehyde, HCN and CO, NNK, and the analysis showed that the method of classifying phenol, Benz [a] Pyrene and ammonia according to the similar variation of H value contribution degree from another group is reasonable, and H value contribution is feasible and effective when applying as a method for distinguishing and analyzing 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 phenol, 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.

### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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