Effects of Glycerol and Propylene Glycol on Smoke Release of Heat-not-burn Tobacco Products

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Abstract. Glycerin and propylene glycol are the main components of the atomizing agent in heat-not-burn tobacco products (HnB), which affect the smoke release of HnB significantly. In this study, the roles of the glycerin and propylene glycol as the atomizing agent on smoke release of HnB were studied by using a fixed-bed reactor system. The effects of glycerin to propylene glycol ratio in the atomizing agent, and the content of atomizing agent in the HnB were investigated. Gas chromatography-mass spectrometer (GC-MS) was used to analyze the condensable components in the released smoke, and gas chromatography (GC) was used to analyze the gaseous products. The results showed that glycerol could promote the thermal cracking of tobacco and smoke release during pyrolysis. The amount of smoke was the largest when the glycerol ratio was 60%, meanwhile the nicotine content in the smoke was also the highest. When using the glycerin and propylene glycol mixture as the atomizing agent, the amount of smoke and concentration of nicotine and CO in the smoke were increased when the content of atomizing agent decreased in the HnB. The results indicated that the interactions between glycerin and propylene glycol, and the interactions between the atomizing agent and the tobacco were both existed during smoking, which could change the characteristics of the atomizing agent and the smoke release property of HnB.

Keywords: Heat-not-burn tobacco; pyrolysis; Atomizing agent; Glycerin; Propylene glycol; Smoke.

1. Introduction
In heat-not-burn tobacco products (HnB), the atomizing agent must be used to promote the smoke release to achieve the similar smoking feelings as the traditional tobaccos. Glycerin and propylene glycol are the main components of the atomizing agent [1, 2]. In tobacco industry, glycerin and
propylene glycol can effectively maintain the moisture of tobacco leaves, increase the softness of the tobacco leaves, and play an important role in atomizing and carrying the smoke released from the thermal cracking of tobacco [3-6]. At present, the researches on the effects of glycerol and propylene glycol on the smoke release of HnB were mainly focused on the toxicological analysis [7, 8], moisturizing performance analysis [3, 9, 10], sensory quality [11-13] and nicotine release [1]. However, the effects of glycerol and propylene glycol on the property of atomizing agent and smoke release characteristics of HnB are not clear yet. On the other hand, the content of the atomizing agent in the tobacco stick also has obvious effects on the smoking feelings [5]. For example, if the atomizing agent content is too high, the concentrations of nicotine and aroma substances in the smoke will be certainly diluted; if the atomizing agent content is too low, the atomizing capacity is insufficient, which will reduce the smoking released. However, the effects of the amount of atomizing agent on smoke release has also not been reported in the literature.

Therefore, this study aims to clarify the effects of glycerin and propylene glycol ratio on smoke release characteristics of HnB, and further explore the effects of atomizing agent loading on the smoke release characteristics. This study can provide a theoretical basis to develop the efficient atomizing agent and high-quality HnB.

2. Materials and methods

2.1. Materials

The original tobacco powder was provided by the Hubei Xinye Reconstituted Tobacco Development Co., Ltd, with the size of 80-120 mesh. The glycerin (HPLC), propylene glycol (HPLC), carboxymethylcellulose (CP), sodium alginate (98%), methanol (HPLC) and dichloromethane (HPLC) were used as received.

2.2. Preparation of tobacco samples

To investigate the glycerol to propylene glycol ratio in the atomizing agent, six atomizing agents with the glycerol to propylene glycol mass ratio of 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, 0:100 were used to prepare raw materials for HnB. The mass ratio of atomizing agent to original tobacco powder was 1:3, as shown in Table 1.

To investigate the atomizing agent content in the tobacco stick on smoke release property, three atomizing agents with the glycerol to propylene glycol mass ratio of 100:0, 70:30 and 0:100 were used. The atomizing agent to original tobacco powder mass ratio of these 3 samples were 1:3, 1:4 and 1:6, as shown in Table 1.

| Atomizing agent to original tobacco powder mass ratio | Glycerol to propylene glycol mass ratio |
|-----------------------------------------------------|---------------------------------------|
|                                                     | 100:0 90:10 80:20 70:30 60:40 50:50 0:100 |
| 1:3                                                 | √      √      √      √      √      √      √      |
| 1:4                                                 | √      √      √      √      √      √      √      |
| 1:6                                                 | √      √      √      √      √      √      √      |

Tobacco powder, atomizing agent, carboxymethylcellulose, and sodium alginate are mixed uniformly at a specific ratio, and then placed in a sealed state for 48 h, and then further equilibrated for 48 h in an environment of 22°C and 60% relative humidity to obtain the raw materials of HnB stick.

2.3. Thermogravimetric analysis (TGA) of tobacco samples

TGA was used to study the thermal release property of tobacco samples. The experimental conditions were as follow: N2 atmosphere with a flow rate of 100 mL/min; heating from room temperature to 330°C (330°C was the typical heating temperature for HnB stick) at the heating rate of 10°C/min, then maintaining for 20 min.
2.4. Pyrolysis experiments of the tobacco samples
The tobacco samples were pyrolyzed in a fixed-bed reactor system (Figure 1). To simulate the actual smoking of HnB, the reactor was designed as a quartz tube with small diameter (10 mm), and the samples were placed in a quartz boat in the central of the quartz tube. The outlet section of the reactor was connected with a condenser (dry ice cooling), a Cambridge filter was also used to collected the smoke. The outlet of the system was connected with a small suction pump.

The experimental procedure of pyrolysis was as follows: the quartz tube was placed in the center of the furnace, and the horizontal tube furnace temperature was set to 330°C. Pyrolysis experiments were performed in a nitrogen atmosphere with a gas flow rate of 100 ml/min (close the actual smoking flow rate). After the temperature was stabilized, a small quartz boat containing 1.5 ± 0.1 g of tobacco sample was quickly pushed into the center of the reactor. After 3 min of pyrolysis, the quartz boat was pushed out and cooled in a nitrogen atmosphere. The experiment of each sample was repeated 10 times to increase the amount of product collected and therefore minimize errors.

Figure 1 Pyrolysis system for the tobacco powder samples (1. Air inlet 2. Flow meter 3. Reaction tube 4. Heating furnace 5. Quartz boat 6. U-shaped condenser tube 7. Dry ice 8. Flange 9. Cambridge filter 10. Air bag)

2.5. Analysis of condensable constituents in smoke
Gas Chromatography-Mass Spectrometer (GC-MS, ThermoFisher, Trace1300/ISQ) was used to characterize the condensable components in smoke [14, 15], the quantification methods of the products were YC/T243-2008 and YC/T246-2008. The capillary column of GC-MS was HP- INNOWax (30 m × 0.25 mm × 0.25 μm). Before the test, the liquid product was diluted with methanol/dichloromethane mixed solution, and the sample solution was filtered by a 0.45 μm filter. 1 μL of sample (concentrated to 1 wt%) was injected into the injection port in a splitless configuration. The column was operated in a constant flow mode using helium as the carrier gas (1 μL/min, purity > 99.99%). The temperature of the injection port was set at 250°C. The column was initially maintained at 40°C for 3 min before it was increased to 250°C at a heating rate of 5°C/min, and thereafter held for 10 min.

2.6. Composition analysis of incondensable gases in smoke
Gas Chromatography (GC, ThermoFisher, Trace1300) was used to analyze the composition of incondensable gases in smoke. High purity argon was used as carrier gas and TCD detector was used. The samples were separated by molecular sieve and two chromatographic columns (HP-PLOT U) with the column pressure of 206.8 kPa and the column temperature of 70°C [16].

3. Results and discussion

3.1. Effects of glycerol to propylene glycol ratio on smoke release

3.1.1. Thermoanomeric analysis. Figure 2 shows the TG and DTG curves of tobacco samples prepared with different atomizing agents. It can be seen that the thermal release of all tobacco samples
includes three stages [4, 17, 18]. The first stage is the evaporation of water in the tobacco. When the atomizing agent is 100% glycerol, the starting temperature of water evaporation is the lowest, which is around 95°C; when the glycerol to propylene glycol ratio is 7:3, the starting temperature of water evaporation is the highest, which is around 103°C. The second stage is mainly the release of atomizing agent, which is also the largest weight loss peak of the tobacco samples, indicating that the main components released during smoking are the atomizing agent. Since the boiling point of propylene glycol is lower than that of glycerin, the release temperature of atomizing agent is the lowest when the atomizing agent is 100% propylene glycol, which is about 159°C. However, release temperature the atomizing agent is not the highest when the atomizing agent is 100% glycerol, and the temperature of maximum weight loss peak is the highest when the glycerol to propylene glycol ratio is 9:1, which is about 243°C. It is worth noting that the weight loss peak is the largest when the atomizing agent is 100% glycerol, indicating that the release rate is the fastest when the atomizing agent is 100% glycerol. The third stage is the thermal decomposition of tobacco at around 330°C. Therefore, in the actual smoking process, the release temperature of atomizing agent should be matched with the thermal decomposition temperature of tobacco (above 300°C) to maximize the atomizing and carrying capacity of atomizing agent.

Figure 2. TG and DTG Figures of the tobacco samples with atomizing agents of different glycerol and propylene glycol ratios
Figure 3. Ss of the residues in TG of the tobacco samples with atomizing agents of different glycerol and propylene glycol ratios

Figure 3 shows the mass of residuals of the tobacco samples after pyrolysis in TG. As shown in Figure 3, as the proportion of glycerol in the atomizing agent increases, the residual mass of residuals in the TG decreases generally. When the proportion of glycerol in the atomizing agent is higher than 90 wt%, the mass of residuals decreases by about 3 wt% compared with that of the sample using pure propylene glycol as atomizing agent. The results show that glycerol can promote the thermal decomposition of tobacco and smoke release better than propylene glycol.

3.1.2. Effects of glycerol to propylene glycol ratio on the yields of pyrolysis products

Figure 4. Product yields of the tobacco samples with atomizing agents of different glycerol and propylene glycol ratios

The yields of solid, liquid and main gases products obtained from the pyrolysis of tobacco samples are shown in Figure 4. Clearly, the higher solid residues yield indicate that the less components of the tobacco sample can be converted into smoke. The liquid products are the condensable components in the smoke, which have significant influences on the actual smoking feelings. When the glycerol ratio in the atomizing agent is 50~100%, the yield of residual solids generally decreases with the increase of glycerol ratio, which is consistent with the results of TG, indicating that the increase of glycerol content in atomizing agent could promote the pyrolysis and smoke release from tobacco. As known
that the atomizing agent would not generate solid residues during its pyrolysis, it can be therefore concluded that the atomizing agent and tobacco samples are not physically mixed, instead there are interactions between them during pyrolysis, which can change the pyrolysis and smoke release behaviors of HnB.

For the sample with the atomizing agents of 100% propylene glycol and 100% glycerol, the liquid product yields are relatively higher, and the solid product yields are relatively lower. For the sample with the atomizing agents of glycerol and propylene glycol mixture, the solid product yields are increased and the liquid product yields are decreased. The results show that there is no linear correlation between the pyrolysis products yields and the proportion of glycerol (or propylene glycol) in atomizing agent, that is, there are interactions between glycerol and propylene glycol during pyrolysis, which change in the properties of the atomizing agent of glycerol and propylene glycol mixture, thus changing the smoke release characteristics of tobacco samples. The results in Figure 4 further indicate that the interactions inhibit release of smoke from the tobacco samples during pyrolysis, resulting in the increase in the solid product yields and the decrease in liquid product yields. The inhibition effects due to the interactions are minimal when the glycerol to propylene glycol ratio in the atomizing agent is 6:4.

For the sample with atomizing agent of 100% propylene glycol, its solid product yield is higher than that of the sample with atomizing agent of 50% glycerol and 50% propylene glycol, which is different from the TG results. The main difference between the pyrolysis reaction system and TG system is the heating rate, this result indicates that the heating rate can significantly affect the pyrolysis of tobacco and the smoke release, resulted in the changes in the atomization effect of atomizing agent.

According to the GC data, the main components of the pyrolysis gas are CO2 and CO. The change of glycerol to propylene glycol ratio in atomizing agent can affect the content of CO. Therefore, it is necessary to simultaneously control the content of harmful CO components in the smoke while increasing the amount of smoke released.

3.1.3. Effects of glycerol to propylene glycol ratio on the release of key components in smoke

![Figure 5. Content of the key components in the smoke of the tobacco samples with atomizing agents of different glycerol and propylene glycol ratios](image)

According to the GC-MS results of the condensable components in smoke, propylene glycol, glycerol and nicotine are the main components in smoke. Among these compounds, propylene glycol and glycerin are the main components of the atomizing agent, nicotine is the key component in the
smoke and its release characteristics significantly affect the smoking feelings. As shown in Figure 5, though the content of atomizing agent in the tobacco samples are the same, but the content of atomizing agent released into the smoke is significantly different. The results show that the atomizing agents with different glycerol to propylene glycol ratios have different release characteristics [4]. For the atomizing agent with glycerol to propylene glycol ratio of 6:4, the atomizing agent content in the released smoke is the highest. For the atomizing agent with glycerol to propylene glycol ratio of 8:2, the atomizing agent content in the released smoke is the lowest. Moreover, the release of atomizing agent is correlated with the nicotine content in the smoke, indicating that the more atomizing agent released in the smoke, the more the nicotine can be carried by atomizing agent. Meanwhile, Figure 4 shows that the liquid products yield and the nicotine content in the smoke are the highest when the glycerol to propylene glycol ratio is 6:4, indicating that the atomization effect of this atomizing agent is the best, which is beneficial to the improvement of the smoking feelings of HnB.

3.2. Effect of atomizing agent content on thermal release characteristics of tobacco samples
In order to investigate the influence of atomizing agent content in tobacco sticks on smoke release, this section compares and analyzes the influence of atomizing agent content on smoke release by reducing the atomizing agent content in tobacco sticks. Six samples were prepared, as shown in Table 1.

3.2.1. Thermogravimetric analysis
Figure 6. TG and DTG of the tobacco samples with different atomizing agents used

Firstly, TGA was used to study the thermal release characteristics of the tobacco samples. The experimental results are shown in Figure 6 and Table 2. When the content of atomizing agent in the sample decreases, the char yield from the pyrolysis of tobacco samples in TG still decreases with the increase of glycerol ratio in the atomizing agent. In addition, when the content of atomizing agent in the sample decreases, the char yield also increases gradually. This is because the pyrolytic char is
generated from the tobacco sample, so the lower the amount of atomizing agent used, the more residual tar left.

Table 2. ss of the residues of the tobacco samples in TG with different atomizing agents used

| Atomizing agent content | Atomizing agent to tobacco mass ratio | Char yield (wt %) |
|------------------------|--------------------------------------|------------------|
| 100% propylene glycol  | 1:3                                  | 36.52            |
|                        | 1:4                                  | 35.04            |
|                        | 1:6                                  | 43.13            |
|                        | 1:3                                  | 34.28            |
| 70% Glycerol to propylene glycol 7:3 | 1:4                                  | 36.00            |
|                        | 1:6                                  | 38.47            |
|                        | 1:3                                  | 33.56            |
| 100% glycerol         | 1:4                                  | 37.04            |
|                        | 1:6                                  | 38.20            |

3.2.2. Effect of atomizing agent content on pyrolysis products yields of tobacco samples

The product yields of tobacco samples with different atomizing agent content are shown in Figure 7. It can be seen in Figure 7 that when the atomizing agent is pure propylene glycol, the liquid product yield decreases gradually with the decrease of atomizing agent content in the tobacco samples. When the atomizing agent is pure glycerol or 70% glycerol propylene, the liquid product yield is the highest when the atomizing agent to tobacco sample ratio is 1:4. The results show that when the glycerol is used in the atomizing agent, appropriately reducing the atomizing agent content can promote the release of smoke.

In addition, when the atomizing agent content in tobacco samples is reduced, the content of CO in the smoke is higher. CO is generated via the cracking of oxygen-containing functional groups such as carbonyl in tobacco during pyrolysis [19]. When the atomizing agent content decreases, the proportion of tobacco increases in the tobacco sticks, so the content of CO in the smoke will therefore increase. Thus, the content of CO in the smoke should be within the standard range when increasing the content of smoke release by reducing the atomizing agent content.
3.2.3. The effects of atomizing agent content on the release of key components in smoke

![Figure 8 Content of the key components in the smoke of the tobacco samples with different atomizing agents](image)

The key components in the smoke (condensable components) produced by pyrolysis of the tobacco samples are detected by GC-MS, the contents of glycerol, propylene glycol and nicotine are shown in Figure 8. The results show that the nicotine concentration in the smoke could be increased by reducing the atomizing agent content in the sample. This is because that as the atomizing agent content decreases, the proportion of tobacco in the tobacco sticks increases and therefore the nicotine concentration in the released smoke increases.

4. Conclusion

In this paper, the effects of the glycerol to propylene glycol ratio in atomizing agent and the content of atomizing agent in the tobacco samples on the smoke release characteristics were studied. The results showed that increasing the proportion of glycerol in atomizing agent could promote the pyrolysis of tobacco samples and increase the amount of smoke released. The amount of smoke released was non-linear related to the glycerol ratio in the atomizing agent. The smoke and the nicotine content in smoke were the highest when the glycerol ratio in atomizing agent was 60%. When the main component of the atomizing agent was glycerol, appropriately reducing the atomizing agent to the tobacco ratio was conducive to release of smoke, and the concentration of nicotine and CO in the smoke were also increased. The interactions between the glycerin and propylene glycol in the atomizing agent existed, as well as the interactions between atomizing agent and tobacco. The interactions changed the property of both atomizing agent and tobacco sticks.

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