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THERMAL DEGRADATION STUDY OF FURFURAL RESINS BY DTA AND DI-PY/MS

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ABSTRACT. The thermal degradation of two furfural's resins has been studied by Differential Thermal Analysis (DTA) and Direct Inlet Pyrolysis-Mass Spectrometry (DI-Py/MS). The identities of main volatile products were established by both electron impact and chemical ionization techniques.

RESUMEN. Se estudió la degradación térmica de dos resinas del furfural mediante Análisis Térmico Diferencial (ATD) y Pirólisis por Introducción Directa en el Espectrómetro de Masas (Py-ID/EM). Se identificaron los principales productos empleando las técnicas de ionización química e impacto electrónico.

INTRODUCTION

Structural characterization of insoluble and infusible polymers and resins is a very difficult task in macromolecular chemistry. Different techniques can be employed for this purpose: non destructives (e.g. ^{13}C NMR magical angle-cross polarization and FT-IR) or destructive (pyrolitic techniques). The rapid extension of destructive analytical techniques (pyrolisis) into diverse fields has been due to progress in the characterization of biological macromolecules and infusible polymers.[1]

Direct Inlet Pyrolisis-Mass Spectrometry (DI-Py/MS is a suitable method for analyzing the initial thermal fragmentation processes ocurring when polymers are degraded by heat. In this technique materials are decomposed by heating on the direct inlet probe and the volatile products are analyzed giving characteristic mass spectra of polymers.[2-4] A qualitative analysis of most polymers can be obtained whithin few minutes.

The use of soft ionization methods contributes to a better identification of thermal degradation products by *mass spectrometry* because they give the posibility to identify molecular species presents in the mixture.[5]

The aim of the present work was to characterize the thermal behavior of insoluble resins from furfural by means of the characteristic mass spectra of their volatile products formed by pyrolysis and thermoanalytical curves of the solid resins.

EXPERIMENTAL PART

Resins

The resins (FH and FAH) were obtained in bulk from fresh vacuum distilled furfural and mixture of furfural and dimethylketone respectively, using strong mineral acid as catalyst. The resins were purified throroughly until elimination of remained monomer and catalyst and afterwards they were dried in high vacuum conditions.

Differential Thermal Analysis

The thermal studies of FH and FAH resins were carried out using a Paulik-Erdey Derivatograph in nitrogen atmosphere. The temperature range was 30 to 1 000 °C with the following parameters:

Thermogravimetric curve (TG) measuring range 0 to 350 mg .
Heating rate: 10 °/min
Nitrogen flow rate: 2,5 cm^3/min
Crucible: platinum

Direct Pyrolysis-Mass Spectrometry

Portions of both resins were ground to powder (ϕ = 0,25 mm) and samples of 20 mg were taken for pyrolysis.

Mass spectra were obtained by sample heating on the direct inlet probe of a JEOL Mass Spectrometer-(DX300) from 80 to 400 °C, using a quartz sample tube. Two different heating rates were used: 16 and 64 °C/min .

Mass spectra were obtained in the Electron Impact (EI) and Chemical Ionization (CI) modes using:

Source temperature	250 °C
Accelerating voltage	3 KV
Emission current	300 μA
Overall mass range	30 to 400

The electron energy employed were 70 and 250 eV by FH and FAH respectively and the reagent gas in chemical ionization was methane.

The Spectra were recorded at 1 decay per second on hard disks (4,56 M) and processed by a JMA-3100 Mass Data Analysis System.

RESULTS

The DTA curves of both samples (Fig. 1) show one endothermic effect around 100 °C which can be attributed to water desorption. From of TG and DTG curves the amount of water loss was evaluated finding that FH and FAH samples losses 5 and 7,4 % of total sample weight respectively.

The thermal decomposition of resins began around 180 °C and maximum decomposition rate was attained at 400 °C . The total weight losses up to 1 000 °C for FH and FAH samples were 43,6 and 49,2 % respectively (Table I) which indicate that FH is thermically more stable than FAH resins.

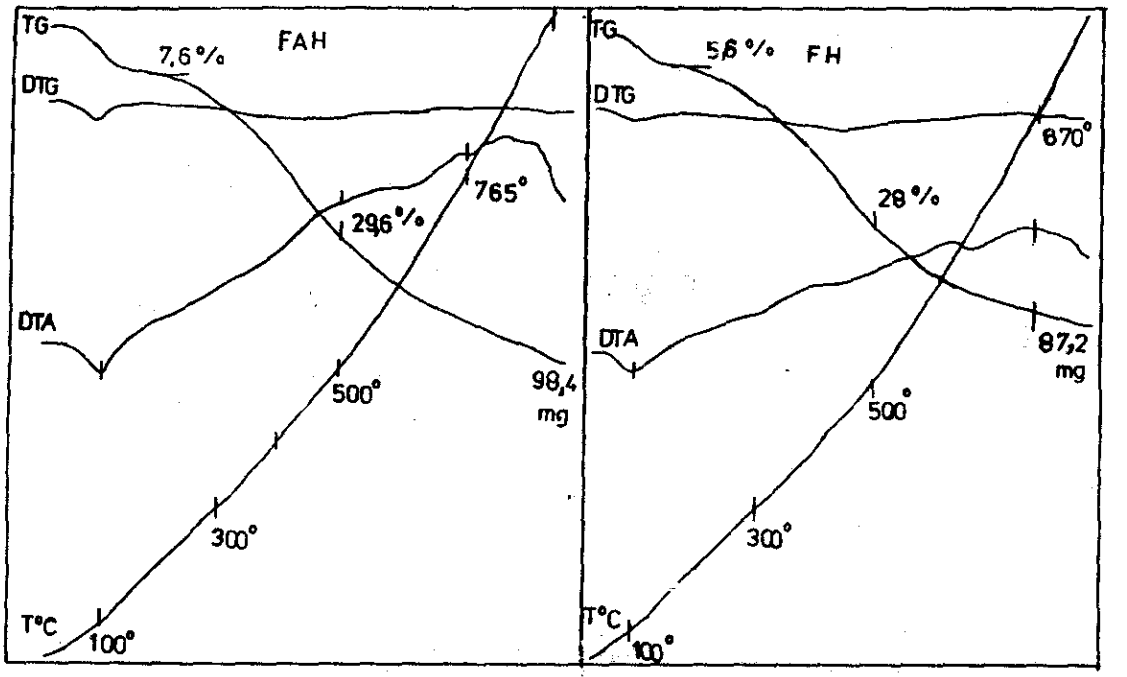

Fig. 1. Thermograms of FH and FAH resins

TABLE I

FAH (sample weight: 200 mg)			FA (sample weight: 200 mg)		
Temperature (°C)	weight (mg)	loss (%)	Temperature (°C)	weight (mg)	loss (%)
100	14,8	7,4	100	10,0	5,0
200	15,2	7,6	200	11,2	5,6
300	22,4	11,2	300	20,0	10,0
400	38,4	19,2	400	36,8	18,4
500	59,2	29,6	500	56,0	28,0
600	72,0	36,0	600	60,4	30,2
1 000	98,4	49,2	1 000	87,2	43,6

The DTA curve of both samples showed two important exothermic effects; at 400 °C, where the rate of thermal decomposition was maximum in both samples and a more broad section between 550 and 990 °C where the weight loss rate decreases and in which it is impossible to define a specific transition in the thermogram. Thermal transition at 400 °C is associated with the decomposition of the most labile structural fragments whereas at higher temperature a more complete decomposition of the most labile structural fragments whereas at higher temperature a more complete decomposition of the material is obtained.

On the basis of these results, a maximum temperature of 400 °C was choosen for pyrolysis experiments.

FAH samples

A plot of Total Ion Courrent (TIC) vs. probe temperature shows a characteristic degradation profile of the material. The TIC corresponds to the amount of volatile products.

The curve of TIC vs. probe temperature presented two relative maxima (one of them was a shoulder) around 300 and 400 °C (peaks 1 and 2 in figure 2) regardless the heating rate employed. Mass spectra corresponding to the second peak is shown in figure 3. These Spectra are reather complex suggesting the presence of a mixture of several degradation products. However, no qualitative differences were observed in mass spectra obtained from peak 1 and 2 of the TIC curve.

The main fragments of these spectra are those corresponding to m/z 44; 58; 60; 68; 82; 96; 110; 136; 148; 162; 176 and 191. This last fragment probably was origined from an ionic species derived from a fragment of higher molecular mass. It can be seen that the relative amounts of fragments of higher m/z were increased at 400 °C .

The thermal degradation profile using CI (Fig. 2b) is quite similar to that obtained with EI.

Mass spectra at 400 °C is shown in figure 3b and from from these spectra were identified, the molecular species presents in the mixture of degradation products from to signals M+1 (45; 59; 69; 83; 97; 111; 137; 149; 163 and 177).

The initial knowledge of the system under study and a comparision of spectra resulting from EI and CI modes allowed us to make the following assignation (Table II).[6]

It is known that the main advantage of DP-MS technique consists on the possible of detection of initial thermal degradation products from pyrolysis. When volatile products are formed into the ion source, under high vacum conditions, they are quickly removed from the heating zone, decreasing the probability of molecular collisions and thus reducing the ocurrence of secondary reactions.[7].

Therefore it is possible to propose some general considerations related to chemical structure of this resin on the basis of experimental results and our assignation of identities.

The relative large amounts of carbon dioxide and acetic acid are indicative of the presence of a high content of carbonyl group in the resin structure.

The detection of several furan derivatives confirm that the furan ring exists in resin structure and remains in a large extent as an unit under the thermal degradation conditions employed.

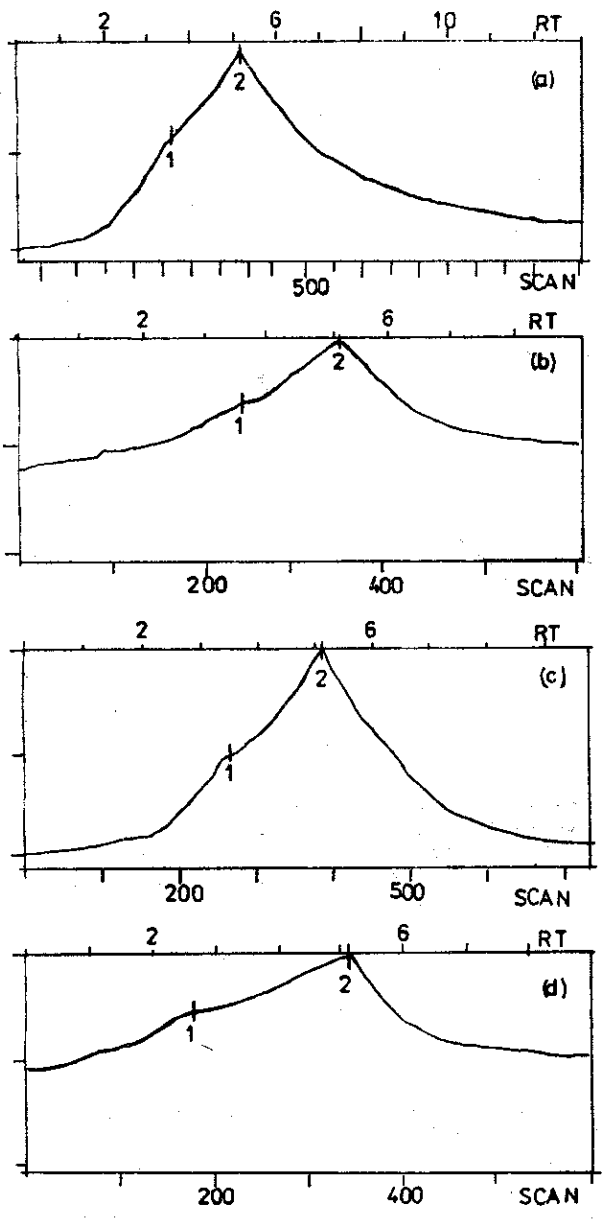

Fig .2. Degradation profile of FAH and FH by EI and CI. a FAH/EI; b FH/CI; c FH/EI and d FH/CI

The fact furfural and acetone, which are the initial monomers for the synthesis of this resin, appeared as important products of the thermal degradation can be explained assuming that they remain as basic structures taking part in the FAH's structure.

The appearence of monomers as pyrolytical products using DP-MS have been demonstrated for several regular polymers and also in carbon-phenol resins.[8]

FH samples

The results obtained in EI and CI modes (Figures 2c y d) were very similar to that of FAH samples. In their points near 300 and 400 °C mass spectra were recorded and following the same procedure already described for FAH samples the spectra (EI and CI, figures 4a y b) were analyzed and pyrolysis products were assigned (Table II).

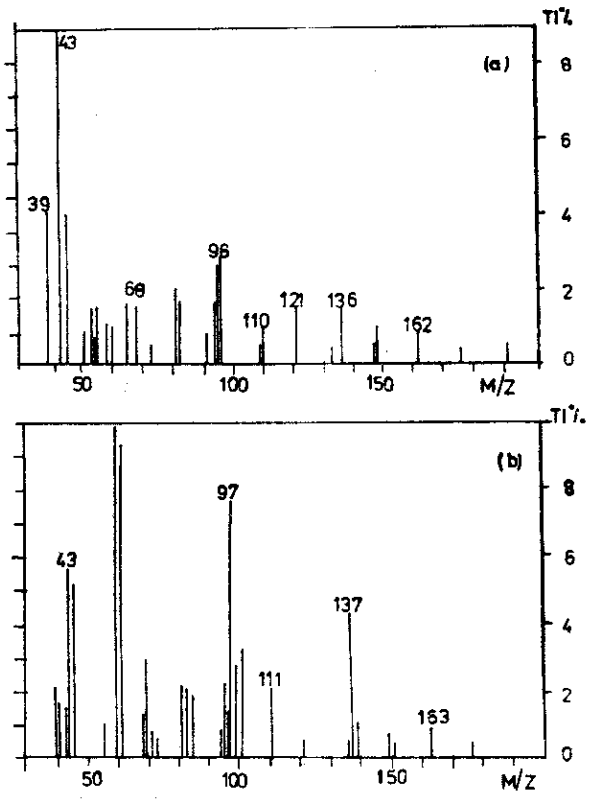

Fig. 3. Mass spectra of FAH (point 2) a EI and b CI

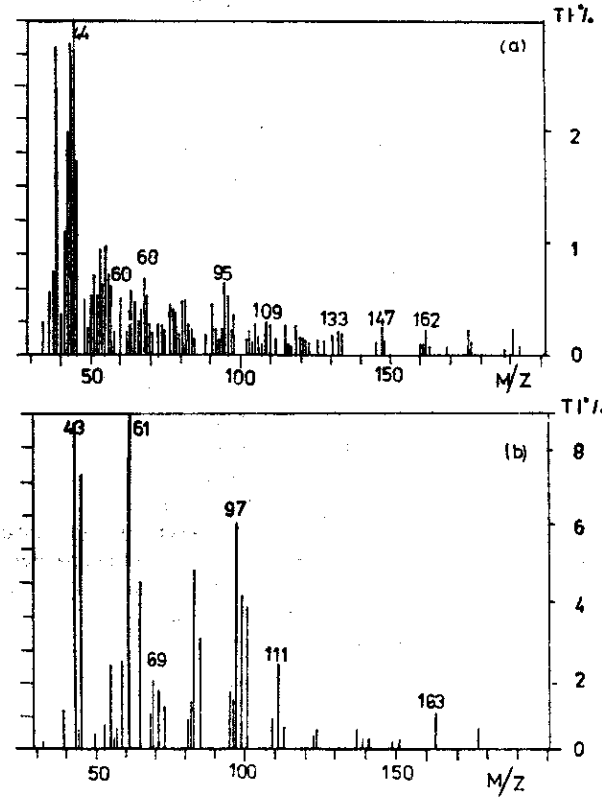

Fig. 4. Mass spectra of FH (point 2) a EI and b CI

TABLE II

m/z (EI)	M+1 (CI)	assignation FAH	FH
44; 43	45	carbon dioxide,	idem
		ethanal	idem
58; 43	59	dimethyl ketone	idem
60; 45	61	acetic acid	idem
68; 39	69	furan	idem
82; 53; 43	83	2-methyl furan	idem
96; 95; 68; 39	97	furfural	idem
96; 95; 81; 53; 43	97	2-5 dimethyl furan	idem
-	101	not identified	
110; 95; 81; 53; 43	111	methyl 2-furil	
		ketone	idem
110; 109; 81	111	-	5-methyl
			furfural
136; 121; 94; 65	137	furfurildenketone	-
148; 120; 94; 91; 81	149	di 2-furil methane	idem
162; 119; 91; 43	163	2-[(5-methyl furyl)	
		furyl methane	idem
176	177	not asignated	idem

The main fragments which appeared in these spectra are similar to those obtained in FAH samples.

An interesting experimental result in both samples is the existence of similar relative amounts of methyl 2-furylketone independently of the presence or not of acetone as initial reactant in the synthesis.

It could be observed that fragment with m/z ratio 136 is not present among major FH's fragments while the pattern fragmentation for 5-methyl furfural (m/z 110) is a characteristic feature in mass spectra of this resin.

These differences in pyrolysis products point to structural differences between FAH and FH resins which will be discussed in more detail in further papers.

CONCLUSIONS

FH resin is thermicaly more stable than FAH resin.

Employing DP-MS/EI and DP-MS/CI techniques structural differences between both resins and identities of main pyrolysis products could be estabilshed.

The existence of several furan derivatives as pyrolysis products of FAH and FH resins suggested that these compounds contribute in a large extent to the structure of these resins.

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