Preliminary Studies on Evaluation and Change Trends of Dominant Components in New Types of Tobacco Sheets by Thick Pulp Process

Hao SHU[1,2,3], Xiangbing TANG[1,2,3]*, Ziwei WANG[1,2,3], Xinge ZHANG[4], Wanxia WANG[1,2,3], Dan LI[1,2,3], Qunshan YAN[1,2,3], Tongfu SU[5], Yanqiu JING[4], Song GAO[1,2,3]*, Bin XIONG[1,2,3]

1. China Tobacco Hubei Industrial Co., Ltd., Wuhan 430040, China; 2. Hubei Xinye Reconstituted Tobacco Development Co., Ltd., Wuhan 430212, China; 3. Applied Technology Research of Reconstituted Tobacco Hubei Province Key Laboratory, Wuhan 430040, China; 4. College of Tobacco, Henan Agricultural University, Zhengzhou 450002, China; 5. College of Science, Henan Agricultural University, Zhengzhou 450002, China

Abstract [**Objectives**] This study was conducted to deeply understand the effects of production process on the quality of new types of tobacco sheets with different flavors. [**Methods**] Based on the pilot production process of thick pulp method, four different flavors of tobacco sheets were sampled at several links in the production process, for the detection of the contents of the main components in the samples, including propylene glycol, glycerol, menthol and glyceryl triacetate, so as to explore the change trends of various components in the thick pulp process. [**Results**] The change laws of propylene glycol and glycerol contents had a very high similarity, showing a trend of first decreasing and increasing then. The changes of menthol content and glyceryl triacetate content were greatly affected by the specific flavor formula. As one of the indexes of the new tobacco evaluation system, the alcohol-to-ester ratio data need to be further improved in the actual production and application process. [**Conclusions**] This study provides basic data support for improving the quality of tobacco sheets.

Key words New tobacco product; Thick pulp process; Heat-not-burn tobacco product; Tobacco sheets; Changing trend

In recent years, as countries around the world continue to increase their efforts to control smoking in public places, and the market share of traditional tobacco products is decreasing. Major tobacco companies around the world have gradually shifted their research direction to the field of new tobacco products[1], rapidly seizing more market shares, and the development trend is very rapid[2-4]. New types of tobacco products generally include four categories: heat-not-burn tobacco products, electronic cigarettes, snus and other categories[2]. Compared with traditional cigarette products, there are fewer kinds of main harmful components in the heat-not-burn tobacco products, and the release amount is also significantly reduced[5]. Meanwhile, due to no combustion, the heating temperature is below 500 ℃, generally about 350 ℃, and there is almost no sidestream smoke during the suction gap[6]. There have been many reports on the research of heat-not-burn tobacco products. The research team of Ma Pengfei *et al.* carried out a more detailed study on the physical and chemical properties and thermal cracking characteristics of tobacco raw materials and heat-not-burn tobacco sheets[7], and proved the thermal cracking behavior of cellulose, lignin and other substances in tobacco sheets. Li *et al.*[8] have made a full study on the effects of water on the chemical composition of different types of heat-not-burn tobacco sheets. The results showed that water not only affected the stability of tobacco sheet structure, but also affected the amount of moisture released from the smoke, the amount of glycerol released from the smoke, the amount of nicotine released from the smoke, and the weight of particulate matter in the smoke.

Many scholars at abroad have also made corresponding research and reports on the safety of heat-not-burn tobacco products. Romain *et al.*[9] studied the toxicity of aerosol components of new tobacco products on human bronchial epithelial cells. Gavriella *et al.*[10] conducted a detailed and in-depth study on the impact of new tobacco products on oxidative stress. Wojciech Baran *et al.*[11] studied the effects of heat-not-burn tobacco waste on microbial organisms, while Cintia *et al.*[12] studied the toxic mechanism of heat-not-burn tobacco on rheumatoid arthritis. These studies focus on the toxicology of heat-not-burn tobacco products to organisms, while there are also many reports on toxicology of new tobacco products[13-15]. Meanwhile, many scholars have made many researches on aerosol detection of new tobacco products and development of smoke systems[16-17]. These studies provide reliable and detailed data for improving the safety of heat-not-burn tobacco products, and provide guidance for reducing the harm of related products to human health.

Although heat-not-burn cigarettes have been studied and discussed in many aspects, it is still in the initial stage. As the basic raw material for heat-not-burn tobacco products, tobacco sheets can achieve different tastes by adding different essence and spices. However, the thick pulp method for preparing special tobacco sheets for heat-not-burn cigarettes has many advantages, such as large capacity of atomizer, good physical properties, *etc.*, and it is the new focus of research in the field of heat-not-burn cigarettes at present. However, the research on the effects of thick pulp production process on the quality of heat-not-burn cigarettes is rarely reported. On the basis of the thick pulp tobacco sheet

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Hao SHU (1991 -), male, P. R. China, master, devoted to research about reconstituted tobacco and new type of tobacco.
* Corresponding author. E-mail: tangxb@hbtobacco.cn; gaosong@hjl.hbtobacco.cn.

production technology on a pilot production scale, this study detected the main components in the production process of four different flavors: grape flavor, mint flavor, green tea flavor and pineapple flavor, including the content changes of propylene glycol, glycerol, menthol and glyceryl triacetate. Through the detection of four chemical components in the whole process from raw materials to finished products, the effects of the process on the changes of dominant chemical components in different flavors were found out, aiming to improve the quality and safety and meet the market demand.

Materials and Methods

Materials, reagents and instruments

Production line: Pilot production line of Hubei Xinye Reconstituted Tobacco Development Co., Ltd., 10 000 t/year.

Formula: Hubei Xinye Reconstituted Tobacco Development Co., Ltd. provided the formula and conducted pilot production.

Products: Four samples of grape flavor, mint flavor, green tea flavor and pineapple flavor.

Reagents: 1,2-Propanediol, glycerol, 1,3-butanediol, n-butanol, menthol, glyceryl triacetate (analytically pure, Sinopharm Chemical Reagent Co., Ltd.); isopropanol (chromatographically pure, Thermo Fisher Scientific Co., Ltd.).

Instrument: 7890B gas chromatograph (Agilent Technology Co., Ltd.); HY-5A digital cyclotron oscillator (Changzhou Jintan Liangyou Instrument Co., Ltd.); electronic balance ME104/02 (Mettler Toledo International Co., Ltd.).

Sampling link: The common tobacco powder raw material of tobacco sheets with different flavors were taken and recorded as samples at A. Materials collected at the link where the thick pulp was poured were record as samples at B. Sampling was performed at the outlet of the pre-drying process to obtain samples at C. Also, samples at D were obtained by sampling at the outlet of the late drying process. The finished products were sampled and recorded as samples at E. After sampling, the samples were sealed in vacuum bags and kept away from light, and submitted for inspection.

Detection methods

Referring to QB/HBZY. ZJ301.4, the main components in the samples were detected by gas chromatography. The main ingredients of different flavors in this study included propylene glycol, glycerol, menthol and glyceryl triacetate.

Gas chromatographic conditions: Elastic quartz capillary column DB-1701 (30 m × 0.32 mm × 1.0 μm); carrier gas: high-purity helium; injection port temperature 260 ℃; split ratio 10∶1; column flow 1.5 ml/min; temperature programme: the initial temperature of 80 ℃, which was maintained for 2.5 min, and increased at 40 ℃/min to 250 ℃, which was maintained for 3 min.

Sensory evaluation method

The method for sensory evaluation referred to China Tobacco Yunnan Industrial Co., Ltd. enterprise standard "Sensory Evaluation Method for New Types of Cigarettes" (Q/YNZY. J04.022-2015) in reference[18]. The sensory quality evaluation was completed by College of Tobacco, Henan Agricultural University.

Results and Analysis

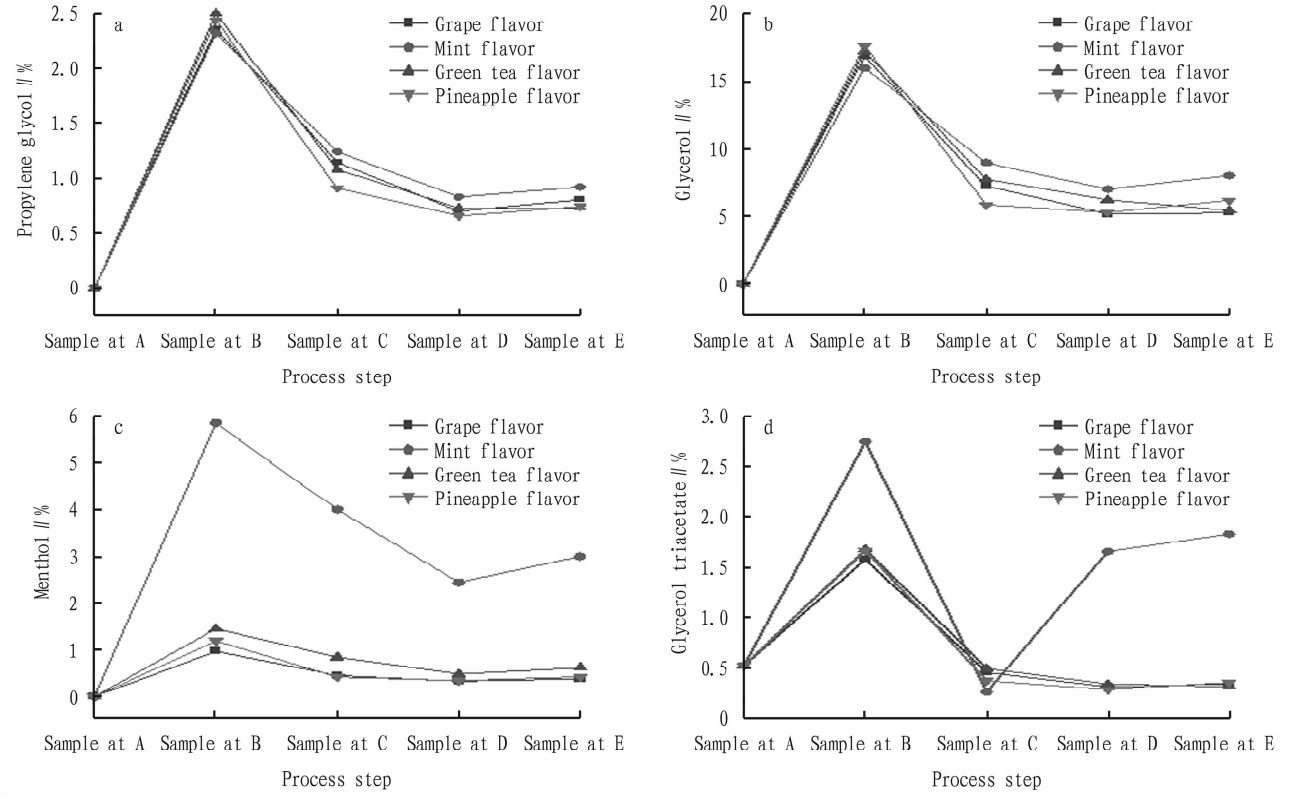
Change laws of dominant components in samples with four different flavors

In this study, four different products, grape flavor, mint flavor, green tea flavor and pineapple flavor, were sampled at different process nodes, and the samples were detected by gas chromatography. The measured chemical component contents were all relative contents on the basis of dry weights of samples. The specific test results are shown in Table 1 below.

Table 1 Detection results of main chemical components of each sample %

Flavor	Component	Sample at A	Sample at B	Sample at C	Sample at D	Sample at E
Grape flavor	Propylene glycol	0.00	2.35	1.15	0.70	0.80
	Glycerol	0.00	16.89	7.25	5.17	5.26
	Menthol	0.00	0.97	0.45	0.33	0.38
	Glyceryl triacetate	0.53	1.58	0.46	0.32	0.35
Mint flavor	Propylene glycol	0.00	2.32	1.24	0.83	0.92
	Glycerol	0.00	16.02	9.01	7.00	8.05
	Menthol	0.00	5.86	4.00	2.45	3.01
	Glyceryl triacetate	0.53	2.75	0.27	1.66	1.83
Green tea flavor	Propylene glycol	0.00	2.49	1.08	0.73	0.73
	Glycerol	0.00	17.26	7.76	6.21	5.44
	Menthol	0.00	1.44	0.84	0.48	0.62
	Glyceryl triacetate	0.53	1.68	0.50	0.35	0.32
Pineapple flavor	Propylene glycol	0.00	2.44	0.91	0.66	0.74
	Glycerol	0.00	17.69	5.85	5.29	6.18
	Menthol	0.00	1.19	0.42	0.34	0.42
	Glyceryl triacetate	0.53	1.67	0.38	0.29	0.36

Table 1 shows that low content of glyceryl triacetate was detected in the raw material of cigarette powder, but no components such as propylene glycol, glycerol and menthol were detected. The subsequent process needs to continue to add essence and flavor to meet the requirements for different flavors and quality and make up for the lack of raw material tobacco powder in quality. Due to different types of essences and spices added at different contents to products of different flavors, the loss of different main ingredients in products of different flavors was different in the process of thick pulp process, and the change laws were also different. The change trends of the leading ingredients in products with different flavors are shown in Fig. 1.



a. Changing trends of propylene glycol; b. Changing trends of glycerol; c. Changing trends of menthol; d. Changing trends of glycerol triacetate.

Fig. 1 Changing trends of main components of four types of samples

Fig. 1 shows the change trends of the main components in the four different flavors of tobacco sheets in the process. Fig. 1 (a) and Fig. 1 (b) show the content changes of propylene glycol and glycerol in tobacco sheets of different flavors in the thick pulp process. In the products with different flavors, the change trends of propylene glycol and glycerol were very similar. After the pulp entered the drying stage, the contents gradually decreased, while the contents of both components slightly increased after approaching the finished products. It might be that in the late drying stage, the contents of these two components were both at a low level, and they could be better combined with the physical structure of the sheets and were not easy to lose.

Fig. 1 (c) shows the effects of thick pulp process on menthol content in tobacco sheets. It could be seen that, in order to meet the demand of mint flavor, the content of menthol in tobacco sheets with mint flavor was significantly higher than those of samples with other three flavors, but its change trend was generally similar to those of propylene glycol and glycerol, that is, decreasing first and then increasing at the last stage. Fig. 1 (d) shows the change trend of glyceryl triacetate in the process. It could be seen that the content of glyceryl triacetate gradually decreased with the progress of the drying stage in the process, but after the sample at C, the content in the product with mint flavor increased sharply, much higher than those in other samples. The reason might be that glyceryl triacetate interacted with the components in tobacco sheets to form stable substances, and the drier the sheets were, the less likely they were to be lost.

Preliminary study on the evaluation of products with four different flavors

For tobacco sheets with different flavors, sensory evaluation was conducted referring to the Yunnan Chinese Tobacco Enterprise Standard " Sensory Evaluation Method for Novel Cigarettes " (Q/YNZY. J04. 022-2015) in the literature[18]. The tobacco sheets with different flavors were preliminarily evaluated, and the evaluation results are shown in Table 2.

It could be seen from the evaluation results in Table 2 that the amount of smoke of the mint flavor was sufficient, and the strength was appropriate. Meanwhile, the aroma was full, but slightly irritating. These characteristics were closely related to the contents of propylene glycol and glycerol serving as smoking agent and humectant in the cut tobacco with mint flavor. The cause of irritation might be related to the high content of menthol and/or

glyceryl triacetate, and it might be caused by one or both of them. Tobacco sheets with other three different flavors were lack of smoke, strength and coordination. Increasing the content of glyceryl triacetate may help to improve the sensory quality of cigarettes.

Table 2 Results of smoke panel test

Sample name	Smoke amount	Aroma	Strength	Coordination	Irritation
Grape flavor	Relatively sufficient smoke	Full and delicate	Relatively appropriate	Relatively coordinated	No irritation
Mint flavor	Relatively sufficient smoke	Full and delicate	Slightly weak	Relatively coordinated	No irritation
Green tea flavor	Relatively sufficient smoke	Full and delicate	Relatively appropriate	Coordinated	No irritation
Pineapple flavor	Sufficient smoke	Full and relatively delicate	Appropriate	Coordinated	Slightly irritative

Alcohol-to-ester ratio in sensory evaluation of tobacco sheets with different flavors

The main components affecting tobacco sheets generally include propylene glycol, glycerol, menthol and glyceryl triacetate. As an important component of tobacco sheets, the content of glyceryl triacetate in tobacco powder samples is about 0.5%. To improve product quality, a certain amount of glyceryl triacetate should be added to the liquid material, and the content should be reduced to about 0.5% after drying. In practical application, we believe that glyceryl triacetate is one of the important leading components that affect the sensory quality of tobacco sheets. Therefore, the concept of "alcohol-to-ester ratio" was proposed and used as one of the important indicators for chemical quality evaluation of tobacco sheets. The "alcohol" here is propylene glycol and glycerol, and the "ester" is glyceryl triacetate. The so-called "alcohol-to-ester ratio" based on the original content of glyceryl triacetate of 0.5% refer to the ratios of the contents of propylene glycol and glycerol in the finished product to this value, which are called, respectively, diol-to-ester ratio and triol-to-ester ratio, both of which are called alcohol-to-ester ratio (represented by "R-OH/RCOO-R"). In this study, the alcohol-to-ester ratios of tobacco sheets with different flavors are shown in Table 3.

Table 3 Ratios of R-OH/RCOO-R of sheets with different flavors

No.	Name	Alcohol-to-ester ratio	
		Diol-to-ester ratio	Triol-to-ester
1	Grape flavor	1.60	10.52
2	Mint flavor	1.84	16.10
3	Green tea flavor	1.46	10.88
4	Pineapple flavor	1.48	12.36

Propylene glycol and glycerol in tobacco sheets are commonly used as the humectant and smoking agent. It is appropriate to control diol-to-ester ratio and triol-to-ester ratio at 1.5 – 2.0 and 10.0 – 20.0, respectively, and control the content of glyceryl triacetate in tobacco sheets at more than 0.5% and that of tobacco sheets with some special flavors at more than 1%.

Discussion and Conclusions

Discussion

Among the four components, propylene glycol, glycerol, menthol and glyceryl triacetate, propylene glycol and glycerol, as the humectant and smoke agent in tobacco sheets, have a large content, and play an important role in the strength and comfort of heat-not-burn cigarettes[19], which is mainly reflected in the infiltration of smoke on the mouth and throat, which can alleviate the drying of oral mucosa to a certain extent and improve coordination. Menthol is an important tobacco flavor, which can produce a cool feeling in the process of smoking. Glycerol triacetate is an important aroma component, which is used as a fixative in essence and flavor because of its role in delaying flavor volatilization. Within the range of glyceryl triacetate content in the samples analyzed in this study, it might be closely related to the strength, aroma, coordination and irritation of cigarettes. The specific impact results need to be further studied.

The contents of propylene glycol and glycerol in the main components of tobacco sheets increased first and then decreased, and the component contents in various sampling links during the production of tobacco sheets with four different flavors were basically the same. In this study, it was considered that it is better to control the content of glyceryl triacetate above 0.5%, and the alcohol-to-ester ratios, including diol-to-ester ratio and triol-to-ester ratio, should be controlled at 1.5 – 2.0 and 10.0 – 20.0 respectively. For the sheets with special flavors, the basic content of glyceryl triacetate can be appropriately increased, which needs to be comprehensively evaluated in combination with the results of smoke panel tests.

Conclusions

To sum up, the main components of tobacco sheets of different flavors obtained by the thick pulp method, including propylene glycol, glycerol, menthol and glyceryl triacetate, were lost to varying degrees in the process, and the contents tended to be stable in the finished product stage. Meanwhile, it was also found that the changes of menthol content and glyceryl triacetate content in mint flavor series samples showed an upward trend, which was different from those of other components that gradually decreased. It was believed in this study that the alcohol-to-ester ratio can be used as one of the important indicators for chemical quality evaluation of new tobacco sheets. In the quality control of products, glyceryl triacetate should be taken as an important leading component, the content of which should generally be more than 0.5%, and can be controlled at more than 1% in high-quality tobacco sheets, and the diol-to-ester ratio and triol-to-ester ratio of different products should be controlled at 1.5 – 3.0 and 10.0 – 20.0 respectively. How to use the alcohol-to-ester ratio better in tobacco sheet evaluation system needs further research and discussion.

References

[1] LIU YL, WANG JB, ZHENG XZ, *et al.* Current status and prospect of heat-not-burn tobacco products [J]. Acta Tabacaria Sinica, 2018, 24(4): 91 – 106. (in Chinese).

(Continued on page 133)

Chinese Medicine, 2012, 13(2): 147 – 148. (in Chinese).
[34] LIU FW. Cisapride plus Chenxiang Huaqi Pill in the treatment of constipative irritable bowel syndrome[J]. Zhejiang Journal of Integrated Traditional Chinese and Western Medicine, 2005, 15(3): 166 – 167. (in Chinese).
[35] TANG LQ. Analysis of 80 cases of senile functional constipation treated with Maren Soft Capsule and Chenxiang Huaqi Capsule[J]. Chinese Journal of Traditional Medical Science and Technology, 2012, 19(5): 460 – 461. (in Chinese).
[36] ZHANG H, MA JL, ZAN NL, *et al.* Study on sesquiterpenoids from *Aquilaria sinensis*[J]. China Journal of Chinese Materia Medica, 2022, 47(16): 4385 – 4390. (in Chinese).
[37] LIANG YQ, LIU JM, WEI G, *et al.* GC-MS analysis of the volatile oil from the medicinal material agarwood[J]. Lishizhen Medicine and Materia Medica Research, 2006, 17(12): 2518. (in Chinese).
[38] TIAN YZ, MI XY, PIAO XL. Studies on chemical constituents, pharmaceutical effects and clinical application of *Aquilaria sinensis*[J]. Journal of Minzu University of China: Natural Science Edition, 2010, 19(1): 77 – 81. (in Chinese).
[39] ZHOU FQ, TIAN SY, PAN JL, *et al.* Contrastive study on the pharmacological action of alcohol extract *Caulis cinnamomi* camphorae and *Lignum aquilariae* sinensis[J]. Acta Chinese Medicine, 2013, 28(12): 1849 – 1850, 1859. (in Chinese).
[40] RYAN CA. Protease inhibitors in plants: Genes for improving defenses against insectsand pathogens[J]. Annu Rev Phytopathol, 1990, 28(2): 425 – 449.
[41] JONES DG, DANGL JL. The plant immune system[J]. Nature, 2006, 444(17): 323 – 329.
[42] PENPUN WETWITAYAKLUNG, NAPAPORN THAVANAPONG, JUREE CHAROENTEERABOON. Chemical constituents and antimicrobial activity of essential oil and extracts of heartwood of *Aquilaria crassna* obtained from water distillation and supercritical fluid carbon dioxide extraction[J]. Silpakorn U Sci&Tech J, 2009, 3(1): 25 – 33.
[43] WEN LM, YAN BZ, JIAO W, *et al.* Chemical composition and anti-MRSA activity of the essential oil from Chinese agarwood[J]. Journal of Chinese Pharmaceutical Science, 2008, 34(17): 225 – 229.
[44] LEI ZD. Study on the antimicrobial activity constituents of the *Aquilaria sinensis*[D]. Guangzhou: Guangdong Pharmaceutical University, 2015. (in Chinese).

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(Continued from page 129)

[2] CHEN CY. Change and challenge: Outlook for development of new tobacco products[J]. Acta Tabacaria Sinica, 2017, 23(3): 14 – 18. (in Chinese).
[3] KANG D, ZHAO H, LIU YS, *et al.* The development and prospect of novel tobacco products[J]. Science and Technology & Innovation, 2020(6): 87 – 89. (in Chinese).
[4] GONG SG, LIU W, HUANG P, *et al.* Puff-by-puff release of main aerosol components from two commercial heat-not-burn tobacco products[J]. Tobacco Science & Technology, 2019, 52(2): 62 – 71. (in Chinese).
[5] PAN X, SONG XY, WEI M, *et al.* Study on physicochemical properties and pyrolysis properties of heated non combustion tobacco sheet[J]. Food & Machinery, 2020, 36(11): 39 – 45. (in Chinese).
[6] HS, WANG WW, ZHANG L, *et al.* Study on pyrolysis behavior of different tobacco materials[J]. Guangzhou Chemical Industry, 2019, 47(9): 76 – 81, 103. (in Chinese).
[7] MA PF, LI QL, LIN K, *et al.* Study on pyrolysis characteristic of the heat-not-burn reconstituted tobacco[J]. Food & Machinery, 2018, 34(4): 71 – 74. (in Chinese).
[8] LI CJ, JIN Y, ZHOU CX, *et al.* The effect of moisture content on chemical components of different types of heat-not-burn tobacco products[J]. Food & Machinery, 2019, 35(10): 35 – 39, 149. (in Chinese).
[9] ROMAIN D, GIANNI Z, MARIE V, *et al.* Comparison of the chemical composition of aerosols from heated tobacco products, electronic cigarettes and tobacco cigarettes and their toxic impacts on the human bronchial epithelial BEAS-2B cells[J]. Journal of Hazardous Materials, 2021: 401.
[10] KOSTELLI G, KOUREA K, IKONOMIDIS I. Effects of combustible tobacco smoking and novel tobacco products on oxidative stress: Different sides of the same coin? [J]. Current Opinion in Toxicology, 2020: 20 – 21. (prepublish).
[11] WOJCIECH B, DARIA M-K, ANDRZEJ S, *et al.* The influence of waste from electronic cigarettes, conventional cigarettes and heat-not-burn tobacco products on microorganisms[J]. Journal of Hazardous Materials, 2020, 385(C).
[12] HELUANY CS, SCHARF P, SCHNEIDER AH, *et al.* Toxic mechanisms of cigarette smoke and heat-not-burn tobacco vapor inhalation on rheumatoid arthritis[J]. The Science of the total environment, 2021: 809.
[13] SCHARF P, DA ROCHA GUSTAVO HO, SANDRI SILVANA, *et al.* Immunotoxic mechanisms of cigarette smoke and heat-not-burn tobacco vapor on Jurkat T cell functions[J]. Environmental Pollution, 2021: 268(PB).
[14] HORINOUCHI T, MIWA S. Comparison of cytotoxicity of cigarette smoke extract derived from heat-not-burn and combustion cigarettes in human vascular endothelial cells[J]. Journal of Pharmacological Sciences, 2021: 147(3).
[15] WANG LY, LIU XY, CHEN LS, *et al.* Harmful chemicals of heat not burn product and its induced oxidative stress of macrophages at air-liquid interface: Comparison with ultra-light cigarette[J]. Toxicology Letters, 2020: 331(C).
[16] KIM YONG-HYUN, AN YOUNG-JI. Development of a standardized new cigarette smoke generating (SNCSG) system for the assessment of chemicals in the smoke of new cigarette types (heat-not-burn (HNB) tobacco and electronic cigarettes (E-Cigs)[J]. Environmental Research, 2020: 185 (prepublish).
[17] ANNETTE D, THOMAS CB, ANYA T, *et al.* Development of a novel method to measure material surface staining by cigarette, e-cigarette or tobacco heating product aerosols[J]. Heliyon, 2020: 6(9).
[18] DAI L, SHI CY, LU XB, *et al.* Difference analysis on physical characteristics and chemical components of reconstituted tobacco used in traditional cigarettes and heat not burn tobacco products[J]. Acta Tabacaria Sinica, 2017: 23(1): 20 – 26. (in Chinese).
[19] TANG PP, ZENG ST, LU S, *et al.* Effects of glycerol on thermal property and smoke release of tobacco leaves under heating[J]. Tobacco Science & Technology, 2015, 48(3): 61 – 65. (in Chinese).

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