

## The investigation of thermal decomposition pathway and products of poly(vinyl alcohol) by TG-FTIR

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**ABSTRACT:** A generalized form of a semiquantitative method has been developed based on the multilinear least-squares regression technique applied on the entire FTIR absorbance spectrum of a gaseous mixture to determine components concentration. Thermal degradation of poly(vinyl alcohol) samples with high, PVA(98), and low degree of hydrolysis, PVA(80), has been investigated by TG-FTIR simultaneous analysis performed in an inert atmosphere. Analysis of gaseous products was carried out using a routine developed in Matlab and this routine returns the product concentration with a reasonable RMS error. The correlation coefficients of the original mixture spectrum with the mixed output were obtained at some specific peak temperatures using irAnalysis software. The first process is the loss of physically adsorbed water which followed by two main processes of thermal degradation. In spite of the similarity of evolved gaseous products, two samples showed some differences in components concentrations identified in the volatile mixture. Acetaldehyde has been identified as the main volatile product in the first thermal degradation step of PVA(98) and PVA(80). The second major degradation product of PVA(80) is acetic acid due to presence of more residual acetate group while 2-butenal have been identified for PVA(98). Water was mainly produced in the first stage of thermal degradation of PVA(98) while it was identified in the first and second stages for PVA(80). This might be attributed to existence of a competition between water and residual acetate group for elimination that postpones the complete elimination of OH group to the second degradation stage. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42117.

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### INTRODUCTION

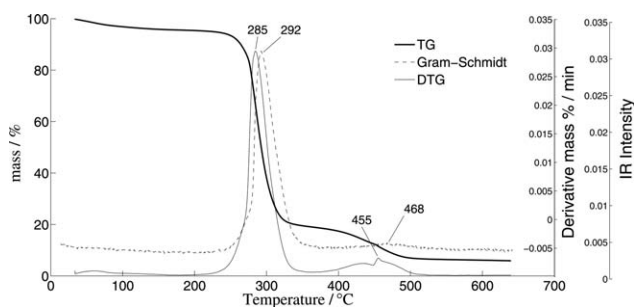
Polyvinyl alcohol (PVA) is a water-soluble, odorless, nontoxic, nonionic biodegradable, biocompatible synthetic polymer produced in large scale around the world with many interesting characteristics including excellent film forming, emulsifying, and adhesive properties, resistant to oil and grease, minimal cell, and protein adhesion property.<sup>1–4</sup> PVA exhibits a strong hydrophilic and hydrogen bonding characteristic due to its hydroxyl groups, thus it is able to form cross linked hydrogels.<sup>5</sup> Polyvinyl alcohol as a polymer with side groups has also been used to prepare conjugated polymers such as polyacetylene (PA) which are types of polymers with long conjugated double bonds and have spectacular properties and used in the areas of optical, electrical, magnetic and, in recent years, photo-catalysis fields.<sup>6–10</sup>

Polyvinyl alcohol is produced by either acid or base catalyzed alcoholysis (the term 'hydrolysis' is often used to describe this process) of poly(vinyl acetate), since vinyl alcohol monomer does not exist in the free state. The degree of hydrolysis, and

hence the residual acetate content which are themselves controlled by varying the catalyst concentration mainly affects PVAs properties. The degree of hydrolysis is the molar percentage of repetitive units with hydroxyl groups within the total repetitive units in the chain. It should be emphasized that it is the most important property of PVA since it defines its solubility in water and its surface activity. Similarly, the molecular weight is another important parameter of a polymer and is usually related to the viscosity of the aqueous form, even though the viscosity can also be affected by other factors.<sup>11</sup>

The study of thermal degradation of polymers has many interesting aims since the thermal resistance as the most dominative properties for polymer materials, affects the mechanical properties, durability, spectral stability, shelf lives, and life cycles of polymers. Evidently, as the thermal degradation begins, the above properties will gradually deteriorate.<sup>12–15</sup>

Various thermal analysis methods such as thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal



**Figure 1.** The curves of TG, DTG and the total FTIR absorbance intensity of evolved gases obtained during the poly vinyl alcohol (PVA98) pyrolysis process by TG-FTIR (heating rate  $15^{\circ}\text{C min}^{-1}$ ;  $\text{N}_2$  flow rate  $50 \text{ mL min}^{-1}$ ).

analysis (DTA), and differential scanning calorimetry (DSC), have been used for investigation of the thermal and thermo oxidative stabilities of some types of PVA.<sup>16–20</sup> Alternatively, thermal analysis coupling systems are the leading methods to reveal the thermal degradation mechanisms of polymers. For example, Fourier transform infrared/thermogravimetric analysis (FTIR/TGA) enables simultaneous quantification and identification of evolved degradation products during pyrolysis and provides well worth information on the thermal degradation of polymers and on the development of heat resistant materials.

It has been established that during the thermal degradation of PVA in the inert atmosphere, the shape of mass loss curve is consistent with the generally accepted two-step mechanisms. The first step is the result of dehydration (elimination of water) accompanied by polyene formation and the second one is pyrolyzation producing some organic volatiles products.<sup>19–21</sup> More precisely, the mechanism of the thermal degradation of PVA comprises two groups of reactions: the ones only affect functional groups (inter- or intramolecular dehydration) and those accompanied by a scission or a modification of the main chain.<sup>22</sup> As all these reactions occurs concurrently, the degradation mechanism will depend on the characteristics of the sample including molecular weight, polymerization process, contents of residual acetate groups (degree of hydrolysis) and also on heating conditions of the sample (heating rate and the surrounding atmosphere).

In this work, initially the principal of our mixture analysis routine written in the MATLAB to identify gaseous species from their characteristic absorbance by using multilinear least-squares regression is introduced. Then, the proposed method is applied to the thermal degradation of polyvinyl alcohol with two different molecular weights and degree of hydrolysis in inert atmosphere. Using this technique, the stages of thermal degradation are identified in details for two polyvinyl alcohol samples.

## THEORY

In spectroscopy, absorbance is an additive function, i.e., the absorbance of a mixture is a sum up of its components. For a mixture containing  $n$  components, the Beer–Lambert law relates the IR absorbance,  $A$ , in a specific wave number to the concentrations,  $c_i$ , of the components according to the following relation:

$$A = l \sum_{i=1}^n \varepsilon_i c_i \quad (1)$$

where  $\varepsilon_i$  is the molar absorption coefficient of the component and  $l$  is the light path length. To compute the concentration of  $n$  components, one needs to measure IR absorbance in at least  $n$  different wave numbers.

Gongwer *et al.* used both a non-negative least squares (NNLS) method<sup>23</sup> and a quadratic programming (QP) least squares optimization<sup>24</sup> to obtain the components concentration from a time series of IR spectra using a set of absorptivity matrices. The algorithm has utilized a constraint that prevents solutions with negative product concentrations.

In the recent work, Jie *et al.*<sup>25</sup> have used a semiquantitative method to determine the concentration using the FTIR absorbance spectrum of some gaseous mixtures. After identifying gaseous products from the FTIR reference spectra available on the standard web resources such as NIST<sup>26</sup> and SADTLER,<sup>27</sup> the IR absorbance ( $B_j$ ) of the mixture at a common wave number ( $\lambda_j$ ) were expressed as a linear combination of its products ( $A_{ij}$ ) at the same wave number. The coefficients of the linear combination (or contribution value of each product in the mixture) can be obtained by solving the inverse problem.

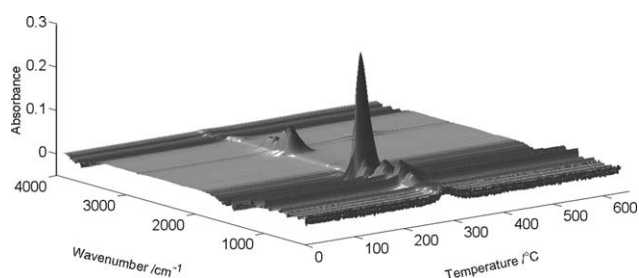
We have developed a generalized form of this method and written a mixture analysis routine in the MATLAB to determine the concentration using the entire FTIR spectrum of identified products rather than few common wave numbers. Moreover, one can add as many components to this routine as required to achieve more precise results. Our routine can be used to analyze a single FTIR spectrum obtained at a specific temperature (or time) as well as the whole TG-FTIR data can be used to obtain the concentration of each individual component versus temperature (or time).

Ignoring the difference between the experimental condition in which the standard spectra and the mixture spectrum were obtained, the total spectrum of the mixture,  $B$ , at a specific temperature can be described as

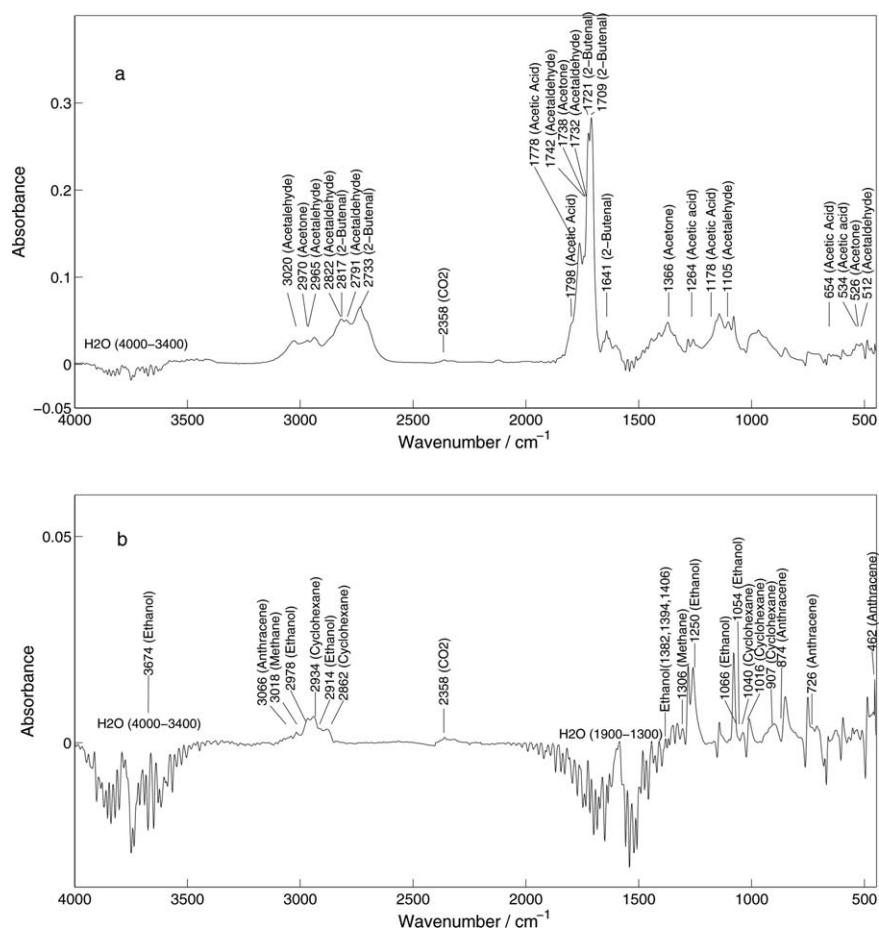
$$B_j = \sum_{i=1}^n k_i A_{ij} = l \sum_{i=1}^n k_i \varepsilon_i c_i \quad (j = 1, 2, \dots, m) \quad (2)$$

or in a matrix form as

$$A \cdot K = B \quad (3)$$



**Figure 2.** The 3D surface graph for the FTIR spectra of the evolved gases produced by polyvinyl alcohol (PVA98) pyrolysis (heating rate  $15^{\circ}\text{C min}^{-1}$ ;  $\text{N}_2$  flow rate  $50 \text{ mL min}^{-1}$ ).



**Figure 3.** The FTIR spectra of evolved gases from decomposed polyvinyl alcohol (PVA98) in  $N_2$  measured at different temperature by online-coupled TG-FTIR (heating rate  $15^\circ\text{C min}^{-1}$ ;  $N_2$  flow rate  $50\text{ mL min}^{-1}$ ): (a) at  $293^\circ\text{C}$ ; (b) at  $472^\circ\text{C}$ .

where  $k_i$  is the contribution value of component  $i$ ,  $n$  is the number of components, and  $m$  is the total wave numbers. Since the number of components are much less than that of wave numbers, there is no unique solution for  $K$ . Therefore, one of the following methods can be used to calculate the contribution values:<sup>28</sup>

1. multilinear least squares regression formulation, i.e.,

$$K = (A^T \cdot A)^{-1} \cdot A^T \cdot (B + e) \quad (4)$$

2. pseudoinverse method, i.e.,

$$K = \text{pinv}(A) \cdot (B + e) \quad (5)$$

3. matrix division method, i.e.,

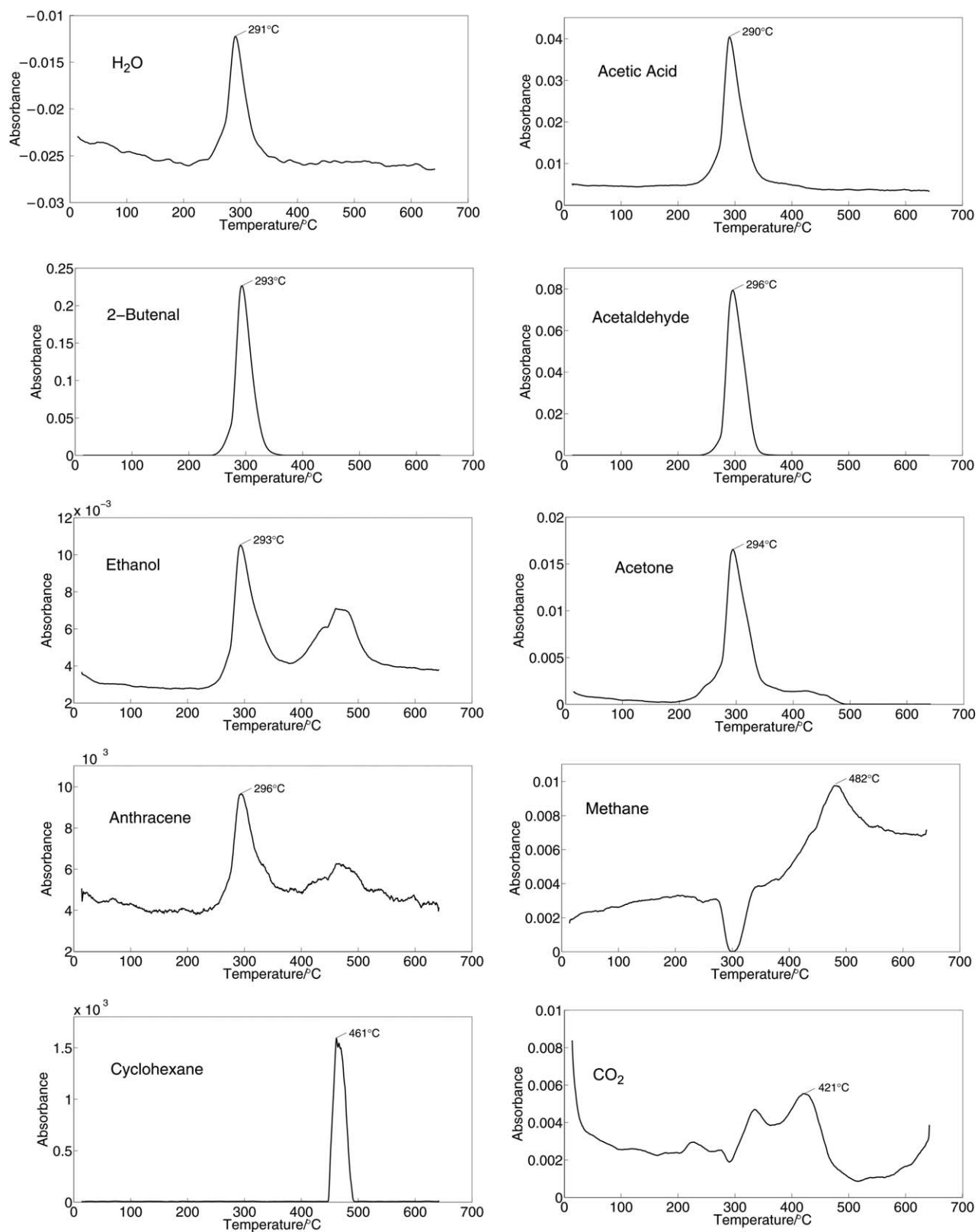
$$K = (B + e) / A \quad (6)$$

In this work, the first method has been used in which a small fraction of noise ( $e$ ) is also added to the mixture spectrum. Similar to work of Gongwer *et al.* only positive values are accepted. It should be noted that although the  $k_i$  can represents the contribution value of the selected product, the comparison

of  $k_i$ 's is meaningless since light absorbance coefficients,  $\epsilon_i$ 's, are different for the various gas products. After calculating the contribution values, an output spectrum file is generated by mixing the components with their associated contribution. The comparison between the original spectrum and the mixed output one over the entire wave number range is returned as an RMS error value. The better matching between the computed combination of the selected components and the original mixture spectrum could results in a lower value of error. This used as a measure in our work to select an appropriate combination of the product from a given list of potential candidate products in each stage of the IR analysis.

For initial identification of each product within a mixture and to compare the output mixed spectrum from the MATLAB to the original mixture, we have used irAnalyze IR spectrum interpretation software from LabCognition.<sup>29</sup> All spectral manipulations on the original mixture spectrum such as baseline correction and format conversion have also been performed using this software. The comparing algorithm was the correlation coefficients and the resulted quality parameter is reported here.

To evaluate the concentration at each temperature, the absorbance of each component is calculated at its characteristic wave



**Figure 4.** IR absorbance vs. temperature curves of identified evolved gaseous species evolved from polyvinyl alcohol (PVA98) decomposed in  $N_2$ , measured by online-coupled TG-FTIR system (heating rate  $15^\circ C \text{ min}^{-1}$ ;  $N_2$  flow rate  $50 \text{ mL min}^{-1}$ ).

**Table I.** Gas Phase Mixture Analysis Results for Characteristic Spectra Curve of PVA (98) at 292°C

Product	Concentration (ppm)
2-Butenal	1179
Acetaldehyde	1611
Acetic acid	120
Acetone	328
H <sub>2</sub> O	1161
Anthracene	18
Ethanol	235
CO <sub>2</sub>	4

number where it has the highest value of the molar absorption coefficient,  $A_{\max}$ , multiplied to its contribution value and then divided to the maximum molar absorption coefficient of the component,  $\epsilon_{\max}$  and to the light path length, i.e.,

$$c_i = k_i A_{\max} / l \epsilon_{\max} \quad (7)$$

The maximum molar absorption coefficients were obtained from the standard web resources such as NIST<sup>26</sup> and PNNL<sup>30</sup> and from related literatures.<sup>31,32</sup> It is worth to mention that both  $A_{\max}$  and  $\epsilon_{\max}$  depends on temperature, however, we have used the  $\epsilon_{\max}$  value at 296 K.

## EXPERIMENTAL

### Materials

Poly vinyl alcohol with an average molecular weight,  $\bar{M}_w$ , 72,000 g mol<sup>-1</sup> and hydrolysis grade >98%, PVA(98), was purchased from Merck. Polyvinyl alcohol with an average molecular weight,  $\bar{M}_w$ , 9000–10,000 g mol<sup>-1</sup> and hydrolysis grade of 80%, PVA(80), was purchased from Sigma-Aldrich.

### Measurements

Thermogravimetric-FTIR measurement was carried out with a Perkin Elmer Pyris STA 6000 thermo-gravimetric analyzer and Spectrum 1 FTIR spectrometer. Samples (~10 mg) were placed in an aluminum crucible, and heated from the room temperature to 650°C in a 50 mL/min flow of nitrogen. TGA and FTIR apparatuses were connected by a heated transfer line, TL 8000 from Perkin, having a silcosteel-coated copper tube wrapped with heating coils, surrounded with insulation and length of 1 m. It was heated to 270°C in order to prevent the gas condensation. The lag time was nearly 5 s. FTIR spectra were collected

with 2 cm<sup>-1</sup> resolution in the range of 4000–400 cm<sup>-1</sup>. The IR cell with a path length of 100 mm was used.

## RESULTS AND DISCUSSION

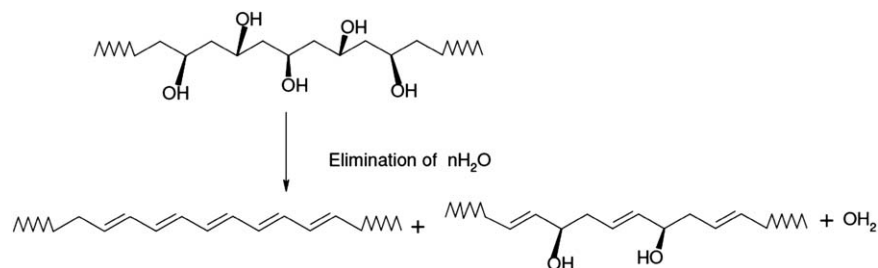
### Thermal Decomposition of PVA(98)

Figure 1 illustrates weight loss (TG), associated derivative thermogram (DTG), and total infrared absorbance (Gram–Schmidt curve) profiles of polyvinyl alcohol as a function of temperature at the heating rate of 15°C/min. In this figure, the lag time of the evolved gases passing through the IR cell has been subtracted. The TG curve shows three distinct weight loss stages. The first stage which occurs at temperature up to 150°C and is attributed to the loss of the physically absorbed water. The major part of weight loss occurs at temperature between 200 and 300°C followed by further weight loss (third stage) between 350 and 450°C, leaving a residue of approximately 10%.

For the last two stages, a comparison of the Gram–Schmidt curve with the DTG one indicates that the temperature of IR absorbance peaks at 292 and 468°C respectively coincide with those of the DTG peaks at 285 and 455°C.

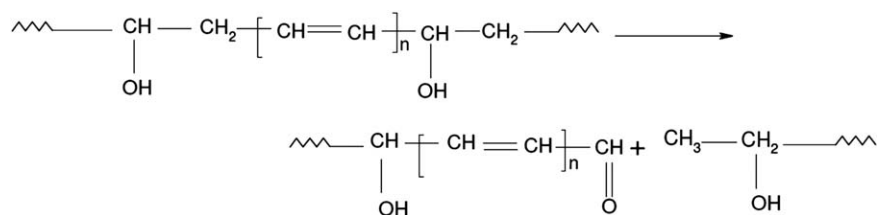
The 3D FTIR spectrum of the volatile pyrolysis products of polyvinyl alcohol, PVA98, at different temperature (time) is shown in Figure 2. It can be seen in Figure 2 that water and CO<sub>2</sub> are present over the entire temperature range so it is necessary to apply a baseline correction algorithm when calculating the concentration. The characteristic spectra obtained at 292 and 468°C are depicted in Figure 3.

From this figure, the following small molecular gaseous species were identified from their characteristic absorbance by our mixture analysis routine written in the MATLAB from the potential candidate products reported in literature,<sup>14,33–35</sup> carbon dioxide ( $\nu_{C=O}$  2358 cm<sup>-1</sup>), H<sub>2</sub>O ( $\nu_{O-H}$  3400–4000 cm<sup>-1</sup>,  $\delta_{O-H}$  1300–1900 cm<sup>-1</sup>); 2-butenal ( $\delta_{C-H}$  966 and 1146 cm<sup>-1</sup>,  $\nu_{C=C}$  1641 cm<sup>-1</sup>,  $\nu_{C=O}$  1709 cm<sup>-1</sup>,  $\nu_{C=O}$  1721 cm<sup>-1</sup>,  $\nu_{C-H}$  2733 cm<sup>-1</sup>,  $\nu_{C-H}$  2817 cm<sup>-1</sup>); acetaldehyde ( $\delta_{C-C=O}$  512 cm<sup>-1</sup>,  $\nu_{C-C}$  1105 cm<sup>-1</sup>,  $\nu_{C=O}$  1732 cm<sup>-1</sup>,  $\nu_{C=O}$  1742 cm<sup>-1</sup>,  $\nu_{C-H}$  2791 cm<sup>-1</sup>, and 2832 cm<sup>-1</sup>,  $\nu_{CH_3}$  2965 cm<sup>-1</sup>, and 3020 cm<sup>-1</sup>); acetone ( $\delta_{C-O}$  526 cm<sup>-1</sup>,  $\delta_{CH_3}$  1366 cm<sup>-1</sup>,  $\nu_{C=O}$  1738 cm<sup>-1</sup>,  $\nu_{CH_3}$  2970 and 2946 cm<sup>-1</sup>); acetic acid ( $\gamma_{C-O}$  534 cm<sup>-1</sup>,  $\delta_{O-H}$  1264 cm<sup>-1</sup>,  $\nu_{C-O}$  1178 cm<sup>-1</sup>,  $\nu_{C=O}$  1775 cm<sup>-1</sup>,  $\nu_{C=O}$  1795 cm<sup>-1</sup>); ethanol ( $\nu_{C-O}$  902 cm<sup>-1</sup>,  $\nu_{C-O}$  1054 cm<sup>-1</sup>,  $\nu_{C-O}$  1066 cm<sup>-1</sup>, (CH<sub>3</sub>)  $\delta_{C-H}$  1250 cm<sup>-1</sup>, (CH<sub>2</sub>)  $\nu_{C-H}$  2914 cm<sup>-1</sup>, (CH<sub>2</sub>)  $\nu_{C-H}$  2978 cm<sup>-1</sup>,  $\delta_{O-H}$  1406 cm<sup>-1</sup>,  $\nu_{O-H}$  3674 cm<sup>-1</sup>); methane ( $\delta_{C-H}$  1306 cm<sup>-1</sup>,  $\nu_{C-H}$  3018 cm<sup>-1</sup>); anthracene ( $\gamma_{C-C}$  462 cm<sup>-1</sup>,  $\gamma_{C-H}$  726 cm<sup>-1</sup>,  $\gamma_{C-H}$  874 cm<sup>-1</sup>,  $\nu_{(C-H)}$

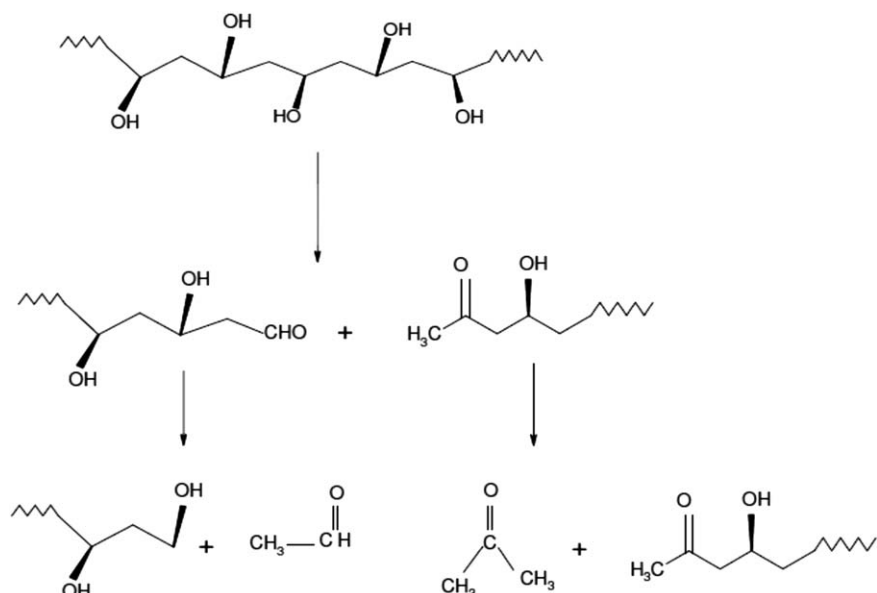


**Scheme 1.** Elimination reaction of H<sub>2</sub>O.





Scheme 2. Chain scission reaction of producing unsaturated aldehydes.

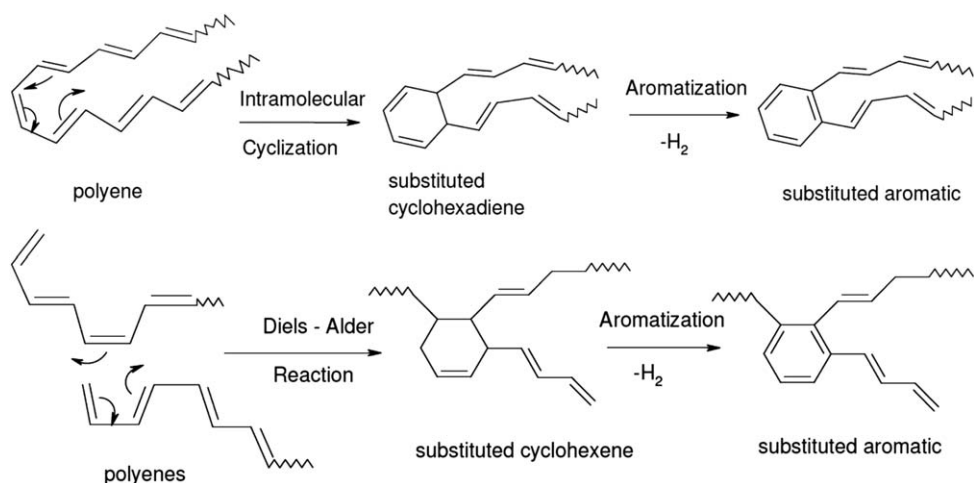


Scheme 3. Chain scission reaction producing saturated aldehydes and ketones.

3066  $\text{cm}^{-1}$ ); cyclohexane ( $\delta_{\text{CH}_2}$  907  $\text{cm}^{-1}$ ,  $\nu_{\text{SCH}_2}$  2863  $\text{cm}^{-1}$ ,  $\nu_{\text{aCH}_2}$  2933  $\text{cm}^{-1}$ ).

Figure 4 illustrates the evolution curves of all identified gases where, except for  $\text{H}_2\text{O}$ , the absorbance at its characteristics wave number was calculated. For  $\text{H}_2\text{O}$ , the absorbance at the maximum point of 3700–4000  $\text{cm}^{-1}$  was used to avoid interferences with the absorbance of other products.

Inspecting the evolution pass of the various products versus temperatures in Figure 4 reveals that the pyrolysis process of PVA(98) is rather complicated. In the first main stage, water is produced by the elimination of side-groups at higher temperatures until 300°C. In addition to water, 2-butenal (of unsaturated aldehydes), acetaldehyde (of saturated aldehydes), acetone (of saturated ketones), anthracene (of benzene derivatives), acetic acid, ethanol, and carbon dioxide are also evolved in this



Scheme 4. Aromatization reactions.

**Table II.** Gas Phase Mixture Analysis Results for Characteristic Spectra Curve of PVA (98) at 468°C

Product	Concentration (ppm)
H <sub>2</sub> O	54
Methane	46
Anthracene	7
Ethanol	127
Acetic acid	1
CO <sub>2</sub>	3
Acetone	8
Cyclohexane	10

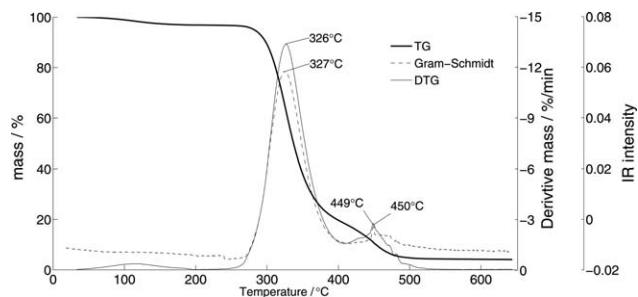
stage. The mixture analysis routine for the FTIR spectra of the evolved gases from PVA(98) at 293°C was applied with 99.1% correlation coefficient value between the original mixture spectrum and the output mixed one. By taking into account the products molar absorption coefficients and the light pass length of the IR cell, the concentrations of the products were calculated according to relation (7) and listed in Tables I and II at the temperature of 292 and 468°C, respectively.

By examining the concentrations of the identified products in Table I and the absorbance values of the products in Figure 3, acetaldehyde, 2-butenal, and water are the main products in this stage. As previously stated in the introduction section, the following mechanisms of several parallel reactions are being suggested for the formation of the products in Table I as in Schemes 1–4. The first groups of reactions step is the elimination reactions, (inter- or intra molecular dehydration) that produce water and traces of acetic acid and conjugated and nonconjugated polyenes (Scheme 1).

The second groups are accompanied by a chain scission and produce unsaturated aldehydes from conjugated polyenes (2-butenal or crotonaldehyde for  $n = 1$ ) (Scheme 2) and saturated aldehydes (acetaldehyde) and ketones (acetone) from poly vinyl alcohols chains (Scheme 3).

As a modification in chain groups of reaction, it has been suggested<sup>22</sup> that the inter and intramolecular reactions produce aromatic derivatives and in turn, they are obtained from polyenes produced from the elimination reactions in the PVA thermal decomposition. From a list of suggested aromatic compounds in literature,<sup>33</sup> even though different aromatics such as toluene, naphthalene, anthracene, and their alkyl derivatives well match the mixture spectrum, however, anthracene was identified with minimum RMS error value from the evolved volatiles and is considered to be produced by the following rearrangement of the chains of polyene groups (Scheme 4)

The last stage occurs at about 475°C which is, in general, suggested to be related to the PVA backbone breakdown by production of mainly hydrocarbons such as  $n$ -alkanes and aromatic hydrocarbons. From a list of small alkanes (C<sub>1</sub>–C<sub>9</sub>) and some alkenes (e.g., ethylene, propene, butene), the identified products were cyclohexane, nonane, and methane which result in minimum RMS error value and have maximum intensity at this

**Figure 5.** The curves of TG, DTG, and the total FTIR absorbance intensity of evolved gases obtained during the poly vinyl alcohol (80) pyrolysis process by TG-FTIR (heating rate 15°C min<sup>-1</sup>; N<sub>2</sub> flow rate 50 mL min<sup>-1</sup>).

region. Since the calculated concentration of nonane was less than 1 ppm, it was omitted from the products list. Moreover, the second minor peaks for ethanol and anthracene are also identified to place in this region. By applying the mixture analysis routine, it was found that ethanol is the main gaseous product of this stage along with the others listed in Table II. The correlation coefficient of this stage was 93.3% due to the presence of some unidentified components. CO<sub>2</sub> is produced from the decomposition of acetate radicals as it has been stated in polyvinyl acetate thermal degradation procedure.<sup>36</sup>

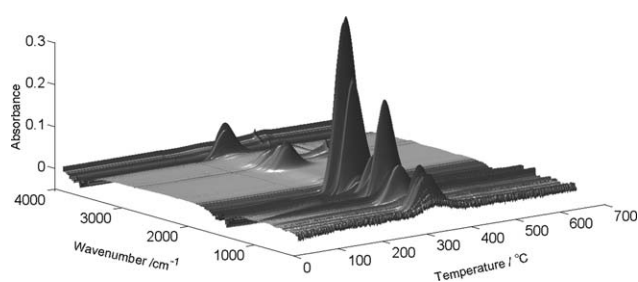


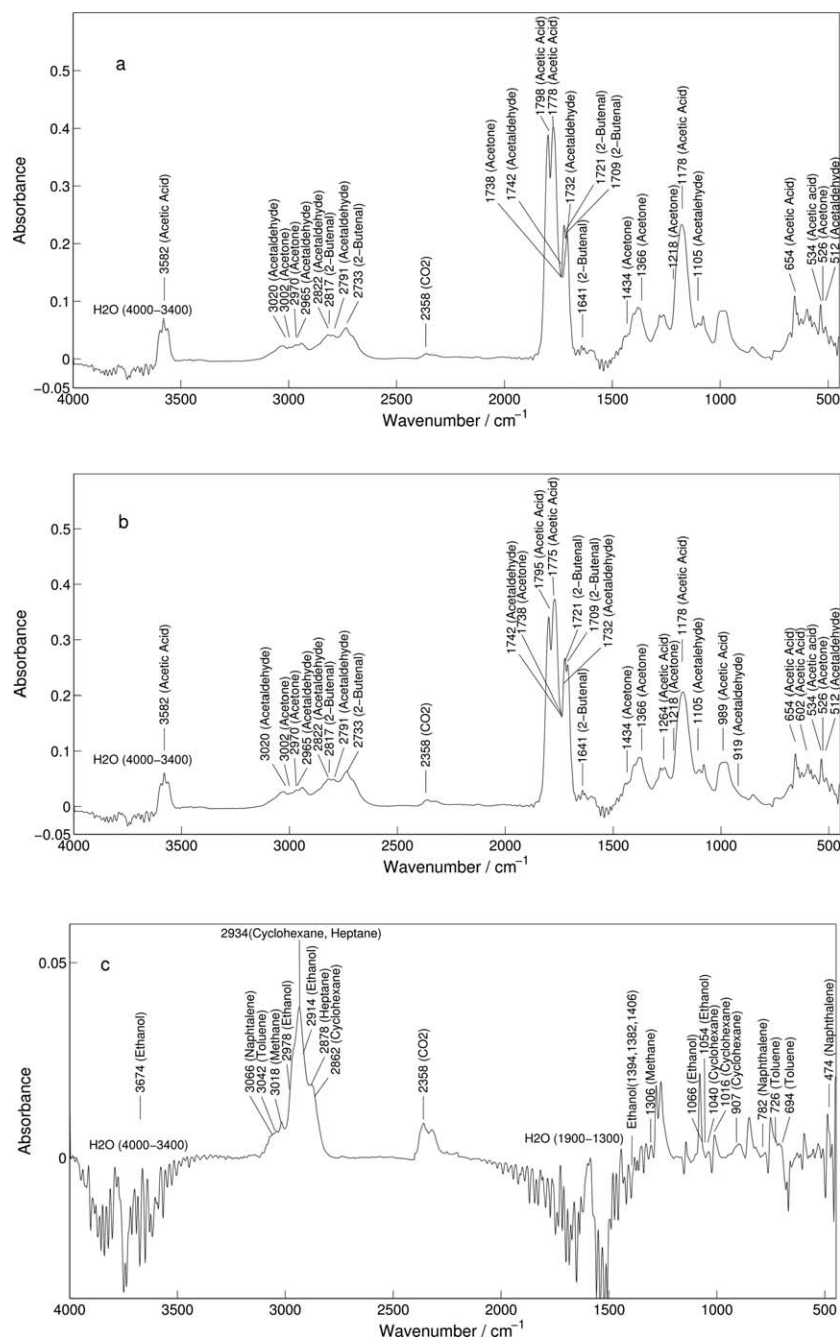
It seems methane and cyclohexane are produced by free radical attacks of polyenes which was formed through elimination reactions. However, some of methane is also appeared to be produced from decomposition of acetate radicals.

### Thermal Decomposition of PVA(80)

The weight loss, the associated derivative thermogram and the total infrared absorbance profile of the poly vinyl alcohol (PVA80) as a function of temperature are shown in Figure 5 at the heating rate of 10°C/min. The lag time of the evolved gases passing through the IR cell has been subtracted. The Gram-Schmidt curve shows a major relatively broad peak existing at 327°C and a minor nearly distinct peak at 450°C.

Three weight loss stages can be located in the TG curve of PVA(80). Similar to PVA(98) thermal degradation path, the first stage in the TG curve observed up to 200°C is attributed to the loss of the absorbed water. The major part of the weight loss occurs at temperature between 300 and 350°C followed by

**Figure 6.** The 3D surface graph for the FTIR spectra of the evolved gases produced by polyvinyl alcohol(80) pyrolysis (heating rate 15°C min<sup>-1</sup>; N<sub>2</sub> flow rate 100 mL min<sup>-1</sup>).



**Figure 7.** The FTIR spectra of evolved gases from polyvinyl alcohol PVA(80) decomposed in  $N_2$  measured at different temperature by online-coupled TG-FTIR (heating rate  $10^\circ\text{C min}^{-1}$ ;  $N_2$  flow rate  $50\text{ mL min}^{-1}$ ): (a) at  $320^\circ\text{C}$ ; (b) at  $330^\circ\text{C}$ ; (c) at  $450^\circ\text{C}$ .

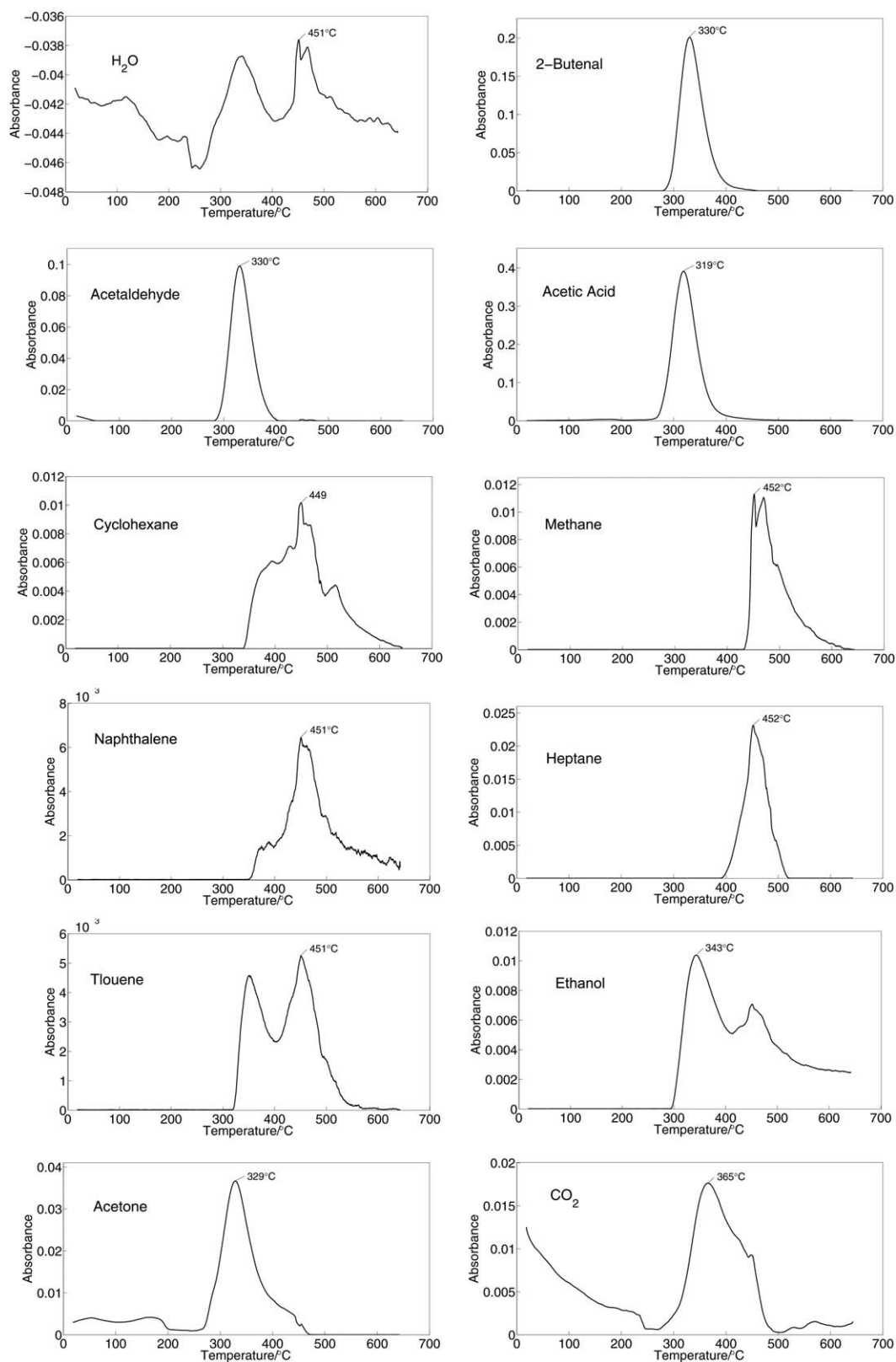
further weight loss between 400 and  $450^\circ\text{C}$  leaving a residue of approximately 13%. The last weight loss stage observed as a peak at temperatures above  $400^\circ\text{C}$  at the DTG curve is related to PVA backbone breakdown.<sup>22</sup> For the last two stages, a comparison of the Gram–Schmidt curve with the DTG one indicates that the temperature of IR absorbance peaks at 327 and  $450^\circ\text{C}$  respectively coincide with those of DTG peaks at 326 and  $449^\circ\text{C}$ .

An examination of the TG curves and the weight loss diagrams in Figures 1 and 5 reveal some significant differences in the samples of PVA(98) and PVA(80) which have different degrees

of hydrolysis. The TG peaks occur at higher temperatures as the degree of hydrolysis decreases. In other words, the weight loss increases with an increase in the content of residual acetate groups.<sup>37</sup> This is due to the elimination of acetic acid, the intramolecular and intermolecular elimination of water, and probably an increase in the extent of scission reactions with the formation of small and more volatile fragments.<sup>38,39</sup>

Figure 6 is the 3D FTIR spectrum of the evolved gases of PVA(80) pyrolysis at different temperature (time), and the characteristic spectrum of all the volatile products produced at 320, 330, and  $450^\circ\text{C}$  are also shown in Figure 7. These points are the





**Figure 8.** IR absorbance vs. temperature curves of identified evolved gaseous species evolved from polyvinyl alcohol(98) decomposed in N<sub>2</sub>, measured by online-coupled TG-FTIR system (heating rate 20°C min<sup>-1</sup>; N<sub>2</sub> flow rate 100 mL min<sup>-1</sup>).

**Table III.** Gas Phase Mixture Analysis Results for Characteristic Spectra Curve of PVA (80) at 320°C

Product	Concentration (ppm)
Acetic acid	1269
2-Butenal	856
H <sub>2</sub> O	500
Acetone	662
Acetaldehyde	1703
Ethanol	192
CO <sub>2</sub>	18

temperatures of the peak points of the deconvoluted curves obtained from partitioning of the derivative thermogram (DTG) into three distinct processes using our new coupled peak deconvolution method.<sup>37</sup>

From this figure, the following small molecular gaseous species were identified from their characteristic absorbance by our mixture analysis routine written in the MATLAB from the potential candidate products reported in literature:<sup>14,33–35</sup> carbon dioxide ( $\nu_{\text{C=O}}$  2358  $\text{cm}^{-1}$ ); H<sub>2</sub>O ( $\nu_{\text{O-H}}$  3400–4000  $\text{cm}^{-1}$ ,  $\delta_{\text{O-H}}$  1300–1900  $\text{cm}^{-1}$ ); 2-butenal ( $\delta_{\text{C-H}}$  966 and 1146  $\text{cm}^{-1}$ ,  $\nu_{\text{C=C}}$  1641  $\text{cm}^{-1}$ ,  $\nu_{\text{C=O}}$  1709  $\text{cm}^{-1}$ ,  $\nu_{\text{C=O}}$  1721  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  2733  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  2817  $\text{cm}^{-1}$ ); acetic acid ( $\nu_{\text{C-O}}$  534  $\text{cm}^{-1}$ ,  $\delta_{\text{CCO}}$  582  $\text{cm}^{-1}$ ,  $\nu_{\text{C-O}}$  1178  $\text{cm}^{-1}$ ,  $\nu_{\text{C=O}}$  1778  $\text{cm}^{-1}$ ,  $\nu_{\text{C=O}}$  1798  $\text{cm}^{-1}$ ,  $\nu_{\text{O-H}}$  3582  $\text{cm}^{-1}$ ); acetone ( $\delta_{\text{C-O}}$  526  $\text{cm}^{-1}$ ,  $\delta_{\text{CH}_3}$  1366  $\text{cm}^{-1}$ ,  $\delta_{\text{CH}_3}$  1434  $\text{cm}^{-1}$ ,  $\nu_{\text{C=O}}$  1738  $\text{cm}^{-1}$ ,  $\nu_{\text{CH}_3}$  2970 and 2946  $\text{cm}^{-1}$ ); acetaldehyde ( $\delta_{\text{C-C=O}}$  512  $\text{cm}^{-1}$ ,  $\nu_{\text{C-C}}$  1105  $\text{cm}^{-1}$ ,  $\nu_{\text{C=O}}$  1732  $\text{cm}^{-1}$ ,  $\nu_{\text{C=O}}$  1742  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  2791  $\text{cm}^{-1}$  and 2832  $\text{cm}^{-1}$ ,  $\nu_{\text{CH}_3}$  2965  $\text{cm}^{-1}$  and 3020  $\text{cm}^{-1}$ ); ethanol ( $\nu_{\text{C-O}}$  902  $\text{cm}^{-1}$ ,  $\nu_{\text{C-O}}$  1054  $\text{cm}^{-1}$ ,  $\nu_{\text{C-O}}$  1066  $\text{cm}^{-1}$ ,  $(\text{CH}_3)$   $\delta_{\text{C-H}}$  1250  $\text{cm}^{-1}$ ,  $(\text{CH}_2)$   $\nu_{\text{S-C-H}}$  2914  $\text{cm}^{-1}$ ,  $(\text{CH}_2)$   $\nu_{\text{C-H}}$  2978  $\text{cm}^{-1}$ ,  $\delta_{\text{O-H}}$  1406  $\text{cm}^{-1}$ ,  $\nu_{\text{O-H}}$  3674  $\text{cm}^{-1}$ ); methane ( $\delta_{\text{C-H}}$  1306  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  3018  $\text{cm}^{-1}$ ); heptane ( $\nu_{\text{C-H}}$  2934,  $\nu_{\text{C-H}}$  2878); cyclohexane ( $\delta_{\text{CH}_2}$  907  $\text{cm}^{-1}$ ,  $\nu_{\text{S-CH}_2}$  2863  $\text{cm}^{-1}$ ,  $\nu_{\text{CH}_2}$  2933  $\text{cm}^{-1}$ ); toluene ( $\nu_{\text{C-H}}$  695  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  728  $\text{cm}^{-1}$ ,  $\nu_{\text{C=C}}$  1498  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  2933  $\text{cm}^{-1}$ , 2868  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  3071  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  3032  $\text{cm}^{-1}$ ); naphthalene ( $\nu_{\text{C-C}}$  462  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  726  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  874  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  3066  $\text{cm}^{-1}$ ).

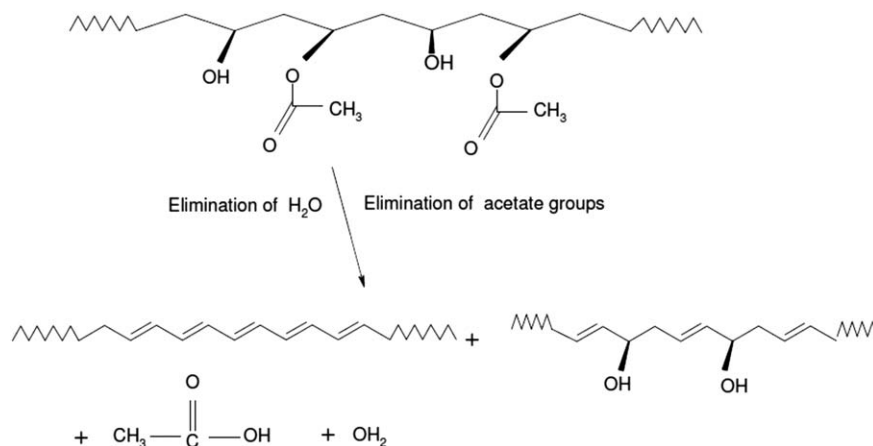
The evolution curves of the all identified gases are shown in Figure 8 which indicate the PVA(80) pyrolysis process is generally similar to that of PVA(98) in products with some differences in details. In the first stage, acetic acid was produced by the elimination of side-groups with peak temperature at 320°C. The mixture analysis routine for the FTIR spectra of the evolved gases from PVA(80) at 320°C was applied with 99.4% correlation between the original mixture spectrum and the output mixed one. The concentrations of the products at this temperature are listed in Table III.

Examining the concentration values of the identified products in Table III and the absorbance values of the products in Figure 8, acetaldehyde and acetic acid rather than water are the main product of this stage. In this case, due to the lower degree of hydrolysis, the presence of more acetate side-groups ready for elimination reaction causes acetic acid dominates to water (Scheme 5).

In the second main stage, starting at temperature about 330°C, as at temperature 320°C, acetaldehyde, acetic acid, water, ethanol, 2-butenal, and acetone have been identified in gaseous phase. The concentration values resulted from applying the mixture analysis routine for the FTIR spectra of the evolved gases of PVA(80) with 99.4% correlation between the original mixture spectrum and the output mixed one are given in Table IV. The major products of the second stage are again acetaldehyde and acetic acid. However, in this stage the increased formation of acetaldehyde and decreased production of acetic acid occurred. Indeed, the peak temperature of acetaldehyde formation took place at 330°C. Further increase in the temperature causes toluene with low intensity peak to be produced.

Finally in the last stage, at about 450°C, heptane, methane, and cyclohexane were observed. The strong peaks of naphthalene and toluene, and the weak peak of ethanol were also occurred in this stage. The concentration values resulted from applying the mixture analysis routine on the FTIR spectra of the evolved gases from PVA(80) with 96% correlation are listed in Table V.

It can be found from Figures 4 and 8 that water was mainly produced in the first stage of thermal degradation of PVA(98) while it was identified in the first and second stages for

**Scheme 5.** Elimination reaction of H<sub>2</sub>O and acetic acid.

**Table IV.** Gas Phase Mixture Analysis Results for Characteristic Spectra Curve of PVA (80) at 330°C

Product	Concentration (ppm)
Acetic acid	1107
2-Butenal	1011
H <sub>2</sub> O	583
Acetone	708
Acetaldehyde	1998
CO <sub>2</sub>	29
Ethanol	270
Toluene	15

PVA(80). The existence of water at high temperature of PVA thermal degradation has already been reported by Khormai *et al.*<sup>40</sup> This may be attributed to existence of a competition between water and residual acetate group for elimination. The competition might prevent the complete elimination of OH group in the first thermal degradation stage of PVA(80) and postpone it to the second stage.

The mechanistic routes of forming naphthalene and toluene may be considered through aromatization reactions similar to anthracene formation path shown in Scheme 4. Comparing the results in Tables II and V, it is obvious that CO<sub>2</sub> was produced in larger amount in this case due to the presence of more residual acetate group.<sup>36</sup>

Identifying toluene or naphthalene in the last stage of thermal degradation of PVA(80) rather than more rings of anthracene in case of PVA(98) may be attributed to the lower molecular weight and the presence of short chains of polymer in PVA(80).

## CONCLUSIONS

TG-FTIR systems provide significant data for investigation of thermal degradation in materials and can arise approaches into solid state reactions from qualitative assessment to a practical quantitative analysis using powerful software techniques as a complementary part of the reactions kinetic studies. In this

**Table V.** Gas Phase Mixture Analysis Results for Characteristic Spectra Curve of PVA (80) at 450°C

Product	Concentration (ppm)
H <sub>2</sub> O	806
Cyclohexane	91
Heptane	219
Methane	65
CO <sub>2</sub>	34
Ethanol	214
Toluene	44
Naphthalene	22
Acetone	30
Acetic acid	13
2-Butenal	4

research work, a generalized form of a semiquantitative method was developed to determine the components concentration in the FTIR absorbance spectrum of gaseous mixtures using the whole FTIR spectrum. This method was applied to the complex process of thermal degradation of Polyvinyl alcohol samples with two different degrees of hydrolysis to identify the volatile products. The concentration of the products and correlation values of the original mixture spectrum and the output mixed one at some specified peak temperatures were also calculated.

The pyrolysis process products of two PVA samples were almost similar in the main stages except for the differences in concentration. For the first main step of thermal degradation of PVA(98) and PVA(80), the main volatile product is acetaldehyde. The second major degradation product of PVA(80) is acetic acid due to presence of more residual acetate group while 2-butenal is the second major product of thermal degradation of PVA(98). In the last backbone cleavage stage of PVA(80) which has lower molecular weight, smaller aromatic compounds were identified compared to the volatile products of thermal degradation of PVA(98) in this stage.

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