Analysis of Pyrolysis Characteristics and Kinetics of Cigar Tobacco and Flue-Cured Tobacco by TG-FTIR *

by

Anran Wang¹, Bin Cai², Lili Fu³, Miao Liang⁴, Xiangdong Shi¹, Bing Wang³, Nan Deng³, and Bin Li³

¹ National Research Base of Tobacco Cultivation Physiology and Biochemistry, Henan Agricultural University, No. 63 Nongye Road, Zhengzhou Jinshui District, Henan, 450002, China

² Haikou Cigar Research Institute of China National Tobacco Corporation Hainan Branch, No. 120 Hongchenghu Road, Haikou City, Hainan, 571100, China

³ Zhengzhou Tobacco Research Institute of CNTC, No. 2 Fengyang Street, Zhengzhou High-Tech Development District, Henan, 450001, China

⁴ School of Food and Biological Engineering, Zhengzhou University of Light Industry, Henan, 450002, China

SUMMARY

Investigation of the detailed pyrolysis characteristics of tobacco raw materials is important for the understanding of product design and consumption. In this work, pyrolysis characteristics and kinetic models of cigar filler tobacco (CFT), cigar wrapper tobacco (CWT), and flue-cured tobacco (FCT) were investigated by using a thermogravimetric analyzer coupled with Fourier-transform infrared spectroscopy (TG-FTIR). The pyrolysis of different tobacco samples could be divided into four stages based on the derivative thermogravimetric analysis (DTG) curves. Flue-cured tobacco underwent a marked decomposition process at lower temperatures (about 200 °C), while the thermal decomposition of cigar tobacco occurs at higher temperatures. During the pyrolysis process, evolved gases including H₂O, CO₂, CH₄, CO, carbonyls, alcohols, phenols and aromatic compounds were detected by FTIR. CWT released more CO₂ than CFT, while the amount of CO₂, CH₄, CO and aromatic compounds released by flue-cured tobacco was lower than that of cigar tobacco. The pyrolysis kinetics of tobacco leaves were further analyzed and compared through the isoconversional FWO (Flynn-Wall-Ozawa) and KAS (Kissinger-Akahira-Sunose) methods. The activation energy of FCT (from 100.1 kJ mol⁻¹ to 192.1 kJ mol⁻¹) was lower than that of CFT (from

207.36 kJ mol⁻¹ to 319.28 kJ mol⁻¹) and CWT (from 160.40 kJ mol⁻¹ to 260.45 kJ mol⁻¹). The thermal decomposition kinetics of different tobaccos were analyzed by MÁLEK and COATS-REDFERN methods. [Contrib. Tob. Nicotine Res. 30 (2021) 29–43]

KEYWORDS

Cigar tobacco; flue-cured tobacco; pyrolysis; kinetics; TG-FTIR

ZUSAMMENFASSUNG

Die Untersuchung der genauen Pyrolyseeigenschaften von Tabakrohstoffen ist für das Verständnis der Gestaltung und des Konsums von Tabakprodukten von Bedeutung. In der vorliegenden Arbeit wurden die Pyrolyseeigenschaften und kinetischen Modelle von Zigarreneinlagetabak, Zigarrendeckblatttabak und heißluftgetrocknetem Tabak mithilfe eines thermogravimetrischen Analysators gekoppelt mit einem Fourier-Transformations-Infrarotspektrometer (TGA-FTIR) untersucht. Auf der Grundlage der derivativen thermogravimetrischen Kurven (DTG-Kurven) kann die Pyrolyse der verschiedenen Tabakproben in vier Phasen

eingeteilt werden. Heißluftgetrockneter Tabak durchläuft bei niedrigeren Temperaturen (ca. 200 °C) einen ausgeprägten Zersetzungsprozess, während die thermische Zersetzung von Zigarrentabak bei höheren Temperaturen stattfindet. Die während des Pyrolyseprozesses entstehenden Gase wie H₂O, CO₂, CH₄, CO, Carbonyle, Alkohole, Phenole und aromatische Verbindungen wurden mittels FTIR nachgewiesen. Bei der Pyrolyse von Zigarrendeckblatttabak wurde mehr CO₂ freigesetzt als bei Zigarreneinlage-tabak, während die freigesetzte Menge an CO₂, CH₄, CO sowie aromatischen Verbindungen bei heißluftgetrocknetem Tabak niedriger war als bei Zigarrentabak. Die Pyrolysekinetik von Tabakblättern wurde näher analysiert und mithilfe der isokonversionellen Methoden von Flynn-Wall-Ozawa (FWO) und Kissinger-Akahira-Sunose (KAS) verglichen. Die Aktivierungsenergie bei heißluftgetrocknetem Tabak (von 100,1 kJ mol⁻¹ bis 192,1 kJ mol⁻¹) war niedriger als die bei Zigarreneinlage-tabak (von 207,36 kJ mol⁻¹ bis 319,28 kJ mol⁻¹) und Zigarrendeckblatttabak (von 160,40 kJ mol⁻¹ bis 260,45 kJ mol⁻¹). Die Kinetik der thermischen Zersetzung unterschiedlicher Tabake wurde mit den Methoden von MÁLEK sowie COATS-REDFERN analysiert. [Contrib. Tob. Nicotine Res. 30 (2021) 29–43]

RESUME

Afin de comprendre leur conception et leur consommation, il importe d'analyser les caractéristiques détaillées de la pyrolyse des matières premières qui composent les produits du tabac. Au cours des présents travaux, les caractéristiques de la pyrolyse et les modèles cinétiques du tabac contenu dans la tripe de cigare, du tabac servant à la cape du cigare et du tabac blond furent étudiés à l'aide d'un analyseur thermogravimétrique couplé à une spectroscopie infrarouge à transformée de Fourier (ATG-IRTF). La pyrolyse des divers échantillons de tabac peut être subdivisée en quatre stades selon les courbes de thermogravimétrie en dérivation (TGD). Le tabac blond subit une décomposition marquée à basses températures (soit environ 200 °C) tandis que la décomposition thermique du tabac pour cigare se produit à des températures plus élevées. Durant le processus de pyrolyse, des gaz émis tels que du H₂O, du CO₂, du CH₄, du CO, des carbonyles, des alcools, des phénols et des composés aromatiques furent détectés grâce à l'IRTF. Le tabac servant à la cape du cigare émet plus de CO₂ que le tabac de tripe tandis que les quantités de CO₂, CH₄, CO et de composés aromatiques libérées par le tabac blond furent inférieures à celles relevées pour le tabac de cigare. La cinétique de la pyrolyse des feuilles de tabac fit l'objet d'études complémentaires et d'une comparaison selon les méthodes d'analyse isoconversionnelle de KAS (Kissinger-Akahira-Sunose) et de FWO (Flynn-Wall-Ozawa). L'énergie d'activation du tabac blond (sur une plage de 100,1 kJ mol⁻¹ à 192,1 kJ mol⁻¹) s'avéra inférieure à celle du tabac de tripe (plage allant de 207,36 kJ mol⁻¹ à 319,28 kJ mol⁻¹) et du tabac de cape (plage allant de 160,40 kJ mol⁻¹ à 260,45 kJ mol⁻¹). La cinétique de la décomposition thermique des divers tabacs fut analysée selon les méthodes de MÁLEK et de COATS-REDFERN. [Contrib. Tob. Nicotine Res. 30 (2021) 29–43]

1 INTRODUCTION

In recent years, cigars have been accepted by many tobacco consumers because of their special aroma and high nicotine release characteristics. According to a statistic report (1), the global cigar market revenue was US Dollar (USD) 17 billion in 2019 and is expected to increase to USD 19 billion by 2023. Cigars are defined as tobacco rolls wrapped in either tobacco leaf or another tobacco-containing substance (2). A burning cigar can be regarded as a chemical reactor. Smoke is produced through complex chemical and physical reactions during the combustion and pyrolysis processes (3), in which the characteristics of cigar smoke can be further studied.

On the other hand, the production of cigarettes and cigars generates about 20% of tobacco waste (4). These cigar tobacco residues are an abundant biomass resource that is discarded as waste without any treatment. The inappropriate disposal of cigar tobacco residues may waste a renewable biomass resource and could cause serious environmental pollution issues (5). An alternative approach for enhancing the value of this resource is by thermochemical conversion methods. For example, these lignocellulosic bioresources can be converted into valuable products, such as bio-oil, fuel gas and solid carbon, through a pyrolysis process (6). Therefore, the pyrolysis behavior of cigar residues is of great significance for the appropriate utilization.

Many studies have focused on the pyrolysis behavior of plant materials (7–9), including tobacco residue (5) via various modern techniques. Among these analytical techniques, thermogravimetric analysis (TG) coupled to Fourier-transform infrared (FTIR) have frequently been used not only in pyrolysis kinetics studies during the thermal decomposition process but were also applied in the characterization of the evolved gas products. With the single-use of TG, CARDOSO *et al.* (10), GUO *et al.* (11) and WANG *et al.* (12) performed research on the pyrolysis kinetics of tobacco including the influence of thermal conditions, heating rate, particle size, and data processing. The thermal degradation of tobacco leaves could be divided into three stages: dehydration, main devolatilization, and continuous devolatilization (10–12). GAO *et al.* (6) showed that the pyrolysis of tobacco is a very complicated chemical reaction, which cannot be represented by a single reaction or reaction combination. VALVERDE *et al.* (13) found that the global mass loss in tobacco dust pyrolysis can be simulated by four independent parallel mass-loss events. By using TG-FTIR technology, the volatile components in the pyrolysis process of bidi tobacco were identified as H₂O, CO₂, CO, NH₃, HCN, NO, NO₂, and some organic volatile compounds (14). However, previous studies have mainly focused on the thermal decomposition of cigarette tobacco. The pyrolysis behavior of cigar tobacco, especially the release of volatiles at different temperatures, has not been fully studied.

Cigar tobacco and cigarette tobacco display different curing methods and chemical compositions, thus their pyrolysis behavior will not be the same. In this study, the pyrolysis behavior of cigar tobacco was comprehensively investigated via thermogravimetric analysis at different heating rates, with the addition of flue-cured tobacco as a contrast. The activation energy was estimated by isoconversional

FWO (FLYNN-WALL-OZAWA) and KAS (KISSINGER-AKAHIRA-SUNOSE) methods. The mechanism functions were established by MÁLEK and COATS-REDFERN methods. Moreover, the release behavior of volatile products during the pyrolysis of cigar tobacco was analyzed dynamically by TG-FTIR. The results can provide theoretical references for the design of cigar products or the processing of cigar residues.

2 MATERIALS AND METHODS

2.1 Material

Three types of tobacco middle leaves were considered in this study: cigar filler tobacco (CFT), cigar wrapper tobacco (CWT) and flue-cured tobacco (FCT). CFT and CWT were cultivated in Hainan Province, China, and collected after air-curing process. FCT was cultivated in Yunnan, China, and collected after flue-curing process. After drying at 40 °C for 5 h, the samples were ground to pass through a 40-mesh sieve and then stored in a sealed container before use. The ultimate analysis of the tobacco was conducted on an Elementar Vario EL cube CHNSO analyzer (Hanau, Germany). Proximate analysis of tobacco was conducted to determine the contents of moisture, volatile matter, fixed carbon and ash by using thermogravimetric method (15). The content of cellulose, hemicellulose and lignin in the samples was determined according to a previous work (16). The nicotine content of the samples was determined according to the methods described in ISO 10315 (17).

2.2 TG-FTIR analysis

Experiments were performed using a thermogravimetric analyzer (Discovery, TA Instrument, Newcastle, DE, USA) coupled with a FTIR spectrophotometer (Nicolet 8700, Thermo Electron, Waltham, MA, USA) through a transfer line. The mass change of the samples with temperature during the pyrolysis was recorded. Approximately 10 mg of the sample were placed in a platinum crucible. The experiments were performed from 40 °C to 900 °C at different heating rates (5 °C min⁻¹, 10 °C min⁻¹, 15 °C min⁻¹, and 20 °C min⁻¹) under nitrogen atmosphere (99.999% minimum purity) with a flow rate of 30 mL min⁻¹. The stainless-steel transfer pipe and the gas cell in the FTIR were both heated to a constant temperature of 210 °C to minimize secondary reactions. The resolution of the FTIR was set at 4 cm⁻¹, spectrum scan frequency was 8 times per minute, and the spectral region was from 600 cm⁻¹ to 4000 cm⁻¹.

The devolatilization index (D_i) is a comprehensive evaluation of volatile release and can reflect the reactivity of the whole pyrolysis process. A greater D_i value implies that it is more reactive. D_i is determined by the following equation (18–20):

$$D_i = (R_{max} \cdot R_{mean}) / (T_S \cdot T_{max} \cdot \Delta T_{1/2})$$

where R_{max} is the maximum devolatilization rate, R_{mean} the average devolatilization rate, T_S the initial volatile release temperature, T_{max} is the temperature corresponding to R_{max} ,

and $\Delta T_{1/2}$ is the temperature interval containing the maximum peak where $R/R_{max} = 1/2$. The devolatilization rate, R , is defined as $R = dw_i/dt$, where w_i is the mass percentage of the raw sample at time t . R_{max} and R can be obtained from the DTG curves.

2.3 Kinetic analysis

For the kinetic analysis, the decomposition rate can be described by the following equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad [1]$$

where α is the extent of conversion, and $\alpha = (m_0 - m_t)/(m_0 - m_\infty)$, m_0 is the initial mass of the sample, m_t is the mass at a given time t , and m_∞ is the final mass of the sample, T is the absolute temperature, $k(T)$ is the reaction rate as function of the temperature and $f(\alpha)$ is the reaction model, which is a function of α . The reaction rate constant is typically described in accordance with the Arrhenius equation, which is a function of T and expressed as:

$$k(T) = A \exp(-E_a / RT) \quad [2]$$

where A is the frequency factor, E_a is the activation energy, and R is the universal gas constant (8.3145 J mol⁻¹ K⁻¹). The heating rate β is defined as dT/dt , which is substituted in Equation [1] to obtain Equation [3]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad [3]$$

The integral form of Equation [3] is expressed as follows,

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT = \frac{AE_a}{\beta R} P(u) \quad [4]$$

where $G(\alpha)$ is the integral form of $f(\alpha)$, $P(u)$ is an approximation, and u is defined as the equation of $u = E_a/R$.

2.3.1 The FLYNN-WALL-OZAWA (FWO) method

The FWO method (21) is one of the most widely used model-free methods derived from DOYLE'S approximation (22). With Equation [4], the final form of the FWO equation is expressed as:

$$\lg(\beta) = \lg\left(\frac{AE_a}{RG(\alpha)}\right) - 2.315 - 0.457 \frac{E_a}{RT} \quad [5]$$

where β is the heating rate, and T is the temperature at conversion α . In a plot of $\lg(\beta)$ versus $1/T$ the slope is $-0.457E_a/R$, where R is the gas constant, and the activation energy E_a can thus be obtained from the slope.

2.3.2 The KISSINGER-AKAHIRA-SUNOSE (KAS) method

The KAS method (23) is also a model-free method to calculate pyrolysis kinetics, which is based on the following expression:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AE_a}{RG(\alpha)}\right] - \frac{E_a}{RT} \quad [6]$$

The plot of $\ln(\beta/T^2)$ and $1/T$ data points obtained from the curves recorded for several heating rates is a straight line. The slope is used to calculate the activation energy E_a .

2.3.3 The MÁLEK method

When the activation energy E_a is known, the pyrolysis reaction mechanism of the solid-stage reactions can be obtained by the MÁLEK method (24, 25). The MÁLEK method works by comparing experimental data with a theoretical reference curve. The theoretical curve can be expressed as:

$$y(\alpha) = \frac{f(\alpha) \cdot G(\alpha)}{f(0.5) \cdot G(0.5)} \quad [7]$$

where the functions $f(\alpha)$ and $G(\alpha)$ are reaction models. The experimental curve can be expressed as follows:

$$y(\alpha) = \left(\frac{T}{T_{0.5}}\right)^2 \frac{\left(\frac{d\alpha}{dt}\right)}{\left(\frac{d\alpha}{dt}\right)_{0.5}} \quad [8]$$

where $T_{0.5}$ and $(d\alpha/dt)_{0.5}$ are the temperature and reaction rate at $\alpha = 0.5$, respectively. Table 2 lists mathematical expressions of several options for $f(\alpha)$ and $G(\alpha)$. The plot of $y(\alpha)$ versus α produces an experimental curve according to Equation [8]. The pyrolysis reaction model can be obtained by comparing the experimental curves with the theoretical master plots.

2.3.4 The COATS-REDFERN method

The COATS-REDFERN (26) integration method uses a single model to analyze the characteristics of pyrolysis kinetics. By integrating the temperature approximation of Equation [4], the COATS-REDFERN equation is derived as follows:

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \quad [9]$$

For the general temperature region and E_a of pyrolysis reaction, $E_a \gg 2RT$, so Equation [9] can be simplified as

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E_a}{RT} \quad [10]$$

The activation energy (E_a) and pre-exponential factor (A) can be obtained from the linear relationship between $\ln[G(\alpha)/T^2]$ and $1/T$.

3 RESULTS AND DISCUSSION

3.1 Composition of tobacco leaves

The composition of different tobacco leaves is summarized in Table 1. The chemical composition of tobacco leaf is affected by factors such as genetics, agricultural practices, soil type, and curing procedures, etc. (27). Cigar tobacco and flue-cured tobacco have significant differences in fixed carbon, ash, nitrogen, oxygen and nicotine content. The nitrogen, nicotine, and ash content of cigar tobacco is higher than that of flue-cured tobacco, while the oxygen and cellulose content is on the contrary. The total content of hemicellulose, cellulose, and lignin in tobacco is from 15% to 20%.

3.2 Thermogravimetric analysis

The TG-DTG curves of CFT, CWT and FCT pyrolysis processes at the heating rate of $10^\circ\text{C min}^{-1}$ are shown in Figure 1. The pyrolysis behavior of tobacco is very complicated, in addition to the decomposition of biopolymers such as cellulose, hemicellulose, pectin, and lignin, further comprising a large number of decompositions of non-polymer compounds. Generally, the decomposition of cigar tobacco can be divided into four stages. In stage I, the decrease in mass occurs primarily due to the evaporation of water, which accounts for almost 3% of the sample. In stage II, the thermal decomposition of hemicellulose in tobacco takes place mainly between 220°C and 285°C (28, 29), the peak at about 270°C could be the maximum decomposition rate

Table 1. Composition of tobacco leaves.

Item	CFT	CWT	FCT
<i>Proximate analysis (wt.%)</i>			
Moisture	2.95	3.84	1.89
Volatile	77.31	75.41	76.79
Fixed carbon	12.80	11.19	16.76
Ash	9.89	13.40	6.54
<i>Ultimate analysis (wt.%)</i>			
C	43.57	42.95	41.83
H	5.88	6.17	6.32
N	3.63	3.77	1.67
S	0.00	0.18	0.17
O	36.52	37.41	43.28
<i>Biochemical analysis (wt.%)</i>			
Hemicellulose	2.25	3.24	2.81
Cellulose	11.35	13.12	14.26
Lignin	2.84	3.65	3.21
<i>Nicotine content (wt.%)</i>			
	2.20	2.33	2.07

CFT = cigar filler tobacco; CWT = cigar wrapper tobacco; FCT = flue-cured tobacco

Table 2. Functional expressions of several common response models.

Mechanisms	Symbol	$G(\alpha)$	$f(\alpha)$
One-dimensional diffusion	D1	α^2	$\frac{1}{2}\alpha^{-1}$
Two-dimensional diffusion	D2	$\alpha + (1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$
Three-dimensional diffusion	D3	$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^2$	$\frac{3}{2}(1-\alpha)^{\frac{2}{3}}\left[1-(1-\alpha)^{\frac{1}{3}}\right]^{-1}$
Avrami-Erofeev	A2	$[-\ln(1-\alpha)]^{\frac{1}{2}}$	$2(1-\alpha)[- \ln(1-\alpha)]^{\frac{1}{2}}$
Avrami-Erofeev	A3	$[-\ln(1-\alpha)]^{\frac{1}{3}}$	$3(1-\alpha)[- \ln(1-\alpha)]^{\frac{2}{3}}$
First-order reaction	F1	$-\ln(1-\alpha)$	$1-\alpha$
1.5-order reaction	F3/2	$2\left[(1-\alpha)^{\frac{1}{2}}\right]-2$	$(1-\alpha)^{\frac{3}{2}}$
Second-order reaction	F2	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$
Contracting area	R2	$1-(1-\alpha)^{\frac{1}{2}}$	$2(1-\alpha)^{\frac{1}{2}}$
3D contracting volume	R3	$1-(1-\alpha)^{\frac{1}{3}}$	$3(1-\alpha)^{\frac{2}{3}}$

Figure 1. TG (a) and DTG (b) curves of CFT, CWT and FCT pyrolysis processes at the heating rate of 10 °C min⁻¹.

of hemicellulose. In addition, some low-temperature volatiles are released, partially due to the decomposition of sugars, pectin, and nicotine, that occurs at this stage (30, 31). The mass loss of CFT and CWT at this stage is 23% and 20%, respectively. In stage III, the temperature range and the temperature of the peak of the DTG curve are very close to the decomposition temperature of cellulose (32, 33). This indicates that stage III of the DTG curve may correspond to cellulose pyrolysis of the cigar tobacco leaves. In this stage, the thermal decomposition rate increases compared with that of stage II. In stage IV, a

shoulder between 420 °C and 600 °C was observed, which could be related to the decomposition of lignin (34). Mass loss after 600 °C may include dehydrogenization and aromatization of residual carbon (3). Among the three components, hemicellulose is the easiest to be pyrolyzed, followed by cellulose, and lignin is the most difficult one. This may be due to differences in the chemical structures and natures of polymeric materials. Hemicellulose is a mixture of various monosaccharides (xylose, mannose, glucose, galactose, etc.) with a low degree of polymerization. In contrast, the cellulose molecule is a very long polymer of

Figure 2. TG-DTG curves of CFT (a), CWT (b) and FCT (c) pyrolysis processes under different heating rates of 5 °C min⁻¹, 10 °C min⁻¹, 15 °C min⁻¹, and 20 °C min⁻¹.

glucose without branches, which results in thermal degradation more difficult than in hemicellulose. Lignin is composed of three kinds of benzene-propane and is heavily cross-linked. Therefore, lignin has high thermal stability and is difficult to decompose (35). The main pyrolysis stages (stage II and stage III) of CFT and CWT contribute to a mass loss of 48.48% and 44.95%, respectively. CWT has been grown under shade treatment conditions that may be unfavorable for the accumulation of organic material in the leaves.

However, it can be seen from the DTG curves that the pyrolysis process of flue-cured tobacco is different from that of cigar tobacco. This may be caused by differences in physical structure and chemical composition. Flue-cured tobacco has an obvious mass loss peak at 200 °C, which corresponds to the decomposition of volatile compounds. The significant difference observed may be due to the difference in sugar content. According to the previous literature (27), flue-cured tobacco has a high sugar content, while in cigars - as air-cured tobacco - their sugars have been virtually depleted via metabolic activities. In addition, flue-cured tobacco has a continuous mass loss peak between 230 °C and 400 °C due to the lower hemicellulose content relative to the cellulose content, while the mass loss peak of cigar tobacco occurs at a slightly lower temperature at this stage. This result shows that the thermal decomposition temperature of biopolymers in cigar tobacco

is lower than that of flue-cured tobacco, which may be due to the lower crystallinity and/or the lower degree of polymerization of the biopolymers in the cigar tobacco (36).

The TG-DTG curves of CFT, CWT and FCT pyrolysis processes at different heating rates are shown in Figure 2. The mass loss at different heating rates during the pyrolysis of samples was obtained from TG-DTG curves and is summarized in Table 3. With the rise of the heating rate, the reaction rate accelerates, and the DTG curves move toward the higher temperature. This may be due to the fact that the time required to reach the final temperature is reduced as the heating rate increases. This results in a decrease in the reaction time experienced by the sample, and thermal hysteresis occurs during the pyrolysis process (37). As shown in Table 3, the mass loss is not strongly dependent upon the heating rate. This suggests that the total mass loss at any stage depends primarily on the basic composition of the sample (38).

The characteristic parameters of pyrolysis (T_s , T_{max} , R_{max} , R_{mean} , $\Delta T_{1/2}$, and D_i) of CFT, CWT and FCT at varying heating rates are summarized in Table 4. At a heating rate of 10 °C min⁻¹, the devolatilization indices D_i of CFT, CWT, and FCT are $6.99 \times 10^{-7}\% \text{ } ^\circ\text{C}^{-3} \text{ min}^{-2}$, $10.62 \times 10^{-7}\% \text{ } ^\circ\text{C}^{-3} \text{ min}^{-2}$, and $27.3 \times 10^{-7}\% \text{ } ^\circ\text{C}^{-3} \text{ min}^{-2}$, respectively. In summary, compared with CFT and CWT, FCT has a lower characteristic temperature of volatiles release, and the $\Delta T_{1/2}$ is narrower. This shows that FCT is more

Table 3. Mass loss at different temperature intervals during pyrolysis of tobacco leaf samples.

Sample	Stage I		Stage II		Stage III	
	Temperature interval (°C)	Mass loss (%)	Temperature interval (°C)	Mass loss (%)	Temperature interval (°C)	Mass loss (%)
<i>CFT</i>						
5	40–130	2.84	130–283	22.60	283–397	26.43
10	40–134	2.88	134–292	23.26	292–411	26.78
15	40–142	3.03	142–296	23.07	296–415	26.77
20	40–146	3.06	146–299	23.35	299–424	27.34
<i>CWT</i>						
5	40–131	2.81	131–273	20.04	273–407	25.33
10	40–140	2.85	140–284	20.83	284–417	24.65
15	40–144	2.84	144–287	20.94	287–419	24.32
20	40–151	2.96	151–291	21.08	291–426	24.44
<i>FCT</i>						
5	40–101	1.29	101–216	21.09	216–401	38.82
10	40–103	1.10	103–227	22.27	227–405	38.41
15	40–108	1.15	108–232	21.76	232–408	38.19
20	40–115	1.27	115–240	22.12	240–416	37.40

CFT = cigar filler tobacco; CWT = cigar wrapper tobacco; FCT = flue-cured tobacco

Table 4. Characteristic parameters of tobacco leaves during pyrolysis.

Sample	T_s (°C)	T_{max} (°C)	R_{max} (% min ⁻¹)	R_{mean} (% min ⁻¹)	$\Delta T_{1/2}$ (°C)	D_i (10 ⁻⁷ % ² °C ⁻³ min ⁻²)	Residue (%)
<i>CFT</i>							
5	130	313	-2.01	-0.43	105	2.02	24.46
10	134	323	-3.96	-0.86	112	6.99	24.73
15	142	330	-5.78	-1.27	121	12.91	25.71
20	146	335	-7.65	-1.68	122	21.61	26.11
<i>CWT</i>							
5	131	297	-2.16	-0.43	72	3.30	24.75
10	140	307	-4.21	-0.83	76	10.62	27.56
15	144	310	-6.22	-1.23	79	21.61	28.25
20	151	315	-8.18	-1.62	82	33.94	28.97
<i>FCT</i>							
5	101	188	-1.82	-0.47	60	7.51	18.75
10	103	197	-3.73	-0.92	62	27.30	20.06
15	108	201	-5.60	-1.36	64	54.80	21.38
20	115	206	-7.30	-1.80	65	85.30	21.82

reactive than CFT and CWT. As shown in Table 4, R_{max} and D_i increase as the heating rate increases. Generally speaking, combustibles with greater D_i value imply that they are more reactive. Thus, increasing the heating rate is in favor of the release of volatile substances.

3.3 FTIR analysis of gas products

The 3D FTIR spectrum of the gases emitted during tobacco pyrolysis are shown in Figure 3. On the whole, the 3D spectra demonstrate similar gas release behavior with some slight differences. Five characteristic absorbance bands with the maximum absorption at 3565 cm⁻¹, 2357 cm⁻¹, 1749 cm⁻¹, 1504 cm⁻¹, and 667 cm⁻¹ are observed for tobacco samples. This result suggests that the gas products corresponding to these five bands are the pyrolysis prod-

ucts. Moreover, each characteristic FTIR peak exhibits several peaks, and the evolution with temperature corresponds to the DTG curves.

In order to identify the components of the gas products, the 2D FTIR spectra at the peak temperature of the four stages are shown in Figure 4. Based on the FTIR spectra, the result of component identification of the gas products is shown in Table 5. To avoid interference from the pyrolyzed mass, the absorbance has been normalized by dividing it by the initial mass of tobacco.

In the first stage (T1), the main volatile component is H₂O, as evidenced by the absorbance band between 3500 cm⁻¹ and 4000 cm⁻¹, which was mainly caused by the evaporation of the sample. In stage II (T2), the bands in the region from 2250 cm⁻¹ to 2500 cm⁻¹ and 580 cm⁻¹ to 700 cm⁻¹ demonstrate the release of CO₂. CO₂ is the dominant

Figure 3. 3D TG/FTIR diagram of pyrolysis products for CFT (a), CWT (b) and FCT (c).

Figure 4. FTIR spectra of volatile products at peak temperature for tobacco samples.

gas during tobacco pyrolysis, and is mainly produced by the cracking and reforming of carbonyl and carboxyl groups (39). Besides, a very small asymmetric absorption peak corresponding to C-O appears in the wavenumber from 1050 cm^{-1} to 1200 cm^{-1} , indicating the existence of alcohols and phenols (40). The C=O stretching vibration in the range from 1710 cm^{-1} to 1800 cm^{-1} is attributed to aldehydes, ketones, and organic acids which contained the carbonyl groups. The bands in the region from 1450 cm^{-1} to 1650 cm^{-1} are the C=C stretching vibration and benzene skeleton vibration. The band at 966 cm^{-1} represents NH_3 . With the pyrolysis temperature increased to T3, the above-mentioned absorbance bands gradually increased in intensity. The band from 2850 cm^{-1} to 3030 cm^{-1} is characteristic of hydrocarbon gases such as CH_4 . The absorption band from 2000 cm^{-1} to 2250 cm^{-1} indicates the presence of CO. The spectrum obtained at T4 shows that the main components of the gases released are CO, CO_2 , and water,

which are caused by the carbonates inherent or generated during pyrolysis (41).

According to the widely used Lambert-Beer law, the absorbance at a specific wavenumber is linearly related to the gas concentration (44). Therefore, changes in absorbance during pyrolysis reflect changes in the concentrations of different gases. Figure 5 compares the evolution of gas products with increasing temperatures during the pyrolysis of tobacco samples. As shown, the gas products (except for CH_4 and CO) are concentrated within the temperature range from $200\text{ }^{\circ}\text{C}$ to $400\text{ }^{\circ}\text{C}$. Moreover, the evolution of released CO_2 with temperature is consistent with the thermogravimetric analysis. The CO_2 released from $200\text{ }^{\circ}\text{C}$ to $400\text{ }^{\circ}\text{C}$ can mainly be attributed to the cracking and reforming of carboxyl groups that CWT exhibit a more intense signal in this stage, whereas above $400\text{ }^{\circ}\text{C}$, the polymerization reaction of solid phase coking is accompanied by the emission of CO_2 as the temperature increases.

Table 5. Identification of gas products during pyrolysis of tobacco based on FTIR spectra.

Wavenumber (cm^{-1})	Functional groups	Compounds	References
3500-4000 (selected:3566)	O-H Symmetrical and asymmetrical stretching	H_2O	(14, 42, 45)
2250-2500 (selected:2359)	Asymmetrical stretching in $\text{O}=\text{C}=\text{O}$	CO_2	(14, 45)
2850-3030 (selected:3016)	C-H Stretching	CH_4	(43)
2000-2250 (selected:2190)	Stretching vibration in CO	CO	(14, 45)
1710-1800 (selected:1749)	C=O Stretching	Carbonyl groups	(14, 45)
1050-1200 (selected:1180)	C-O Stretch	Hydroxyl groups	(14)
1450-1650	Aromatic C=C-C ring stretch	Aromatics	(42, 43)
3070-3130 (selected:3076)	Aromatic C-H in plane bend		
966		NH_3	(42)

Figure 5. Evolution of gas products with increasing temperature in the pyrolysis of tobacco.

Figure 6. Arrhenius plots of FWO method for CFT (a), CWT (b) and FCT (c) at different conversion rates.

Figure 7. Arrhenius plots of KAS method for CFT (a), CWT (b) and FCT (c) at different conversion rates.

The release rate of water varied with the temperature, the band below 200 °C was related to the evaporation of water. The appearance of a maximum at around 320 °C for H₂O can be attributed to the decomposition of hemicellulose and cellulose by the cracking of hydroxyl groups in the lateral chains (45). CH₄ is formed by the cleavage of methoxyl groups and methylene groups. This band shows a maximum at around 540 °C, which is associated with lignin decomposition. For CO, two peaks appear at around 330 °C and 500 °C, indicating that the formation of CO is related to the decomposition of cellulose and lignin, and the release amount of CO above 600 °C increases significantly. The release of CO is consistent with the results reported by BAKER (46), suggesting that the formation of carbon oxide occurs in two regions, a low-temperature region from 100 °C to 450 °C and a high-temperature region from 500 °C to 900 °C. The total amount of carbon oxides is independent of the heating rate, but the relative proportions of CO₂ and CO are strongly dependent on the heating rate. BAKER proposed that CO undergoes some gas phase reactions, and that CO₂ undergoes both gas phase reaction and heterogeneous reaction. The release curves of carbonyl and hydroxyl compounds were consistent in the maximum mass loss range, indicating that the formation of aldehydes and ketones from tobacco pyrolysis went along with the formation of alcohols and phenols. Aromatics were formed at temperatures above 500 °C and with a maximum at around 540 °C, suggesting that the production of aromatic compounds was related to lignin decomposition. Compared with CFT and CWT, FCT had lower decomposition intensity on CO₂, CH₄, CO, and aromatics.

3.4 Determination and comparison of activation energy

To determine the activation energy of the pyrolysis of cigar tobacco and flue-cured tobacco, two different model-free isothermal conversion methods (FWO and KAS models) were used. In the FWO method, the activation energy can be determined from the plots of $\lg(\beta)$ versus $1/T$. In the KAS method, the activation energy can be determined from the plots of $\lg(\beta/T^2)$ versus $1/T$. Figures 6 and 7 show the dependence of the activation energy on the conversion ($\alpha = 0.1-0.9$) for the different tobacco leaves based on the isoconversional FWO and KAS methods, respectively. The corresponding values calculated from the slope and the coefficients of determination R^2 at different degrees of conversion (α) are presented in Table 6. The E_a values of CFT range from 207.4 kJ mol⁻¹ to 319.3 kJ mol⁻¹, that of CWT range from 160.4 kJ mol⁻¹ to 260.5 kJ mol⁻¹, and that of FCT range from 100.1 kJ mol⁻¹ to 192.1 kJ mol⁻¹. Importantly, the coefficients of determination R^2 of all curves are above 0.98 indicating that all linear plots are statistically relevant. The difference between the two methods is less than 2%, indicating the accuracy and reliability of the calculations of the FWO and KAS methods.

Figure 8 depicts the relationship between the activation energy E_a calculated by the FWO and KAS methods at different conversions. The kinetic analysis results show that E_a is highly dependent on α , which indicates that the pyrolysis of tobacco leaf is a complex process including parallel, competitive and consecutive reactions. Taking the results of the CFT as an example, the activation energy

Table 6. Activation energies of cigar tobacco leaves obtained by the FWO method and KAS method.

Conversion	CFT				CWT				FCT			
	FWO		KAS		FWO		KAS		FWO		KAS	
	E_a (kJ mol ⁻¹)	Correlation coefficient R ²	E_a (kJ mol ⁻¹)	Correlation coefficient R ²	Difference (%)	E_a (kJ mol ⁻¹)	Correlation coefficient R ²	Difference (%)	E_a (kJ mol ⁻¹)	Correlation coefficient R ²	E_a (kJ mol ⁻¹)	Correlation coefficient R ²
0.1	207.4	0.984	210.3	0.982	1.40	160.4	0.993	0.993	102.2	0.999	100.1	0.999
0.2	249.9	0.995	254.2	0.994	1.72	206.9	0.987	0.986	120.4	0.999	118.9	0.999
0.3	253.5	0.994	257.6	0.994	1.59	229.3	0.990	0.989	121.4	0.996	119.6	0.996
0.4	252.2	0.995	255.9	0.994	1.42	228.8	0.992	0.991	155.4	0.994	154.7	0.994
0.5	222.2	0.995	224.0	0.994	0.77	215.6	0.993	0.993	172.3	0.996	172.0	0.996
0.6	219.3	0.994	220.6	0.993	0.58	221.9	0.994	0.994	171.9	0.996	171.2	0.996
0.7	266.4	0.999	269.7	0.988	1.21	238.0	0.989	0.988	173.5	0.998	172.5	0.998
0.8	301.3	0.992	305.7	0.991	1.43	234.3	0.994	0.994	162.6	0.984	160.5	0.982
0.9	315.2	0.993	319.3	0.993	1.28	259.3	0.994	0.994	192.1	0.983	190.4	0.980
Average	254.2		257.5			221.6			155.4		151.1	

CFT = cigar filler tobacco

CWT = cigar wrapper tobacco

FCT = flue-cured tobacco

FWO = Flynn-Wall-Ozawa method

KAS = Kissinger-Akahira-Sunose method

Figure 8. Changes in E_a versus α obtained by applying the FWO and KAS methods.

increased rapidly as the conversion value increased from 0.1 to 0.2, and remained approximately at about 250 kJ mol⁻¹ as α increased from 0.2 to 0.4. At this stage, the pyrolysis temperature was not particularly high, and corresponded to the drying of the cigar tobacco and the partial pyrolysis of hemicellulose. Therefore, a higher energy was required to increase the reactivity. As the pyrolysis proceeded and α increased from 0.4 to 0.6, the activation energy E_a decreased from 253.5 kJ mol⁻¹ to 219.3 kJ mol⁻¹ (FWO), this stage was mainly contributed by the thermal degradation of cellulose. Cellulose was initially pyrolyzed into active cellulose, resulting in a decrease in polymerization degree and molecular chain length. Active cellulose continued to degrade into more components with lower molecular weight and required lower activation energy (37). When α was higher than 0.6, the value of E_a increased significantly. This stage corresponded to the lignin pyrolysis in the DTG curve. Since lignin consists mainly of three forms of highly cross-linked benzene-propane (35), its thermal stability is high and the activation energy required for pyrolysis increases. At this stage, coke is produced at the same time, which also increases the activation energy value.

Generally, there are similar variations in the activation energy of the three types of tobacco. Since the conversion rate of flue-cured tobacco is from 0.1 to 0.3, corresponding to the pyrolysis of volatile components such as sugars, the activation energy gradually increases from 100.1 kJ mol⁻¹

to 121.4 kJ mol⁻¹. Comparing the activation energies during the whole process, the activation energy of FCT is relatively lower than that of CFT and CWT. Because the value of the apparent activation energy represents the minimum energy required for a chemical reaction to occur, greater apparent activation energy indicates lower pyrolytic reactivity. These results indicate that the volatile materials of FCT decomposed more easily than the components of the CFT and CWT.

3.5 Determination of reaction mechanism

Heterogeneous reactions usually involve a superposition of several elementary processes such as order-based, the diffusion, the random nucleation and nuclei growth, these reaction mechanisms $G(\alpha)$ are summarized in Table 2. The theoretical curves $y(\alpha)$ versus α were plotted using Equation [7] and are shown in Figure 9. This figure also shows the experimental curves for three types of tobacco leaf, where S1 and S2 are the curves of the sample in stage II and stage III, respectively. As shown in Figure 9, the theoretical curve for $G(\alpha)$ corresponding to the one-dimensional diffusion D1 is consistent with the experimental data of S1 in tobacco. Thus stage II follows one-dimensional diffusion D1, which is in accordance with the results obtained by GAO *et al.* (6) studying flue-cured tobacco. The experimental curve S2 of FCT matched well with the theoretical master plot of two-dimensional diffusion D2. However, the experimental curve S2 of CFT and CWT did not fit very well to any of the theoretical curves, but it was acceptably close to the theoretical curves of 1.5-order reaction F3/2 and second-order reaction F2. In order to determine the reaction mechanism further, the COATS-REDFERN method was used to determine the thermal decomposition mechanism of stage III.

By combining the two mechanism functions, values for E_a , A , and correlation coefficients (R^2) were obtained by the COATS-REDFERN method, and are shown in Table 7. For the pyrolysis of CFT and CWT in stage III, the second-order reaction F2 had higher correlation coefficients (0.997 and 0.984) compared with the 1.5-order reaction F3/2. Simultaneously, the activation energy E_a obtained by the COATS-REDFERN method was close to the activation energy (234.42 kJ mol⁻¹ and 224.65 kJ mol⁻¹) obtained by the FWO and KAS isoconversional methods. Thus, the most likely kinetic mechanism of stage III for cigar tobacco is second-order reaction F2.

Figure 9. $y(\alpha)$ versus α curves at 10 °C min⁻¹ calculated by Equation [8] for tobacco leaves, (a) CFT, (b) CWT, (c) FCT.

Table 7. Kinetic parameters of tobacco thermal decomposition obtained by COATS-REDFERN method.

Sample	Stage	Reaction	Fitted equation	A (min ⁻¹)	E _a (kJ mol ⁻¹)	Correlation coefficient R ²
CFT	II	D1	Y = -10165.86x + 6.09	4.49 × 10 ⁴	84.5	0.995
		F3/2	Y = -23551.40x + 26.44	7.12 × 10 ¹³	195.8	0.990
	III	F2	Y = -28195.40x + 34.48	2.65 × 10 ¹⁷	234.4	0.997
CWT	II	D1	Y = -10305.79x + 5.30	7.74 × 10 ⁴	85.7	0.998
		F3/2	Y = -22403.96x + 25.26	4.17 × 10 ¹³	186.2	0.963
	III	F2	Y = -27020.35x + 33.40	1.73 × 10 ¹⁷	224.7	0.984

The pyrolysis of tobacco is a complex and continuous process, which is affected by different reactions. The thermal decomposition of ligno-cellulosic biomass is initially limited by diffusion mechanisms (47). First-order and second-order reactions typically occur during pyrolysis when cellulose content is higher than the lignin content (48). In stage III, the difference of cigar tobacco and flue-cured tobacco is the temperature range, leading to a different reaction mechanism. It also shows that reaction mechanism may be highly related to the degradation behavior of the main components. In addition, the activation energy of cigar tobacco found in our experiments was higher than that reported in a study on tobacco waste (103.94 kJ mol⁻¹) (10) and tobacco dust (43.6 kJ mol⁻¹ – 227.0 kJ mol⁻¹) (13). The difference could be related to the type of species, growth condition, particle size of tobacco and the different kinetic models.

4 CONCLUSIONS

In this work, the pyrolysis kinetics of cigar tobacco and flue-cured tobacco were investigated at different heating rates. The chemical composition varied with tobacco type, with cigar tobacco having a higher content of nitrogen, nicotine and ash, while flue-cured tobacco had a higher content of oxygen and cellulose. Cigar tobacco pyrolysis could be divided into four stages, consisting of

- Stage I: evaporation of water;
- Stage II: decomposition of hemicellulose and emission of low-temperature volatiles;
- Stage III: decomposition of cellulose;
- Stage IV: decomposition of lignin and the formation of char.

Flue-cured tobacco had obvious mass loss at 200 °C due to its high volatile components such as sugars. During the pyrolysis of different types of tobacco, most of the gas species were released in the second and third stage. H₂O, CO₂, CH₄, CO, carbonyls, alcohols, phenols, and aromatic compounds were identified by FTIR spectra. Generally, the total amounts of CO₂, CH₄, CO, and aromatics released from cigar tobacco pyrolysis are higher than that from flue-cured tobacco pyrolysis. The change tendency of activation energy was quite similar between flue-cured tobacco and cigar tobacco, and the activation energy distribution along with the conversion rate is a comprehensive expression of pyrolysis behaviors of various components. The pyrolysis reaction model for cigar tobacco could be well described by one-dimensional diffusion and a second-order reaction,

and the reaction model for flue-cured tobacco could be described by one-dimensional diffusion and two-dimensional diffusion.

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Corresponding author:

Bin Li, Ph.D.
Zhengzhou Tobacco Research Institute of CNTC
No. 2 Fengyang Street
Zhengzhou High-Tech Development District
15 Henan, 450001, China
E-mail: ztrilibin@163.com