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Effects of Ethyl Acetate, Phytic Acid, and Grape Seed Extract on the Aging of Tobacco Pyrolysis Oil

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Abstract. The tobacco pyrolysis oil derived from the pyrolysis of tobacco waste can effectively enhance the flavor of cigarettes while also providing a safe means of waste disposal. However, the composition of the resulting tobacco pyrolysis oil is complex and prone to aging and degradation. To address this, the present study introduced varying proportions of ethyl acetate, phytic acid, and grape seed extract, under controlled temperature and humidity conditions, to effectively inhibit the aging of tobacco pyrolysis oil. The study found that adding ethyl acetate in concentrations ranging from 1% to 10% effectively stabilized the small molecular compounds in tobacco pyrolysis oil. Compared to the tobacco pyrolysis oil samples after three weeks of aging, the reduction in aldehydes and ketones in the oil with 5% ethyl acetate added is only 4.8% after the same period. Phytic acid, when added in concentrations ranging from 1% to 10%, effectively stabilized the aromatic compounds in tobacco pyrolysis oil. Adding a high concentration of grape seed extract (10%) primarily inhibited the decrease in acid compounds in tobacco pyrolysis oil. In summary, this study proposed a reaction mechanism of the three additives for anti-aging based on the interaction between small molecular compounds and aromatic substances in tobacco pyrolysis oil.

Keywords: Aging, Tobacco pyrolysis oil, Ethyl acetate, Phytic acid, Grape seed extract

1 Introduction

Tobacco is widely cultivated around the world, with the majority of both domestic and international production being used for cigarette manufacturing. However, approximately 25% of tobacco leaves, tobacco dust, and other by-products are classified as tobacco waste and cannot be utilized in cigarette production [1]. Tobacco waste is a hazardous by-product, and its direct disposal can contribute to increased greenhouse

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gas emissions, disrupt soil ecological balance, and lead to a range of other issues, including resource waste [2]. Additionally, tobacco waste contains valuable reusable substances, such as nicotine, acids, and alcohols. Therefore, enhancing the comprehensive utilization of tobacco waste can transform it into a valuable resource, increase the economic income of tobacco farmers, and support the sustainable development of the tobacco industry.

Thermochemical processes are a widely used technology for the large-scale and efficient treatment of waste. Pyrolysis is the first step in all thermochemical conversion processes [3-4]. It is a thermal decomposition reaction that occurs when raw materials are heated in an inert atmosphere, transforming the raw materials into three products: gas, carbon, and oil [5-6]. Among them, the oil obtained by pyrolysis has a high yield, rich materials, and is easy to transport, which has attracted extensive attention from researchers. If tobacco waste can be processed on a large scale to prepare tobacco pyrolysis oil through pyrolysis technology, it can safely handle tobacco waste and further utilize tobacco pyrolysis oil as a flavor additive[7].

However, the components of the prepared tobacco pyrolysis oil are complex, including acids, aldehydes, ketones, phenols, furans, and lignin-derived polymers, which result in high water content, high oxygen content, high acid value, and large polarity differences [8]. Due to the unique physicochemical properties of tobacco pyrolysis oil, its components are susceptible to aging reactions [9-10], leading to product degradation. Over long-term storage, the oil tends to stratify and form viscous sediments that adhere to the container's bottom, resulting in a series of instability issues that hinder the large-scale, stable use of tobacco pyrolysis oil as a flavor additive [11-12].

This study investigated the effects of adding three different proportions (1%, 5%, and 10%) of ethyl acetate, phytic acid, and grape seed extract to the original tobacco pyrolysis oil. These modified oils were compared to the original tobacco pyrolysis oil and subjected to accelerated aging experiments under controlled conditions (constant temperature, humidity, and time). Gas chromatography-mass spectrometry (GC-MS) and Ultraviolet fluorescence spectrometer (UV) analysis were used to characterize the samples. The results demonstrated that the addition of these three additives effectively inhibited the aging of tobacco pyrolysis oil by hindering the interactions among small molecular compounds and aromatic substances in tobacco pyrolysis oil.

2 Materials and Methods

2.1 Experiments

Using a self-made pyrolysis oil enrichment device, tobacco samples were pyrolyzed at 360°C for 30 minutes, and the resulting tobacco pyrolysis oil was then condensed and collected. To accelerate aging, a heating method was used to age the tobacco pyrolysis oil. A specific amount of tobacco pyrolysis oil was placed in a sealed glass bottle and stored in a 50°C constant-temperature chamber for accelerated aging. The oil was stored for 6 hours, 12 hours, 24 hours, 48 hours, 72 hours, 120 hours, 1 week, 2 weeks, and 3 weeks. This group served as the blank control. The tobacco pyrolysis oil before and after aging was weighed, and the chemical composition of the aged oil was analyzed using GC-MS and UV spectroscopy. In the control group, ethyl acetate, phytic acid, and grape seed extract were added at mass fractions of 1%, 5%, and 10%, respectively. The tobacco pyrolysis oil before and after aging was weighed, and the chemical composition of the aged oil was analyzed using GC-MS and UV spectroscopy.

2.2 Product Analysis

The samples were analyzed using a Thermo Scientific Trace 1300 series GC coupled with an ISQ QD MS detector. The capillary column used was an HP-INNOWax (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness). Prior to analysis, the sample solution was filtered through a 0.45 μm oil-based filter. A 1 μL injection volume was used for GC-MS, with an inlet temperature set to 250°C, and high-purity helium (purity > 99.99%) as the carrier gas at a flow rate of 1.0 mL/min. The split ratio was set to 1:1. The temperature program for the column was as follows: an initial hold at 40°C for 3 minutes, followed by a ramp to 250°C at 5°C/min, with a final hold for 10 minutes. The mass spectrometer source temperature was set to 230°C, and the quadrupole temperature was set to 150°C. The mass scan range was 15–500 m/z, and the mass spectral delay time was set to 6.3 minutes. The resulting spectra were compared with the National Institute of Standards and Technology (NIST) database (2014 edition) for compound identification.

For ultraviolet fluorescence spectroscopy, samples were analyzed using an Agilent Cary Eclipse fluorescence spectrometer with constant-energy synchronous fluorescence. To avoid self-absorption effects caused by high concentrations of aromatic compounds, the tobacco essence was diluted to 4 ppm with methanol. At this concentration, the fluorescence intensity was directly proportional to the concentration of aromatic components in the solution. Each sample was scanned twice, and the average value was used as the final result. The fluorescence intensity of the tobacco pyrolysis oil samples was calibrated by multiplying it by the mass concentration of the tobacco essence, which enabled semi-quantitative analysis of the aromatic content in the tobacco pyrolysis oil. In the constant-energy difference (-2800 cm^{-1}) ultraviolet fluorescence spectrum, the fluorescence wavelengths of the tobacco essence spectrum reflect the size of the aromatic rings. Specifically, wavelengths < 290 nm correspond to single-ring aromatic compounds, wavelengths between 290-320 nm correspond to compounds with two benzene rings, and wavelengths > 320 nm indicate compounds with three or more fused rings.

3 Results and Discussion

3.1 Effects of aging Times on Aging Characteristics of Tobacco Pyrolysis Oil

Figure 1 shows the content of aromatic components in tobacco pyrolysis oil after three weeks of aging, along with changes in the levels of small molecular substances detected by coupled GC-MS. The figure shows that under accelerated aging conditions at 50°C, all components in the tobacco pyrolysis oil exhibited a decreasing trend after three weeks of storage. Compared to the non-aged tobacco pyrolysis oil, the reduction rates of various substances in the tobacco pyrolysis oil aged for three weeks are as follows: acids 28.96%, alcohols 34.67%, esters 64.07%, aldehydes and ketones 35.34%, pyridines 30.17%, phenols 62.76%, and aromatics 92.60%, respectively. The largest decrease was observed in aromatic compounds, while the smallest decrease was seen in acids. The results showed that under accelerated aging conditions, the original tobacco pyrolysis oil underwent a significant reduction in the content of various small molecular components as the aging time increased, indicating the onset of noticeable aging characteristics in the tobacco pyrolysis oil.

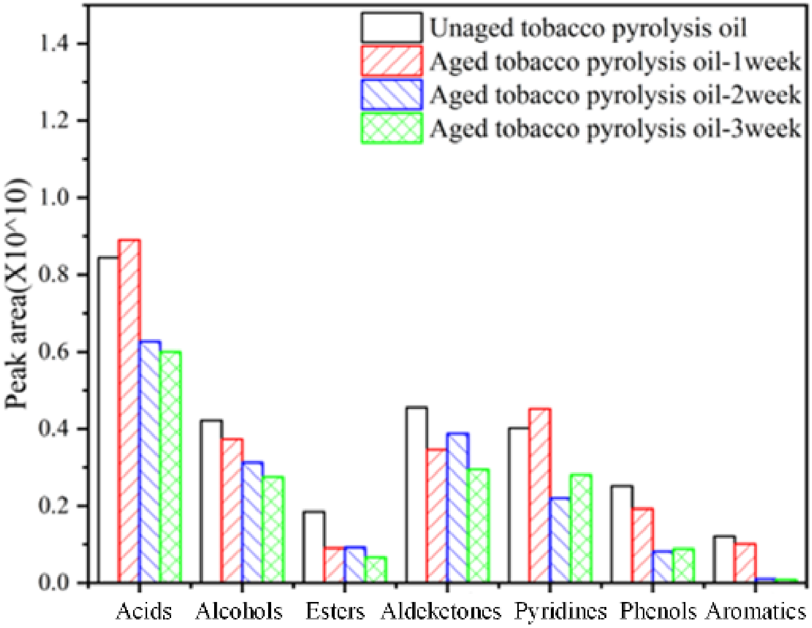

Fig. 1. The peak areas of the compounds in tobacco pyrolysis oil detected by GC-MS at different aging times.

Figure 2 shows the content of aromatic components in tobacco pyrolysis oil at different aging times. The results indicated that the aromatic components remained relatively stable during the first week of aging. However, after one week, the aromatic components in the tobacco pyrolysis oil began to decrease progressively as aging time increased. After two weeks of aging, the content of bi-cyclic compounds was significantly reduced. Combined analysis of GC-MS and UV data revealed a significant reduction in both the detectable light and aromatic components of the tobacco pyrolysis oil during the accelerated aging process. This suggested that interactions among the components in tobacco pyrolysis oil resulted in the formation of polymers with higher molecular weights.

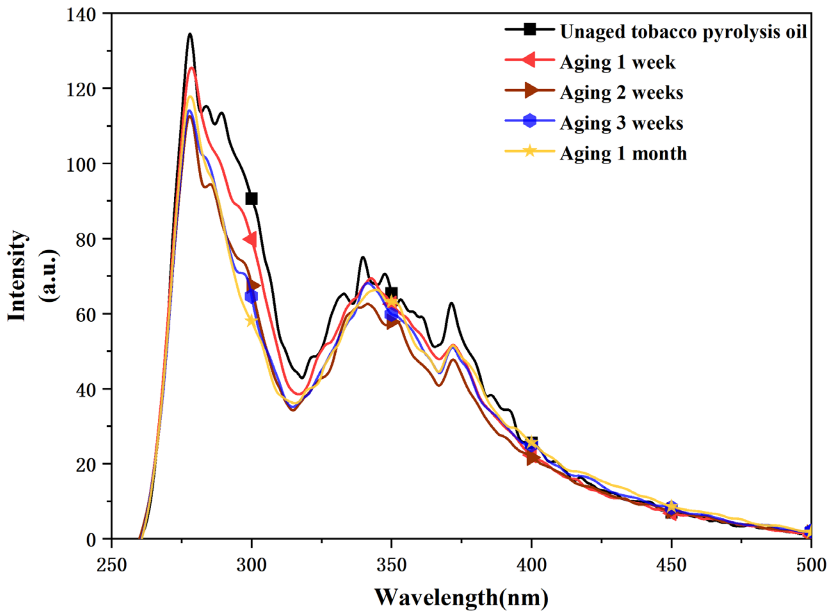

Fig. 2. Content of aromatic components in tobacco pyrolysis oil by UV at different aging times.

3.2 Effects of Different Additives on Aging Characteristics of Tobacco Pyrolysis Oil

Figure 3 illustrates the main components and their contents in tobacco pyrolysis oil with different additives and concentrations (1%, 5%, 10%) at various aging times. For tobacco pyrolysis oil with ethyl acetate added at concentrations of 1% to 10%, the reduction rates of key components were as follows: aldehydes and ketones 4.8% esters 14.4%, and pyridines 14.6%. Compared to non-aged tobacco pyrolysis oil, these substances showed a smaller decrease in content, indicating that ethyl acetate effectively stabilized aldehydes and ketones, esters, and pyridines in the tobacco pyrolysis oil, thereby exhibiting antioxidant effects. When phytic acid was added at a concentration of 5%, the reduction rates of key components in tobacco pyrolysis oil aged for three weeks were as follows: aldehydes and ketones 23.9%, acids 16.4%, and pyridines 34.1%, all showing a smaller decrease in content. However, the addition of 1% and 10% phytic acid to tobacco pyrolysis oil did not exhibit significant anti-aging effects. In contrast, when grape seed extract was added at a concentration of 10%, the reduction rates of key components in tobacco pyrolysis oil aged for three weeks were as follows: acids 18.1%, alcohols 26.8%, and aldehydes and ketones 15.7%. These reductions indicated significant anti-aging effects compared to the 1% and 5% concentrations.

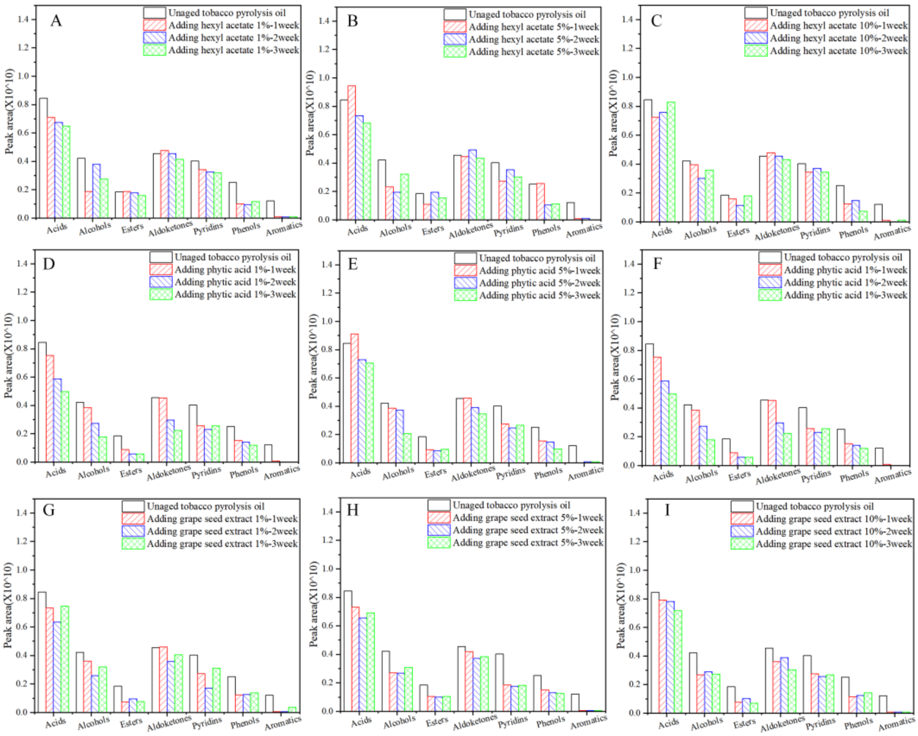

Fig. 3. The peak areas of the compounds in tobacco pyrolysis oil were detected by GC-MS at different aging times with 1%, 5%, and 10% concentrations of additives of hexyl acetate, phytic acid, and grape seed extract.

In summary, during the aging process, ethyl acetate, at a wide range of concentrations, could effectively stabilize esters, aldehydes, ketones, and pyridines in tobacco pyrolysis oil. The addition of high concentrations of phytic acid (≥5%) effectively stabilized aldehydes and ketones, acids, and alcohols, ,while the addition of high concentrations of grape seed extract (10%) primarily inhibited the decrease of acid components in the tobacco pyrolysis oil.

Figure 4 shows the impact of different additives and concentrations (1%, 5%, 10%) on the aromatic compounds in tobacco pyrolysis oil at various aging times. When 1% ethyl acetate was added, the content of bi-cyclic compounds was lower compared to the original tobacco pyrolysis oil aged for two weeks, suggesting that a low concentration of ethyl acetate was insufficient to effectively stabilize the aromatic compounds in the oil. However, when phytic acid was used as an additive at a medium concentration (5%), there was no significant change in the aromatic components of tobacco pyrolysis oil after two weeks of aging, regardless of whether the addition ratio was low (1%) or high (10%). This suggested that phytic acid, as an anti-aging agent, exhibited excellent inhibitory effects on the polymerization of aromatic components in tobacco pyrolysis oil within a relatively wide range of addition concentrations. The results regarded the impact of grape seed extract addition ratios on aromatic compounds in tobacco pyrolysis oil showed that at low (1%) and medium (5%) addition ratios, the aromatic components of the oil underwent more significant changes compared to the other two additives after two weeks of aging. However, at a high addition ratio (10%), the content of aromatic components in tobacco pyrolysis oil decreased to some extent, but the reduction was still less than that observed in the original tobacco pyrolysis oil. This result suggested that although grape seed extract exhibits excellent anti-aging properties, its inhibitory effect on the polymerization of aromatic components in tobacco pyrolysis oil decreased as the concentration increased, eventually failing to prevent the polymerization of aromatic substances. In summary, ethyl acetate at medium and high concentrations (≥5%) could inhibit the polymerization of aromatic substances in tobacco pyrolysis oil. Phytic acid was effective at inhibiting the polymerization of aromatic substances across a relatively wide range of concentrations (1%-10%). However, grape seed extract did not effectively inhibit the polymerization of aromatic substances in tobacco pyrolysis oil.

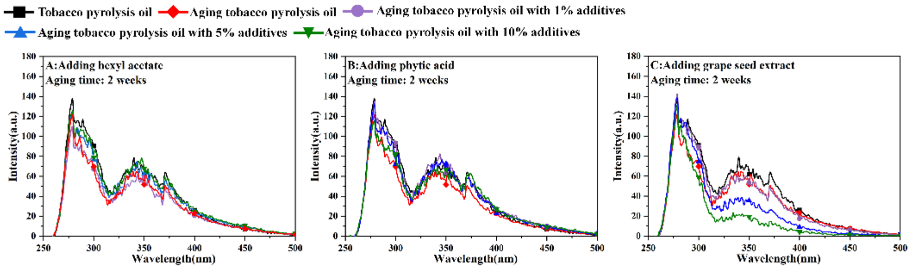

Fig. 4. Constant energy (-2800 cm-1) synchronous spectra of the tobacco pyrolysis oil with 1%, 5%, and 10% concentration additives after aging 2 weeks (a)Adding hexyl acetate, (b)Adding phytic acid, (c)Adding grape seed extract.

3.3 Mechanism of Additives on the Aging of Tobacco Pyrolysis Oil

Figure 5 illustrates the mechanism behind the evolution of the aging process in tobacco pyrolysis oil, based on the interactions between its components. Tobacco pyrolysis oil could be primarily classified into small molecular compounds and aromatic components based on molecular size and functional groups. Due to the complexity of its components, tobacco pyrolysis oil exhibited physical and chemical characteristics such as high water content, high oxygen content, and a high acid value. Therefore, the small molecular and aromatic components in tobacco pyrolysis oil were prone to interactions, leading to aging reactions that generate large molecular polycyclic polymers. This results in the formation of insoluble solids and caused the pyrolysis oil to deteriorate. The results showed that ethyl acetate stabilized small molecular substances such as aldehydes, ketones, esters, and pyridines, while phytic acid stabilized compounds like aldehydes, ketones, acids, and alcohols. Grape seed extract primarily stabilized acid compounds. These additives effectively stabilized the functional group activity of small molecular substances or aromatic components, inhibiting interactions between components and thus achieving anti-aging effects.

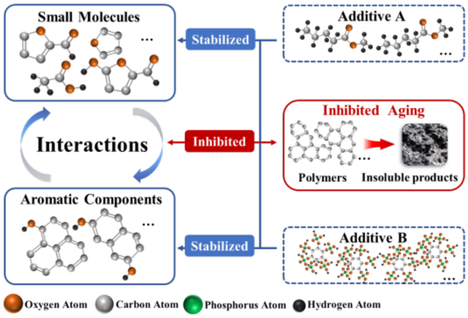

Fig. 5. The mechanism of additives inhibiting the aging of tobacco pyrolysis oil.

4 Conclusions

To investigate the impact of additives on the aging of tobacco pyrolysis oil, accelerated aging experiments were conducted under controlled temperature and humidity conditions on both the original tobacco pyrolysis oil and samples with varying proportions of ethyl acetate, phytic acid, and grape seed extract. The results of the accelerated aging experiments on the original tobacco pyrolysis oil indicated that, as aging time increased, there was a significant reduction in the content of various small molecular components, and the oil began to exhibit distinct aging characteristics. Furthermore, as the aging progresses, interactions between the aromatic components and other small molecular compounds promote polymerization reactions, contributing to the aging process.

The results of experiments with different concentrations of additives showed that the addition of ethyl acetate at various concentrations effectively inhibited the decrease in aldehydes and ketones, esters, and pyridines in tobacco pyrolysis oil. High concentrations of phytic acid (≥5%) effectively prevented the reduction of aldehydes and ketones, acids, and alcohols, while high concentrations of grape seed extract (10%) mainly inhibited the decrease of acid components in the tobacco pyrolysis oil. Further analysis of the changes in specific components revealed that high concentrations of ethyl acetate (≥5%) could inhibit the polymerization of aromatic substances in tobacco pyrolysis oil, whereas phytic acid could suppress polymerization across a wide range of concentrations (1%-10%). However, grape seed extract did not inhibit the polymerization of aromatic substances in the tobacco pyrolysis oil.

The findings of this study demonstrated that additives could effectively inhibit the interactions between small molecular substances and aromatic compounds by stabilizing them, thereby achieving anti-aging effects in tobacco pyrolysis oil. This research provided a theoretical foundation for regulating the stability of tobacco pyrolysis oil and for developing advanced, stable, and modular technologies for its utilization.

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