Application progress of two-dimensional correlation spectroscopy in biomass

Tianliang Gao¹, Chuanshan Zhao^{1, a} and Qijun Ding¹

¹State Key Laboratory of Biobased Material and Green Paper making, Qilu University of Technology, Shandong Academy of Sciences, Jinan, Shandong, 250353, China

Abstract: As a renewable resource, biomass resources have been widely concerned. The internal structure and changes of the graduate students play an important role in the utilization of biomass. Compared with conventional spectroscopy technology, two-dimensional correlation spectroscopy (2D-COS) can provide not only the characteristic information of each functional group, but also the interaction information between each functional group. Therefore, the application of two-dimensional correlation spectroscopy in biomass has attracted increasing attention. First introduced the 2D-COS technology, focusing on the application progress of 2D-COS in the internal structure of graduate student molecules and molecules, biomass energy utilization technology and other aspects. Finally, the existing problems and future prospects are analyzed.

1 Introduction

In recent years, biomass resources have gradually come into people's vision, which can not only be used for combustion power generation, but also be converted into bioethanol, biodiesel and other transportation fuels. Compared with fossil fuel, its environmental pollution is small and renewable. Biomass is an organism formed by photosynthesis. It includes all plants, animals and microbes. Biomass is a renewable resource with little environmental pollution, so it is widely concerned^[1]. Biomass can be divided into herbs, woody plants, agricultural and forestry wastes, domestic garbage and animal manure according to the main characteristics. Plants rich in sugar, fat and fiber are often used for the development and utilization of biomass energy^[2]. The biomass mentioned in the following paper mainly refers to these biomass, and the components of biomass mainly include cellulose, hemicellulose and lignin. In recent years, biomass based new energy has the potential to replace petroleum energy.

In the process of developing biomass, it is particularly important to study the chemical structure changes. One dimensional spectroscopy is a common analytical method to study the internal structure of biomass, but it has some limitations. Compared with conventional spectroscopy technology, 2D-COS can not only provide the characteristic information of functional groups, but also provide the interaction information between functional groups. Therefore, it is applied to biomass development. In this paper, the 2D-COS technology is introduced firstly, and the application progress of 2D-COS in the research of biomass molecular internal structure, biomass energy utilization

technology and other aspects of biomass application are mainly introduced. Finally, the existing problems and future prospects are analyzed.

2 2D-COS

2.1 Background and principle of 2D-COS

2D-COS was first used in the field of nuclear magnetic resonance (NMR). An important reason hindering the development of two-dimensional technology is that the time scale of ordinary spectrum is much shorter than that of nuclear magnetic resonance^[3]. In 1986, based on 2D-NMR theory, Noda^[4] proposed that the multiple RF excitation in the experiment is regarded as an external disturbance to the system. By analyzing 2D-NMR with this idea, it is easy to design completely different 2D-COS experimental techniques. In 1989, Noda^[5] applied mathematical correlation analysis technology to infrared spectroscopy to obtain two-dimensional correlation infrared spectroscopy. Until 1993, Noda^[5] modified the theory, extended 2D-COS technology from narrow sense to broad sense, and extended 2D-COS technology to near-infrared, Raman, fluorescence and other optical spectrum technologies^[3,5,6,7,8,9,10,11,12,13,14].

In 2D-COS, a set of spectra $a(v_j, T_i)$ is a function of the spectral variables v_j and T_i , where $j=1, 2, \dots, N$ and $i=1, 2, \dots, m$. Through simple mathematical correlation analysis, a series of dynamic spectra generated by external disturbances are collected and converted into a set of two-dimensional correlation spectra, as shown in Fig. 1.

^a Corresponding author: ppzcs78@163.com

Figure 1. a general method for constructing generalized two dimensional correlation spectra

The dynamic frequency spectrum (v_j, T_i) caused by external disturbance is defined as follows in the observation interval between T_1 and T_M :

$$\tilde{A}(v_j, t_i) = A(v_j, t_i) - \bar{A}(v_j) \quad (1)$$

Where $\bar{A}(v_j)$ is the reference spectrum. The average spectrum is usually selected as the reference spectrum:

$$\bar{A}(v_j) = \frac{1}{m} \sum_{i=1}^m A(v_j, t_i) \quad (2)$$

The two-dimensional correlation synchronous matrix $\Phi(v_1, v_2)$ and the two-dimensional correlation asynchronous matrix $\Psi(v_1, v_2)$ are given by the following formula:

$$\Phi(v_1, v_2) = \frac{1}{m-1} \sum_{i=1}^m \tilde{A}(v_1, t_i) \cdot \tilde{A}(v_2, t_i) \quad (3)$$

$$\Psi(v_1, v_2) = \frac{1}{m-1} \sum_{i=1}^m \tilde{A}(v_1, t_i) \cdot \sum_{k=1}^m N_{ik} \tilde{A}(v_2, t_k) \quad (4)$$

Where N_{ik} is Hibert-Noda matrix.

$$N_{ik} = \begin{cases} 0 & i = k \\ \frac{i}{\pi(k-i)} & i \neq k \end{cases} \quad (5)$$

2.2 Spectral properties and spectrum reading methods of 2D-COS

2.2.1 Spectral properties

There are two kinds of two-dimensional correlation spectrum, one is two-dimensional synchronous correlation spectrum, the other is two-dimensional asynchronous correlation spectrum. Two dimensional synchronous correlation spectroscopy mainly studies the changes of functional groups in matter with external disturbance under the effect of disturbance (Fig. 2a). It is symmetrical about the diagonal. The peaks formed on the diagonal are called automatic peaks, and the automatic peaks are all positive. The peaks formed outside the diagonal are called cross peaks. The cross peaks can be divided into positive and negative ones. If the intensities of absorption peaks under two wave number variables are the same (increase or decrease at the same time) with external disturbances, the cross peaks formed are positive peaks, otherwise they are negative peaks. According to the positive and negative cross peaks of the synchronous spectrum, the source of the functional groups can also be determined. The positive peak indicates that the two

functional groups may have the same source, and the negative peak indicates that the source may be different [3-14].

Two dimensional asynchronous correlation spectroscopy was used to study the difference of each functional group with external perturbation. In this paper, the order of the intensity of absorption peaks at the two variables with external disturbance is studied (Fig. 2b). The two-dimensional asynchronous correlation spectrum is antisymmetric with respect to the diagonal, and the peaks formed are all cross peaks, which can be divided into positive and negative ones. The two-dimensional asynchronous correlation spectrum is interpreted mainly according to the two-dimensional correlation analysis method proposed by no do [3-14].

Figure 2. Schematic diagram of 2D correlation spectrum

2.2.2 Reading rules

The two-dimensional correlation spectrum reading rules are divided into two. First, if $H(v_1, v_2) > 0$, the corresponding functional groups at the wave numbers of v_1 and v_2 have the same trend with the external disturbance. If $H(v_1, v_2) < 0$, the change trend of corresponding functional groups at wave numbers v_1 and v_2 is opposite [3-14].

Secondly, in the asynchronous correlation spectrum, if the $J(v_1, v_2)$ in the asynchronous spectrum is the same as that in the synchronous spectrum, the change of v_1 is faster than that of v_2 . On the contrary, if the positive and negative conditions of $J(v_1, v_2)$ in asynchronous spectrum are different from that of $H(v_1, v_2)$ in synchronous spectrum, then the change of v_1 is slower than that of v_2 (where $v_1 > v_2$), and when $v_2 > v_1$, it is completely opposite to the above [3-14].

2.3 Technical method of 2D-COS

With the development of generalized correlation spectrum theory, three new correlation spectroscopy techniques have been developed: sample two-dimensional correlation, hybrid two-dimensional correlation analysis and moving window two-dimensional correlation analysis [15]. The sample two-dimensional correlation technique takes the sample as the external disturbance, which can provide the relationship between the concentration changes of different components in the system [8]. The common 2D-COS technology is usually carried out under the same external disturbance condition, but in fact, in many

cases, it is carried out under two or more external disturbances. The spectral intensity under two external disturbances is expressed as a (V, T, t) (T, t denotes two different external disturbances). We call this system "hybrid two-dimensional correlation analysis technology"^[16-17]. Moving window two-dimensional correlation analysis technology characterizes the change of spectral intensity in the direction of external disturbance variable in large spectral data, and determines the characteristic disturbance point of spectral intensity with external disturbance mutation, which has advantages in the study of phase transition process and determination of phase transition point^[18-19]. Among them, the moving window two-dimensional correlation analysis technology has been applied in biomass fuel ethanol technology, mainly in the application of its phase change advantages.

The generalized 2D-COS has two kinds of spectra, synchronous and asynchronous. Combining the two kinds of spectra, we can not only analyze the characteristics of the internal functional groups, but also analyze the changing order of the functional groups with external disturbances. But in practice, especially in the case of a large number of cross peaks, this method is not efficient and easy to make mistakes. In order to solve this problem, many improved methods have been proposed, such as 2d-cds technology, full phase angle spectrum, modified asynchronous two-dimensional correlation spectrum and fused two-dimensional correlation spectrum^[20]. Two dimensional component correlation spectroscopy (2D-CDS) technology was developed in 2014^[21], which can directly provide the distribution and concentration change order of components in the dynamic process of the system to be analyzed.

Generalized 2D-COS has a strong ability to extract feature information, but sometimes overlapping peaks in the system are difficult to analyze. Noda^[22] proposed "projected two-dimensional correlation spectrum technology", which can extract overlapped peaks in complex systems and conduct spectral analysis. In 2010, Noda^[23] proposed double two-dimensional correlation analysis technology, which mainly solves the problem of low resolution of overlapping peaks in synchronous spectrum.

3 Application of 2D-COS in biomass research

3.1 Application of 2D-COS in the analysis of biomass molecular structure

3.1.1 Cellulose

In the early years, there were more researches on the internal structure of cellulose. Cellulose molecules are connected by hydrogen bonds. The types of hydrogen bonds can be divided into two types: intramolecular hydrogen bonds O-3-H-3...O-5, O-2-H-2...O-6, and intermolecular hydrogen bonds O-6-H-6...O-3. With the development of 2D-COS technology, some scientists

have used this technology to analyze the internal hydrogen bonds of cellulose.

Barbara^[24] et al. Analyzed the hydrogen bond in cellulose by dynamic mechanical measurement (DMA) and 2D-IR. It was found that O-6-H-6...O-3 was mainly distributed in 3230-3310 cm^{-1} band, O-3-H-3...O-5 was mainly distributed in 3340-3375 cm^{-1} band, and O-2-H-2...O-6 was mainly distributed in 3410-3460 cm^{-1} band. This is the first time to use 2D-IR to study the hydrogen bond structure of cellulose, and then to study the sequence of internal hydrogen bond breaking with external disturbance. Serge^[25] et al. Explored the change of hydrogen bond with temperature in 3800-2800 cm^{-1} band by PCA and 2D-IR. It is found that the O-6-H-6...O-3 inter chain hydrogen bond breaks first in the range of 40-150°C, O-3-H-3...O-5 first breaks in the range of 250-325°C, followed by O-2-H-2...O-6. This laid a foundation for further utilization of cellulose.

Cellulose contains water. The study of the interaction between cellulose and water plays an important role in chemistry, physics, cellulose separation and processing technology (such as papermaking). Watanabe^[26-27] et al. Studied the interaction between microcrystalline cellulose (MCC) and water by 2D-IR and 2D-NIR, respectively. It was found that water was mainly combined with hydrogen bond O-6-H-6...O-3 between MCC and water during drying process. By studying the interaction between MCC and water during drying process, it was found that water content of 3-7wt% would affect the inter chain and intra chain hydrogen bonds of MCC. Li^[28] et al. Studied the thermal behavior of regenerated MCC with water content of 2.4wt% by 2D-IR. The main purpose was to reveal the sequence of different hydrogen bonds changing with temperature. It was found that when the temperature was higher than 250°C, the intramolecular hydrogen bonds had been completely broken, which also suggested that the factor of water should be considered in the preparation of fibroin. Cellulose has a strong hydrophilicity, so it has excellent water absorption capacity. Shinzawa^[29-30] used 2D-NIR to study the water absorption behavior of cellulose with time at 20 and 60 MPa. 2D-COS showed that the significant difference in water absorption was due to the way in which water molecules were intercepted by the cellulose polymer structure. The compression of cellulose essentially led to the crystal disintegration, and eventually led to the change of hydrogen bond structure between and within the chain caused by the interaction between water and cellulose.

3.1.2 Lignin and hemicellulose

Sugii^[31] et al. Used NIR spectroscopy technology combined with PCA and 2D-COS to study the change of wood chemical structure under the condition of moisture as external disturbance during drying process. 2D-NIR revealed the order of chemical structure transformation under different water content. Li^[32] et al. Analyzed the chemical structure changes of teak under the treatment temperature from 120°C to 220°C by combining FT-IR spectrum with sd-ir spectrum, correlation coefficient and

2D-IR spectrum. After mathematical calculation, the apparent resolution of the original infrared spectrum can be improved by combining the FT-IR spectrum with sd-ir spectrum and 2D-IR spectrum, and more accurate and comprehensive information of sht wood structure can be obtained. 2D-IR showed that the sensitivity of sht wood to thermal disturbance initially increased with the increase of treatment temperature, and then decreased. The results showed that the wood treated with sht at 180°C was the most sensitive to thermal disturbance. The strength of the automatic peak at 1493 cm⁻¹ and 1465 cm⁻¹ increased, indicating the structural degradation of lignin during sht. Popescu^[33] et al. Analyzed lime wood samples treated at 140°C and about 10% relative humidity for 504 hours by IR, principal component analysis (PCA) and 2D-IR. Through 2D-IR analysis, it was observed that the methoxyl side chain of lignin was cleaved first, but the degree was very small. With the increase of treatment time, the degradation of lignin structure was more obvious, and the methyl group was depolymerized and recondensed.

3.2 Application of 2D COS in biomass thermochemical transformation technology

Modern biomass energy technologies mainly include biomass direct combustion technology, biogas technology, biomass gasification technology, biomass fuel ethanol technology, biomass pyrolysis technology, biomass hydrogen production and indirect liquefaction technology, vegetable oil and bio oil technology. 2D-COS is mainly used in biomass fuel ethanol technology and pyrolysis technology.

3.2.1 Biomass fuel ethanol technology

When ethanol is used as a power fuel, it is called fuel ethanol. The fuel ethanol generated from biomass mainly goes through two steps, which are converted into sugar by hydrolysis, and then converted into ethanol by fermentation. Hydrolysis is a necessary step in the production of fuel ethanol. It refers to the process of decomposing cellulose and hemicellulose into monosaccharide under the action of certain temperature and catalyst (acid or cellulase)^[34]. Yellow^[35] et al. Analyzed lignin and xylan substituents in wheat straw after hydrothermal pretreatment by 2D HSQC-NMR, and obtained the following conclusions from the hydrothermal pretreatment of 1000 mg of wheat straw based on 2D HSQC-NMR: (1) β -aryl ether bond decreased by 60%; (2) Natural acetyl bond decreased by 81%; (3) From 4-O MeGlcA The results showed that the glucuronic acid of meglca decreased by 95%; (4) Meglca had acylation effect on coumaric acid ester and ferulic acid ester. Teramura^[36] et al. Used 2D HSQC-NMR spectroscopy to analyze the changes of lignin and polysaccharide components of 13 rice straw varieties after dilute acid pretreatment. 2D HSQC-NMR spectra showed that both lignin and polysaccharide decreased. During dilute acid pretreatment, starch was an important source of glucose and an important source of

fermentation inhibitors in liquid hydrolysates. These observations will help to screen rice varieties suitable for downstream bioethanol production. Gandolfi^[37] et al. Analyzed the separation of hemp residue by organic solvent pretreatment and its effect on lignin and sugar production. FTIR and 2D HSQC-NMR spectra were used to characterize the pretreated biomass and separated lignin. 2D HSQC-NMR spectrum showed that pyranoside was the main carbohydrate related to hemp lignin. When dilute acid and organic solvent are pretreated, some environmental pollutants are produced, which are difficult to degrade. Recently, as a kind of green solvent, deep eutectic solvent has been widely used in the pretreatment stage. The results of 2D HSQC-NMR showed that the dissociation of aryl ether bond (i.e. β -O-4) was dominant in the process of Des pretreatment. With the increase of pretreatment temperature, aliphatic hydroxyl groups were acylated or dehydrated. The chemical properties of lignin revealed in the process of Des pretreatment will help to optimize the pretreatment process and help in the current biorefinery process^[38]. Liu^[38] et al. Pretreated with triethylbenzylammonium chloride/lactic acid deep eutectic solvent improved the enzymatic hydrolysis and lignin extraction rate of wheat straw. In addition, 2D HSQC-NMR spectra showed that the regenerated lignin (purity 75.69 $\pm$ 1.32%) was mainly composed of eugenol unit and guaiacyl unit. In general, the results of this study provide an effective and simple pretreatment method for lignocellulosic biomass waste to enhance enzymatic hydrolysis and saccharification.

Biomass fuel ethanol technology mainly uses 2D hsqc-nmr to analyze the changes of its internal functional groups, while other 2D-COS has not been applied to this technology. I believe that more scientists will carry out this research in the future.

3.2.2 Biomass pyrolysis technology

The purpose of the technology of producing fuel ethanol from biomass is to convert it into a kind of high-quality gas and liquid fuel with low conversion efficiency. However, biomass pyrolysis technology can break the organic molecular chain of biomass by heat treatment, which can realize the application of all components of biomass, and convert biomass into gas, liquid and solid fuels. In recent years, Professor Yang Haiping applied 2D-IR pyrolysis technology in biomass pyrolysis process. On this basis, the correlation and formation mechanism of gas, liquid and solid products were explored^[40].

Agricultural straw should be baked when it is used. 2D-COS was used to study the chemical structure changes in the baking process. Wang^[41] et al. Combined with 2D-IR, compared the dry baking (DT) and wet baking (WT, hydrothermal carbonization) of corn straw and analyzed the pyrolysis of biomass. It was found that WT dehydration mainly occurred between the free hydroxyl group and methyl group in the branched chain structure, and retained a large number of hydroxyl groups in the cellulose chain. This is conducive to the production of high yield bio oil with high sugar content and high yield of CO₂ and H₂. Song et al. Used tg-ftir-ms

and 2D-COS to study the pyrolysis kinetics, evolution gas and mechanism of bagasse pyrolysis. The results of 2D-TG-FTIR / MS-COS showed that the response order of each gas was $\text{H}_2\text{O}/\text{CH}_4 > \text{phenol}/\text{alkane}/\text{aromatic hydrocarbon}/\text{alcohol} > \text{carboxylic acid}/\text{ketone} > \text{CO}_2/\text{ether} > \text{aldehyde}/\text{acetaldehyde}$. The response sequence of gas is suitable for the combination of sequence, diffusion and chemical reaction mechanism in the degradation of components. Mahdiyanti^[42] et al. Used near infrared and two-dimensional correlation to analyze the thermal degradation of wood, and 2D NIR was used to study the chemical changes of observed color changes during the thermal degradation of wood. The change of 2D NIR spectral strength shows that different chemical components are the cause of color change during heat treatment and accelerated wood aging. Under dry heat treatment, the content of hemicellulose decreased with the color change, while under wet heat treatment, the cellulose and lignin extracts decreased.

Because of the advantages of simple structure and single composition of cellulose, cellulose pyrolysis is the earliest and most studied.

Dai^[43] et al. Revealed the initial pyrolysis mechanism of cellulose, and characterized the evolution of functional groups by combining infrared Fourier transform spectroscopy (Swift) with 2D IR. The results show that the degradation of carbon skeleton is prior to the dehydration of free hydroxyl group after the hydrogen bond network is destroyed during pyrolysis. The thermal stability of cellulose containing C-O was $< \text{C-O}$ between glucopyranous ring and hydroxyl group in the glucopyranopyranous ring. Chen^[44] et al. Used 2D-IR to reveal the pyrolysis mechanism of lignocellulosic biomass. 2D-IR analyzed the functional group evolution of bamboo charcoal during the pyrolysis process from 250 to 600°C. The results showed that the hydrogen bond network in the macromolecular structure of biomass was destroyed below 250°C, and the branching structure was destroyed in hydration and decarboxylation reactions at 250 -300°C, resulting in the formation of H_2O , acetic acid and carbon dioxide, with the temperature of 300-350°C Various phenols were formed between due to the cleavage of ether bridge in lignin structure. The results of 2D-IR analysis show that aromatic rings with adjacent substituents are easy to form double active sites after the branching structure breaks. These structures are easy to form fused ring systems at temperatures below 400°C. dehydrogenation and polycondensation reactions occur at temperatures above 400°C, which can promote the formation of fused rings without adjacent substituents. Cellulose pyrolysis is often carried out under certain external conditions, such as slow pyrolysis at low temperature and subsequent deoxygenation degradation. Leng^[45] et al. Used in-situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy combined with two-dimensional perturbation correlation infrared spectroscopy (2D-PCIS) to analyze the functional group evolution of crystalline and amorphous cellulose during low-temperature slow pyrolysis. During the pyrolysis of cellulose, the intramolecular and intermolecular hydrogen bonds break when the temperature is higher

than 120°C, resulting in free hydroxyl groups. For both cellulose samples, the intramolecular H-bond is not as stable as the intermolecular H-bond. Due to the weakening of hydrogen bonds, various functional groups begin to decompose, especially amorphous cellulose. In the process of cellulose pyrolysis, saturated carbonyl groups are firstly produced by dehydration reaction. Since the formation temperature of saturated carbonyl group of amorphous cellulose (240°C) is lower than that of crystalline cellulose (270°C), the initial temperature of amorphous cellulose during pyrolysis is lower. When the temperature is higher than 270°C, the H-bond in the amorphous cellulose will be significantly reduced, which further promotes the decomposition of various functional groups (glycosidic bond and glucopyranosyl ring), resulting in more double bonds (i.e., carbonyl, carboxyl and conjugated olefins). Mei^[46] et al. Studied the effect of the deoxidation temperature of cellulose on the composition of liquid products obtained from subsequent pyrolysis. 2D-COS was used to analyze the evolution of functional groups in the process of low-temperature deoxidation. The main deoxidation temperature range of cellulose was determined to be 290–320°C, corresponding to the deoxidation rate of 46.32%. Under these conditions, the functional groups (such as oh and glycosidic bonds and glucopyranosyl rings) in cellulose gradually disappear and are replaced by new functional groups (such as carbonyl and carboxyl groups). This is similar to the change of functional groups during low temperature pyrolysis.

The 2D-COS analysis method is also used in the pyrolysis of hemicellulose and lignin. However, due to a large number of chemical connections between hemicellulose and lignin, they should be destroyed during the pyrolysis process. Wang^[47] et al. Explored the influence of baking process on the structural characteristics and pyrolysis behavior of hemicellulose, and carried out two-dimensional perturbation correlation analysis based on diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to characterize the structural evolution. The main reactions at low baking temperature are dehydration of hydroxyl group and dissociation of side chain, while the reactions at high baking temperature are depolymerization of hemicellulose and breakage of monosaccharide residues. The change of hemicellulose structure leads to the change of pyrolysis behavior. After baking, the activation energy of degradation reaction increased, while that of condensation reaction decreased, and the contribution of condensation reaction to devolatilization increased. In addition, the production of typical pyrolysis products, such as acids, furans, alicyclic ketones, etc., decreases after baking. Wang^[48] et al. Studied the pyrolysis characteristics of guaiacol lignin and analyzed the in-situ FTIR spectra by introducing two-dimensional perturbation correlation infrared spectroscopy (2D-PCIS). It was found that the decomposition of alcohol or phenol co bond was the main reaction of g-lignin decomposition, and methacrylate methoxy group could be easily removed from methoxy group to form CH_4 . Based on 2D-PCIS, three ways to describe lignin pyrolysis were

proposed: ①cleavage of α -O-4 chemical bond. Firstly, 3-(1-hydroxyethyl) - 4-hydroxyphenylethanol was prepared, then 2-hydroxy-5-methylacetophenone was formed by C-C bond cleavage and dehydrogenation reaction, then p-hydroxytoluene was formed by decarboxylation reaction; ②5-5'bond was cleaved. At first, 2-methoxyphenol is formed, and then it is converted into catechol through demethylation reaction. Finally, phenol and benzene are formed with the increase of temperature. ③The fracture of β -O-4 bond. The main product is coniferol, which is further converted into 2-methoxyphenol and cresol.

Pyrolysis technology is an important technology to utilize biomass, and it is also the focus and hotspot of current research. However, it is still relatively few to use 2D-COS to analyze the structural changes in the pyrolysis process. At present, some domestic scientists are mainly engaged in the research, while foreign research is relatively less. In the future, with the further popularization of 2D-COS technology, it is believed that it will be better used in biomass pyrolysis.

3.3 Application of 2D-COS in other aspects of biomass

3.3.1 identification doping test

It is difficult to distinguish different kinds of wood biomass when they are ground into powder. Two kinds of wood can be identified by 2D-COS technology. Huang^[49] et al. Quickly identified poplar and Eucalyptus from broad-leaved trees by two-dimensional infrared spectroscopy, and found that the one-dimensional infrared spectra of the two kinds of wood have great similarity, and their two-dimensional infrared spectra are in the range of 1500-1800cm⁻¹. There are great differences in the intensity and number of automatic peaks, and the number and positive and negative of cross peaks are also different, which can quickly identify poplar and Eucalyptus. Leguminosae is a unique species of Dalbergia in Hainan Province of China. It is also known as Hainan Huanghua pear wood. It has very good medicinal value, but some species of Dalbergia odorifera are very similar to him, so it is difficult to identify them. 2D-COS method is used to identify them quickly. Zhang^[50] et al. Quickly identified sandalwood and Dalbergia odorifera by 2D-IR, and found that they had different peaks on 2D-COS, which could be easily identified. Wang^[51-52] et al. Studied the identification of Dalbergia odorifera miscible tree species based on infrared spectroscopy and two-dimensional correlation spectrum. They analyzed three different kinds of sandalwood, i.e. Dalbergia odorifera, Pterocarpus erinaceus and dalbergia Belize, and selected two-dimensional synchronous correlation infrared spectra of 1100-1300cm⁻¹ band, and found that their two-dimensional correlation spectra were different, so as to distinguish them. Liu^[53] et al. Identified radix sophorae tonkinensis and radix sophorae tonkinensis by 2D-NIR. It was found that there was significant difference in 2D-NIR between the two herbs under the

condition of temperature as external disturbance and in the band of 7500-4000cm⁻¹, so it can be used as an important means to identify the two kinds of traditional Chinese medicine. Chen^[54] et al. Identified 4 kinds of vegetable edible oils by 2D-NIR under the condition of external disturbance. It is found that the 2D-NIR of 4220-4310 cm⁻¹ band has obvious difference, which can realize the identification of four kinds of vegetable oil in the concentration of external disturbance.

2D-COS has been well studied in some adulteration problems. Agarwood resin (ALR) is a kind of biomass with high medicinal value. For economic consideration, some businesses adulterate it. Qu^[55-56] et al. Used Fourier transform infrared (FT-IR) spectroscopy and 2D -IR spectroscopy to analyze and screen adulteration of agarwood. The standard ALR and adulterated samples were identified by FT-IR and 2D-IR spectra. It was found that the standard ALR had a strong peak at 1658 cm⁻¹, which refers to the conjugated carbonyl group of the resin, but there was no such peak in the adulterated samples, which indicated that the ALR contained resin components, but there were almost no or different resin components in the three adulterated samples. The position, intensity and shape of the automatic peaks of real and adulterated ALR are quite different in synchronous 2D-IR spectra with thermal disturbance. The results show that FT-IR and 2D-COS can be used as a simple and accurate method for ALR quality control. Chen^[57] et al. Used 2D-NIR analysis to identify the application of natural green cotton doping, respectively studied four groups of different proportions of natural green cotton and dyed green cotton doping, and carried out 2D-NIR analysis in the range of 4000-5500 cm⁻¹. It is found that there are great differences in the number and intensity of the automatic peaks and in the cross peaks among the four different proportions of dopants.

3.3.2 cellulose modification

After modification of cellulose, the resulting materials can also be analyzed by two-dimensional correlation analysis, and the most common analysis is the analysis of cellulose composite membrane. Popescu^[58] et al. Studied the structure and adsorption properties of PVA membrane reinforced by CNC. 2D-IR showed that the change of CH group occurred after the OH group of PVA and CNC, the co group and COH and co group distributed to the amorphous region and primary alcohol of PVA changed, which indicated the formation of H bond between PVA chain and CNC and the change of molecular conformation arrangement. Li^[59] et al. Analyzed the effective water permeability resistance of cellulose nanocomposite films, and proposed an effective method to inhibit the adsorption through hydroxyl crosslinking of epichlorohydrin (ECH). Meanwhile, graphene oxide (GO) nanosheets were used to prolong the vapor permeation pathway. 2D-COS revealed for the first time that the crosslinking of ECH does not change the permeation direction, while go can significantly act as a barrier to the formation of bound water, thus changing the sequence of the first interaction vapor

regions from crystal to crystal. Amorphous region. Free trade volume is the destination of penetration. The blocking effect of go in the amorphous region leads to the improvement of vapor barrier. Water molecules penetrate into the free volume region from the crystalline and amorphous regions. When go is added, the permeation path changes, which leads to the change of amorphous region faster than that of crystal region, which changes the permeation trend from amorphous to crystal, and then to free volume region. The mutual improvement of adsorption and diffusion processes eventually leads to a significant improvement of vapor barrier performance, which corresponds to the reduction of hydroxyl number and the extension of permeation pathway.

The application of 2D-COS in other aspects of biomass is mainly in identification, adulteration and cellulose modification. Because identification and doping are relatively mature, the research tends to be saturated, and the analysis of cellulose modified materials is just starting, which is also a direction of future development. Through 2D-COS, we can understand the change of molecular structure of cellulose during the modification process.

4 Conclusion

As a new analytical method in recent decades, two-dimensional correlation spectroscopy has been widely used in food, environment, medicine and other fields, and the application in biomass is one of them. In this paper, two-dimensional correlation spectroscopy in the study of internal molecular structure of biomass, thermochemical conversion technology and identification, doping and other three aspects of content, so that we have a further understanding and understanding of two-dimensional correlation spectroscopy.

1) The two-dimensional correlation spectrum is not directly measured by the instrument, but by measuring its one-dimensional correlation spectrum, and then through mathematical correlation analysis. PCA mentioned in this paper is a kind of mathematical analysis. In the future, looking for more other mathematical analysis methods can make us get more and more comprehensive information through spectrogram.

2) The application of two-dimensional correlation spectroscopy in biomass thermochemical conversion is mainly applied in the combustion of ethanol technology and pyrolysis technology, and we found that the combustion of ethanol technology mainly uses 2D HSQC-NMR technology, while pyrolysis technology mainly uses two-dimensional infrared correlation spectrum. Therefore, the utilization of other two-dimensional correlation spectra in biomass thermochemical conversion will be the focus of future research.

3) In recent years, the preparation of cellulose modified materials is the focus and focus of research. We see that two-dimensional correlation spectroscopy has been applied in cellulose modified membranes. So the application of two-dimensional correlation spectroscopy

in other cellulose modified materials will be the focus of future research.

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