Article

Study of Analytical On-line Pyrolysis of Oils from Macauba Fruit (*Acrocomia sclerocarpa* M) via GC/MS

I.C.P. Fortes[a], and P.J. Baugh[b]

[a]*Departamento de Química, ICEx, Universidade Federal de Minas Gerais,*

31270-901 Belo Horizonte - MG, Brazil

[b]*Department of Chemistry and Applied Chemistry, University of Salford,*

Salford M5 4WT, UK

Estudos pirolíticos dos óleos vegetais das partes (endocarpo mais mesocarpo e epicarpo) do fruto da Macauba (*Acrocomia sclerocarpa* M.) foram realizados sob atmosfera de hélio usando-se um pirolisador de filamento modelo Girdel 75 -Py -1, conectado diretamente a um CG/EM.

Os experimentos foram realizados em diferentes temperaturas e tempos de pirólise, para avaliar como estes parâmetros afetam o processo pirolítico de obtenção dos produtos bem como a sua reprodutibilidade.

A pirólise dos óleos gerou grande número de compostos tais como hidrocarbonetos, aldeídos e ácidos carboxílicos, este último refletindo a composição original dos óleos.

A identificação de alguns compostos foi feita com o uso de um banco de dados , dos padrões de fragmentação das classes de compostos e dos cromatogramas de massas de alguns íons específicos tais como m/z 83, 85 e 60.

O modo de ionização química positiva foi utilizado para confirmar as massas molares dos constituintes gerados a partir das pirólises, tendo como gás reagente, o metano, (CH4-CI).

Pyrolytic studies of vegetable oils of Macauba (Acrocomia *sclerocarpa* M.) fruit's parts (endocarp plus mesocarp and epicarp) were undertaken under a helium atmosphere using a filament pyrolyser, Girdel Pyrolyzer 75-PY-1, coupled directly to a GC/MS.

The investigation was performed using different temperatures and pyrolysis times to evaluate how these parameters affect the yield products and the reproducibility of the pyrolytic process.

The pyrolysis of both oils yields a large number of compounds such as hydrocarbons, aldehydes and carboxylic acids, the latter reflecting the original composition of the oils.

The identification of some compounds was carried out using a mass spectral library data base search (NIST) together with recognition of fragmentation pattern and mass chromatograms of some specific ions such as m/z 83, 85 and 60.

The CH4-CI mode was used to confirm molecular weights of the constituents generated from pyrolysis, in some instances.

Keywords: *PY/GC/MS, Macauba fruit* (Acrocomia sclerocarpa *M.), on-line pyrolysis, vegetable oils*

Introduction

The need for different alternative sources of energy and technology using Brazilian natural resources have motivated many studies of *biomass* as a renewable energy source[1]. In addition, *biomass* is the only renewable source of raw material to the chemical industry and represents the only long term source of carbon[2]. Therefore it is important, in order to preserve in some ways our environment, to direct our efforts towards developing new technology to increase the use of derivatives from biomass in the chemical industry.

Biomass is, however, generally poorly suited for direct energy use and pre-treatment is necessary to change its physical and chemical forms[1].

Pyrolysis of *biomass*, in particular, vegetable oils, has been studied since World War II. At that time studies

concerning the chemical composition of the volatile compounds obtained were not completed, owing to the limitation in instrumental and analytical methods[3]. The direct thermal cracking of fatty acids (FFAs) and triglycerides (TGs) in the presence or absence of a catalyst, such as bentonite[4], lignin[5], calcium oxide[6-8] and zeolites[9-10] has been reported. During the last decade, the research into new concepts and processes for higher oil yields and new analytical techniques to elucidate the mechanisms of formation and constitution of the resulting pyrolysates has undergone a technological renaissance of the investigations in the area of pyrolysis[1,11].

A natural source of a composite mixture of triglycerides (TGs) is the oleaginous plants, which comprises a large part of the vast and diversified flora of Brazil. The plant of interest here is the Macauba tree (*Acrocomia sclerocarpa* M), in particular, the oils from the Macauba fruit. This tree is native to different regions in Brazil, which are located mainly in the centre of the country and, in particular, in the state of Minas Gerais[8].

We report herein a study carried out with a filament pyrolyser coupled to a GC/MS, using a flash pyrolysis procedure, employing the oils from Macauba fruit to investigate the effects of pyrolysis time and temperature on the yields of a particular pyrolysate composition. Experiments were performed to obtain information on the influence of these parameters upon the mechanism of pyrolysis of these oils, which is still largely unknown.

Materials and Analysis

Sampling

The Macauba fruit has a spherical slightly flattened shape with an external diameter in the range of 3 to 6 cm and colour of the fruit varying from brownish to yellowish green[12-13].

The fruit comprises an epicarp or external shell, a mesocarp or pulp and an epicarp or kernel which envelopes one or two nuts[12-13].

The Macauba fruit was divided into two parts. The outer part comprised a mixture of external shell and pulp and the inner part, the endocarp nut. Both were dried at 80 °C to constant weight, ground into powder, extracted with hexane under a Soxhlet reflux for 72 h and concentrated by distillation to give the vegetable oil extracts[8].

The composition of each oil, obtained after their esterification with BF_3 in methanol is summarised in Table 1.

Conditions and methodology

Pyrolysis was performed using a Girdel Pyrolyser 75-Py-1, a filament pyrolyser connected to a GC/MS (Finnigan Mat 1020). A gas and power control unit, a cable and a probe comprise the Girdel Pyrolyser 75-Py-1. Helium was used as the carrier gas. The system was purged for a short

Table 1. Composition in percentage of fatty acids present in inner and outer oils from Macauba Fruit (*Acrocomia sclerocarpa* M).

Fatty acids	Relative Percentage	
	Inner	Outer
Caprylic acid	2.10	Traces
Capric acid	3.72	Traces
Lauric acid	38.89	2.93
Myristic acid	11.00	1.88
Palmitic acid	17.35	22.30
Palmitoleic acid	-	5.28
Margarinic acid	-	4.34
Stearic acid	4.34	5.75
Oleic acid	22.60	52.82
Linoleic acid	-	4.69

time (30 s) with the carrier gas before each injection and the probe connected directly to the GC injector. The sample was dispensed, as a thin film onto the filament and the solvent was allowed to evaporate before starting the pyrolysis procedures. The carrier gas was diverted through the control unit and probe ensuring that the volatile pyrolysate wad transferred from this device to the GC/MS equipment without any loss.

Preliminary experiments were performed in triplicate using different temperatures (400 to 1000 °C) and pyrolysis times (10, 20 and 30 s). Further experiments were carried out at a given temperature (700-800 °C) and different pyrolysis times (10, 20 and 30 s) to study the behaviour , reproducibility of the pyrolytic process.

GC/MS analysis

Electron impact (EI) mode

General profiles of the pyrolysates were carried out using EI mode. Analyses were conducted on a Finnigan Mat model 1020 automated GC/MS using a fused capillary column (14 m x 0.25 mm; d_f = 0.15 μm; DB1, J & W Scientific) with dimethylsiloxane as the stationary phase. Helium was used, as the carrier gas, at a flow rate of 1 mL/min. Aliquots of 1 μL of the sample in hexane together with 1μL of a mixture of standard compounds (d_{10} - biphenyl, d_{10} - anthracene, d_{10} - pyrene) at 100 μg/mL as internal standard were spread onto the filament for pyrolysis. This set was employed as a parameter to locate the molecular weights of the compounds when the library search was performed as well as to confirm the reproducibility of the pyrograms.

The injection mode was short splitless with a 1s delay. The column was held at 35 °C for 2 min and then heated to 300 °C, at 20 °C/min. The final temperature was held constant for 2 min.

Chemical Ionisation (CI) mode

Analyses, in a PCI (positive chemical ionisation) mode, were carried out on a GC model HP 5890 series II and MS model VG Trio 1000, using a fused capillary column (11 m x 0.32 mm, d_f = 0.25 μm, DB5, J &W Scientific), and helium as the carrier gas and methane as the reagent gas. The GC conditions used were the same as for EI mode.

Compounds identification

The presence of different classes of compound from pyrolysates was confirmed using the total ion chromatogram (TIC) and mass chromatogram (MC) analyses, in addition to fragmentation patterns[16-19] and library search (NIST). Identification was carried out according to pre-established criteria for the analysis of the data[17].

Data analysis

To obtain the data from the different experiments the following steps were undertaken:

• TIC of each experiment at a specific condition : mode of injection, temperature and pyrolysis time;

• Preliminary identification of the main peaks using the computer library data. The peaks were considered identified when the library response for purity was > 900 and fit was > 975. Positive chemical ionization (CH_4- CI) was also used in an attempt to confirm the molecular weight of compounds;

• Identification of classes of compounds to which the main peaks belonged;

• A specific m/z characteristic of each class of compound was selected, for instance, alkane (m/z 85), alkene (m/z 83), alkynes or dienes (m/z 81), fatty acids (m/z 60 and 73), derivatives of cyclohexene (m/z 54 and 67);

• Identification of the target compounds (however, in some cases only the base peak was identified);

• Quantification of the peaks in terms of relative percentage was done using a software from the data system: SR and QL-QR-MQ-EQL;

• The resulting data from quantification were compared for all replicate experiments, by a Fortran programme, at a given condition such as mode of injection, temperature and pyrolysis time;

• Answers are registered into new files called RESULTS which were transferred to a spreadsheet. Statistical parameters such as mean, standard deviation, variance and error were calculated;

• Each class of compound was classified according to its characteristic m/z and after that, constituents which belong to each class were added up to give a global view of the yield of products obtained.

Results and Discussion

Studies were carried out to evaluate the influence of the temperature and pyrolysis time on the behaviour and reproducibility of the process as well as the changes in the yield of products of both oils from Macauba fruit.

It has been reported[7,14,15] that a mixture of triglycerides submitted to a thermal cracking process, should undergo to decarboxylation, disproportionation and successive elimination of ethylene molecules yielding to some classes of compounds such as hydrocarbons and carbonylic compounds. In addition, the sample can undergo many different reactions such as hydrogenation and oxidation, the latter one providing the greatest difference between the cracking of vegetable oils and petroleum as the latter does not generate carbonyl groups in products[14,15].

Preliminary studies

It was observed that the samples underwent a desorption like process rather than pyrolysis at lower temperatures (400 °C to 600 °C) and fixed pyrolysis time. The real pyrolytic process took place in the temperature range between 700 °C and 1000 °C, which could be observed by the changes in the total ion chromatogram (TIC), which become more complex as the temperature was increased, as shown in Fig. 1.

The pulp and nut oils only underwent partial pyrolysis. The pulp was more resistant to this process probably due to higher degree of unsaturation. Both oils led to carboxylic acids compounds generated from triglycerides of which the original oil is composed (see Table 1). A major peak (m/z 44), at the beginning of the chromatographic run, indicated the presence of carbon dioxide, probably originated from decarboxylation of fatty acids[9].

A general feature of the pyrolysates of the pulp and nut oils is summarised in Fig. 2 , which shows the presence of several compounds, some of which were identified as indicated in Tables 2 e 3.

Analysis by EI mode

The driving force in the cracking of the pulp oil under helium atmosphere was the formation of aldehydes, cycloalkanes, alkenes, and dienes. The paramount product generated was 2-propenal or acrolein, a known product when triglycerides are pyrolysed[15]. Some compounds classified as unknown were also detected, which exhibited different base peaks and are reffered to as unknown m/z 55 and unknown m/z 67. In addition, the presence of small amounts of alkanes, alkenynes, alkylbenzene and cycloalkene were also evident (see Table 4).

The pyrolysis of the nut oil leads to alkenes, aldehydes and carboxylic acids as major products, as indicated in Table 5. The pyrolysate also exhibits cycloalkane, alcohol, alkane and some components, with base peaks at m/z 54 or
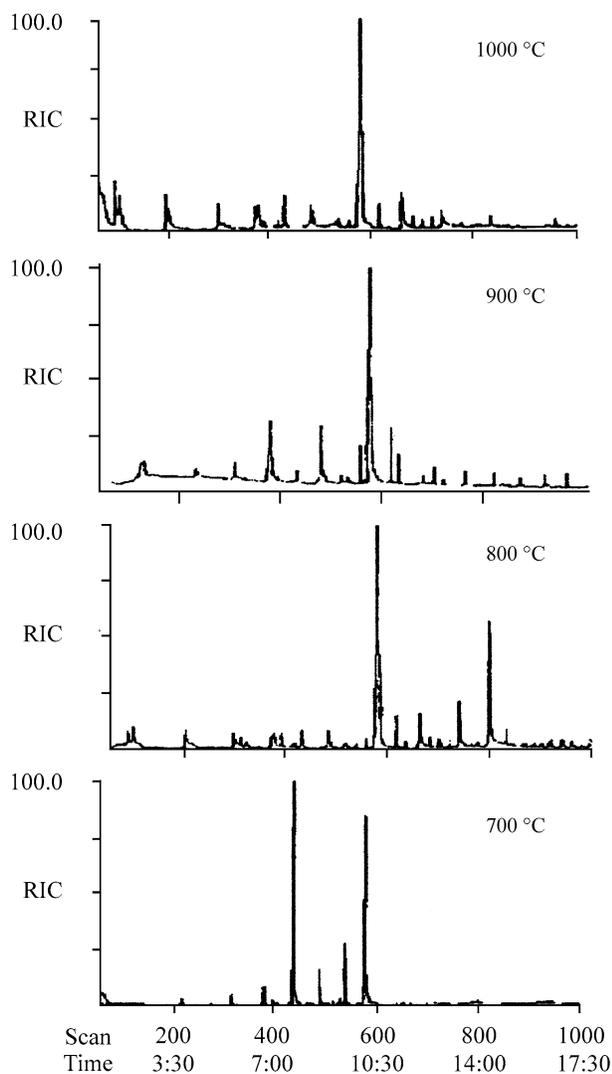
Figure 1. Comparison between pyrogram profiles at different pyrolysis temperatures (700-1000 °C)and the same pyrolysis time(30 s) by PI/CG/MS for nut oil.

67, which are here classified here as unknown. These compounds are considered to be associated with cyclohexene derivatives[20-22]. Other constituents with base peaks, m/z 55 and m/z 57 were also noticed.

Some classes of compounds are common to pyrolysates products such as aldehyde, cycloalkane, alkene , alkane and those reffered as unknown/55 but others are not. These differences should be associated to the composition of the original oils.

The products generated by the pyrolytic process from both oils when compared to their respective calcium soap pyrolysates, are quite different[8,14,15]. In the latter case the main products are comprised of homologue series of n-alkane, 1- alkene and some carbonylic compounds.
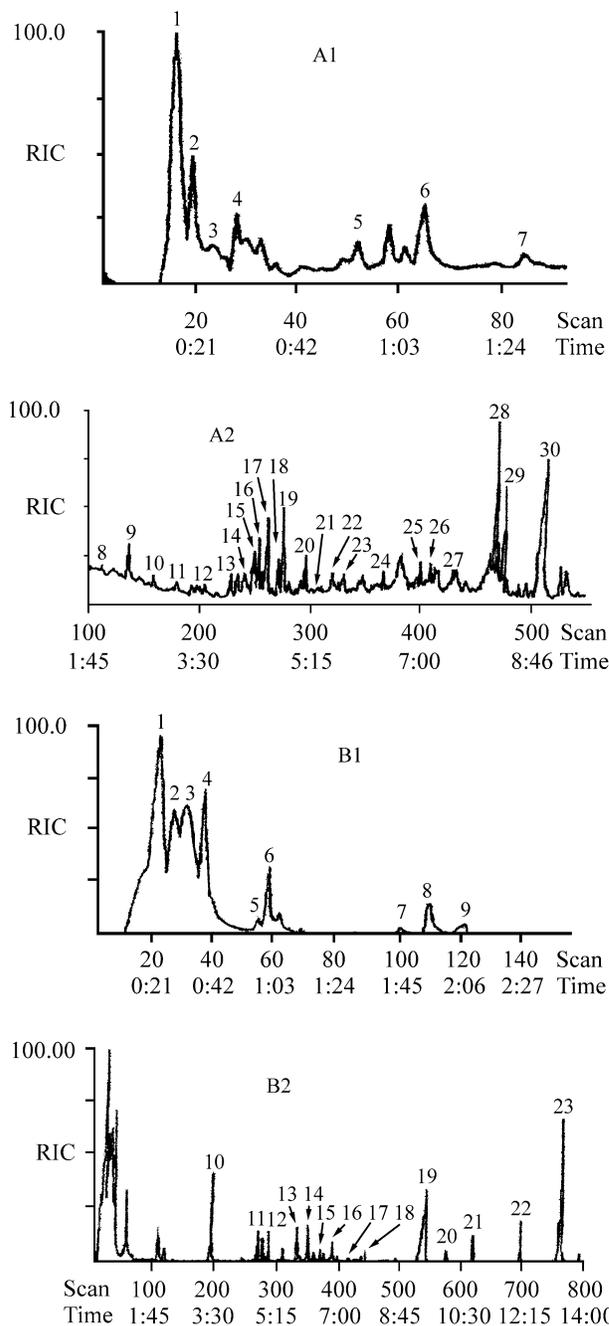
Figure 2. General GC/MS features (TIC) of pyrolysed oils (A1 e A2) Pulp oil; (B1 e B2) Nut oil.

Analysis by CI Mode

The crucial problem with the analysis in EI mode is the lack of molecular weight data for many of the compounds, which made the identification more difficult. CH_4-CI/MS was used to overcome this problem in an attempt to match the identification and the molecular weight of the compound identified using EI mode. To ensure that the compound in EI mode was the same in CI mode the relative

Table 2. Some identified constituents of pulp oil pyrolysate.

No.	Class of compounds	Identification	Relative t_R	t_R	MW	B.Pk	Formula
1	aldehyde	2-propenal	0.043	0.263	56	41	C_3H_7O
2	alkene(diene)	1-3cyclohexadiene	0.052	0.315	80	79	C_6H_8
3	alkene	1-penten-2-methyl	0.057	0.350	84	56	C_6H_{12}
4	cycloalkane	cycloalkane(isomerC_7H_{14})	0.089	0.543	98	56	C_7H_{14}
5	alkene(diene)	1-4-heptadiene-3-methyl	0.115	0.700	110	81	C_8H_{14}
6	unknown	unknown	0.129	0.788	110	67	C_8H_{14}
7	alkene	1-octene	0.144	0.875	112	55	C_8H1_6
8	alkene	1-heptene-3-methyl	0.172	1.050	112	55	C_8H_{16}
9	alkylbenzene	propylbenzene	0.218	1.330	--	91	-----
10	alkene(diene)	1.3nonadiene(-E)	0.256	1.558	124	55	C_9H_{16}
11	unknown	unknown	0.290	1.768	--	54	-----
12	alkene(diene)	2-4nonadiene(E-E)	0.325	1.978	124	81	C_9H_{16}
13	alkene	1-nonene	0.391	2.380	126	55	C_9H_{18}
14	cycloalkane	cyclopentane-1-methyl-2propyl	0.457	2.783	126	55	C_9H_{18}
15	alkylbenzene	butylbenzene	0.494	3.010	134	91	$C_{10}H_{14}$
16	alkene(bycyclo)	bycyclo[2.2.1]heptene-2-2dimethyl	0.537	3.273	136	79	$C_{10}H_{16}$
17	cycloalkene	cyclodecene(-E)-isomers	0.586	3.570	138	67	$C_{10}H_{18}$
18	aldehyde	2-nonenal	0.655	3.990	140	55	$C_9H_{10}O$
19	unknown	unknown	0.667	4.060	--	67	-----
20	unknown	unknown	0.695	4.235	--	67	------
21	cycloalkane	cyclopropane-1-ethenyl-2hexene	0.710	4.323	150	79	$C_{11}H_{18}$
22	cycloalkane	isomer	0.727	4.428	150	79	$C_{11}H_{18}$
23	cycloalkane	isomer	0.753	4.585	150	79	$C_{11}H_{18}$
24	cycloalkane	isomer	0.770	4.690	150	79	$C_{11}H_{18}$
25	alkene	1-undecene	0.779	4.743	154	55	$C_{11}H_{22}$
26	alkenyne	5-dodecen-7yne(E)	0.822	5.005	164	79	$C_{12}H_{20}$
27	alkenyne	5-dodecen-7-yne(Z)	0.868	5.285	164	79	$C_{12}H_{24}$
28	unknown	unknown	0.914	5.565	164	81	-----
29	unknown	unknown	0.934	5.688	--	55	------
30	alkene	1-dodecene	0.046	6.370	168	55	$C_{12}H_{24}$
31	unknown	unknown	1.138	6.930	--	67	-----
32	alkane	decane2-4dimethyl	1.170	7.123	170	57/43	$C_{12}H_{26}$
33	unknown	unknown	1.227	7.473	--	67	-----
34	unknown	unknown	1.236	7.525	--	67	------
35	alkene(diene)	1-2tridecadiene	1.336	8.138	18O	67	$C_{13}H_{24}$
36	unknown	unknown	1.526	9.293	--	67	-----
37	unknown	unknown	1.629	9.923	--	67	-----

retention time to biphenyl (t_R = 6,74 min) was used as a reference.

Pyrolysis behaviour

Studies of the behaviour of the pulp and nut oils at different temperatures and pyrolysis time have shown different trends in profile (see Figs. 3 and 4, and Tables 4 and 5).

Pulp oil

The products of the pyrolysate can be classified into three categories: main products (> 10%), secondary products (3%-10%) and tertiary products (< 3%). The overall trend was the same for both worked temperatures. At 700 °C the main products (aldehyde, cycloalkane, alkene and diene) correspond to 71-79% of the total products; the secondary products (unknowns/55, 67 and others and alkylbenzene) ranging between 19 to 26% and the remaining

Table 3. Some identified constituents of nut oil pyrolysate.

No.	Class of Compounds	Identification	t_R	MW	B.Pk	Formula
01	aldehyde	2 - propenal	0.282	56	41	C_3H_4O
02	alkene	1- pentene - 2 methyl	0.371	84	56	C_6H_{12}
03	alkane	n-hexane	0.438	86	57	C_6H_{14}
04	cycloalkane	cycloalkane (isomer C_7H_{14})	0.577	98	56	C_7H_{14}
05	alkane	heptane/ hexane- 3 methyl	0.598	100	57/43	C_8H_{16}
06	alkene	1-heptene 3 - methyl or cyclopropane 1,2-diethyl	1.068	112	55	C_8H_{16}
07	alkane	octane/hexane 2,4 dimethyl or hexane,3-ethyl	1.114	114	57/43	C_8H_{18}
08	unknown	unknown	1.715	126	56	C_9H_{18}
09	cycloalkane	cyclopentane 1-methyl 2- propyl	1.890	126	56	C_9H_{18}
10	alkane	chain alkane(isomer C_9H_{20})	2.250	128	57/43	C_9H_{20}
11	alkene	1-decene	3.325	140	56/41	$C_{10}H_{20}$
12	alkene	1-undecene	4.410	154	55/41	$C_{11}H_{22}$
13	alkane	n-undecane	4.568	156	57/43	$C_{11}H_{24}$
14	unknown	unknown	4.725	--	54/67	--------
15	unknown	unknown	5.303	--	54/67	--------
16	carboxylic acid	nonanoic acid	5.390	158	60	$C_9H_{18}O_2$
17	aldehyde	2-undecenal	5.728	168	70	$C_{11}H_{20}O$
18	aldehyde	undecenal	6.055	170	55/43	$C_{11}H_{22}O$
19	aldehyde	2-dodecenal	6.493	182	70	$C_{12}H_{22}O$
20	alcohol	1-dodecanol	6.788	186	60	$C_{11}H_{22}O_2$
21	carboxylic acid	undecanoic acid	6.790	186	55	$C_{12}H_{26}O$
22	caboxylic acid	dodecanoic acid	8.050	200	60	$C_{12}H_{24}O_2$
23	unknown	unknown	8.663	--	57	-------
24	alkane	tetradecane,6-methyl	8.803	212	57	$C_{15}H_{32}$
25	carboxylic	tetradecanoic acid	9.153	228	60	$C_{14}H_{28}O_2C$
26	acidcarboxylic acid	hexadecanoic acid	10.203	256	60	$_{16}H_{32}O_2$
27	unknown	unknown	11.078	-	55	--------
28	unknown	unknown	11.200	-	55	---------

products (alkenyne, alkane, cycloalkene) from 3 to 4%. At higher temperature ,however, it was noticed a slight decrease in the main products (61-76%), and a slight increase in the secondary products were noticed (22-34%). The percentage of tertiary products remained constant.

According to Table 4 and Fig. 3. it can be observed that short a pyrolysis time (5 s) tends to favour cyclization and generation of multiple bonds whereas a longer pyrolysis time favours secondary reactions. These trends may be explained by the extent to which the sample underwent secondary reactions (see Table 4).

Nut Oil

In this sample, the composition of the whole pyrolysate was distributed in the following way: main products (aldehyde, alkene and carboxylic acid) corresponding to 59-74%; secondary products (cycloalkane, alkane and unknown/55) varying between 24-37% and tertiary prod-

ucts (unknown/54 and 57 and alcohol) ranging between 5-7%.

The relative percentage of carboxylic acids and unknown/55 increased when the pyrolysis time was raised in both worked temperatures. Other products, such as alkene, aldehyde and alkane have a tendency to decrease (see Fig. 4 and Table 5). This suggests that the generation of these classes of compounds is dependent on the cracking of carboxylic acids whereas the formation of unknown/55 is not. Additional trend is that classes of compounds present in less quantities of the total pyrolysate (unknown/54 and 57 and alcohol) increased with temperature and pyrolysis time enhancement. This fact can be explained by secondary reactions, which should be easier to occur under these conditions.

Short pyrolysis time (10 s) at both temperatures leads to a high amount of alkanes, alkenes and aldehydes instead of carboxylic acids. On the other hand, higher temperature and long pyrolysis time did not favour an extensive pyro-

Table 4. Composition of the Pulp Oil pyrolysate at a given pyrolysis temperature and different pyrolysis times.

Pyrolysis time (s)	Aldehyde	Cyclo alkane	Alkene	Diene	Unknown/55	Unknown/67	Unknown/others	Alkylbenzene	Alkenyne	Alkane	Cycloalkene
					T = 700 °C						
5	34 ± 2	21 ± 2	11.1 ± 0.5	10.7 ± 0.8	9 ± 1	5.5 ± 0.4	2.7 ± 0.5	2.8 ± 0.1	2.58 ± 0.06	0.9 ± 0.4	0.7 ± 0.2
10	34 ± 3	23 ± 1	13 ± 1	8.5 ± 0.4	7.2 ± 0.5	6.1 ± 0.5	2.8 ± 0.2	3.2 ± 0.2	2.30 ± 0.05	0.48 ± 0.04	1.1 ± 0.2
20	29 ± 2	24 ± 4	13 ± 3	7.3 ± 0.3	7.3 ± 0.2	7.3 ± 0.8	3.4 ± 0.2	6 ± 1	0.9 ± 0.2	0.6 ± 0.1	1.2 ± 0.5
30	32 ± 4	23 ± 3	10 ± 1	5.8 ± 0.4	6.9 ± 0.7	5.86 ± 0.05	5.6 ± 0.4	7.4 ± 0.6	1.8 ± 0.3	0.16 ± 0.02	1.48 ± 0.05
Pyrolysis time (s)	Aldehyde	Cyclo alkane	Alkene	Diene	Unknown/55	Unknown/67	Unknown/others	Alkyl-benzene	Alkenyne	Alkane	Cycloalkene
					T = 800 °C						
5	35 ± 3	20 ± 2	8 ± 1	13 ± 2	11.0 ± 0.6	4.2 ± 0.4	2.25 ± 0.08	4.1 ± 0.3	0.9 ± 0.1	1.4 ± 0.4	0.5 ± 0.1
10	26 ± 3	19 ± 1	8 ± 1	16 ± 1	9.6 ± 0.3	5.3 ± 0.6	6.9 ± 0.3	6.8 ± 0.3	1.0 ± 0.2	1.3 ± 0.2	0.46 ± 0.04
20	25 ± 3	18 ± 1	9 ± 1	14 ± 1	7.7 ± 0.4	7.9 ± 0.5	7.8 ± 0.4	8.2 ± 0.3	0.9 ± 0.2	0.9 ± 0.3	1.2 ± 0.4
30	22 ± 3	23 ± 1	6.4 ± 0.5	10 ± 1	8.2 ± 0.8	8.9 ± 0.7	8.2 ± 1	9 ± 1	1.9 ± 0.4	0.8 ± 0.3	1.7 ± 0.4
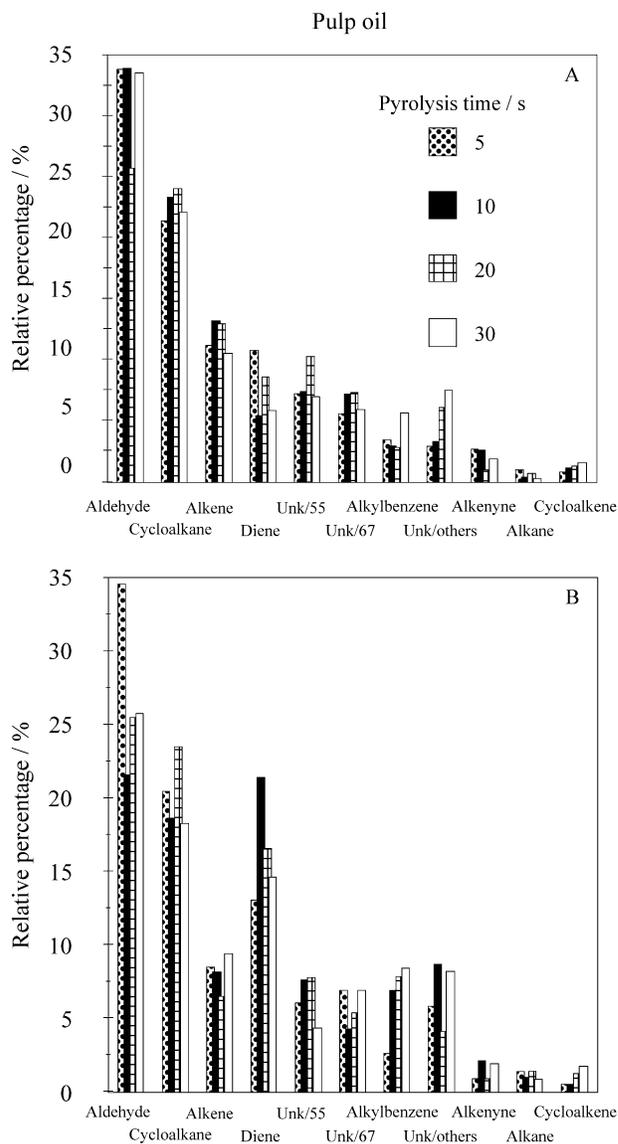
Figure 3. Comparison between profiles at a given pyrolysis temperature and different pyrolysis times for pulp oil.(A) 700 °C; (B) 800 °C.

lysis of this material. In this case, the desorption like process becomes more likely than the pyrolytic process.

Reproducibility of the pyrolytic process

The critical problem with the PI/GC/MS technique is the reproducibility of the experiments. There are several parameters which should be controlled during the experiments such as filament homogeneity and temperature, quantitative transfer of the pyrolysate material, amount of the material dispensed on the filament etc. All these parameters could affect in some way the reproducibility, especially in the quantitative aspect.

To ensure the reproducibility aspect of the experiments perdormed a various temperatures and pyrolysis times a

Table 5. Composition of the Nut Oil pyrolysate at a given pyrolysis temperature and different pyrolysis times.

T = 700 °C									
Pyrolysis Time (s)	Alkene	Aldehyde	Carboxylic acid	Unknown/ m/z 55	Cyclo alkane	Alkane	Unknown/ m/z 54	Alcohol	Unknown/ m/z 57
10	41 ± 3	25 ± 4	8.2 ± 0.4	8 ± 2	6.0 ± 0.9	10.3 ± 0.6	1.1 ± 0.4	0.4 ± 0.2	0.15 ± 0.02
20	37 ± 3	18 ± 1	11.7 ± 0.7	16 ± 1	8.4 ± 0.8	6.5 ± 0.4	1.8 ± 0.6	0.5 ± 0.2	0.33 ± 0.03
30	25 ± 3	16 ± 1	17.4 ± 0.9	24 ± 2	10.2 ± 0.7	2.9 ± 0.6	3.4 ± 0.4	1.0 ± 0.4	0.34 ± 0.02

T = 800 °C									
Pyrolysis Time (s)	Alkene	Aldehyde	Carboxylic acid	Unknown/ m/z 55	Cyclo alkane	Alkane	Unknown/ m/z 54	Alcohol	Unknown/ m/z 57
10	30 ± 6	21 ± 3	14 ± 1	10 ± 2	9 ± 1	15 ± 3	1.4 ± 0.3	0.32 ± 0.06	0.49 ± 0.07
20	27 ± 5	14 ± 3	24 ± 4	15 ± 3	8 ± 1	8 ± 2	2.7 ± 0.4	1.1 ± 0.4	0.57 ± 0.03
30	18 ± 2	15 ± 1	36 ± 3	19 ± 3	2.7 ± 0.3	3.1 ± 0.2	2.8 ± 0.2	2.5 ± 0.3	2.01 ± 0.6
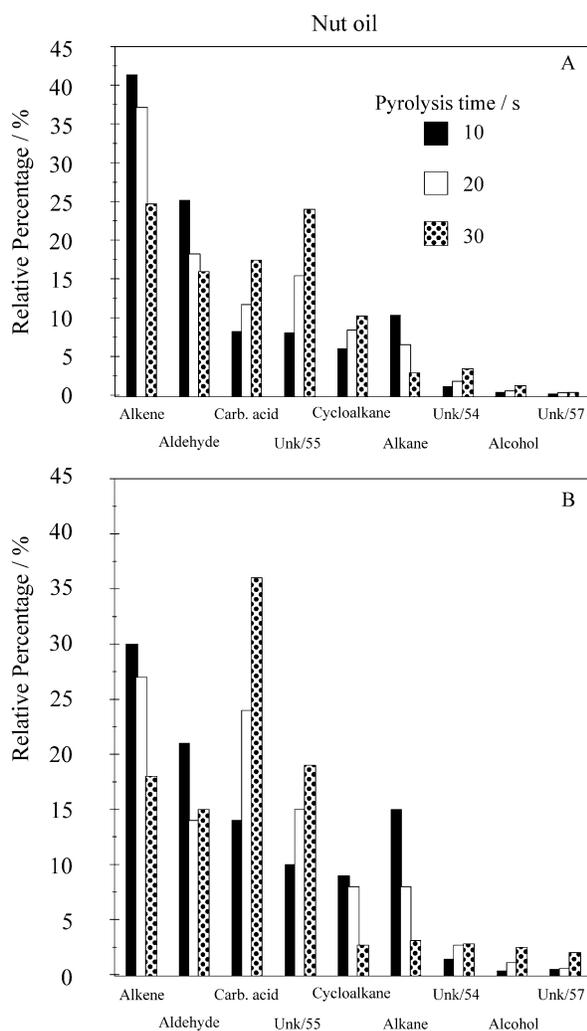
Figure 4. Comparison between profiles at a given pyrolysis temperature and different pyrolysis times for nut oil. .(A) 700 °C; (B) 800 °C.

number of observations were made: (1) reproducibility of the caracteristic features of the pyrograms for each pyrolysate; (2) reproducibility of the trends for the applied conditions; (3) reproducibility in terms of semi-quantitative analysis of the products (classes of compounds) obtained during the pyrolytic process.

To verify the first assumption a set of internal standards comprising biphenyl, anthracene and pyrene) was used which were pyrolysed together with the samples. The chromatographic features were quite reproducible as illustrated in Fig. 2.

The second assumption was studied after obtaining the semi quantitative data presented in Tables 4 and 5 and Figs. 3 e 4, in an analogous manner the previously described procedure. These data allowed the evaluation of the observed trend of the yield of products when temperature and pyrolysis time were varied. The pyrolysate composition at each set of conditions was found to be quite reproducible. This means that the parameters of the pyrolysis systematically affected the pyrolytic process.

The third assumption was verified by calculation of the relative errors from replicate analysis. In the less representative classes of compounds the estimated errors were > 20% and for the main classes these values were ranging between 4 and 20%.

Conclusion

The technique of PY/GC/MS has been demonstrated to be a good analytical tool for identifying the main constituents generated from pyrolysis of the original oils from macauba fruit using the direct analysis with capillary GC/MS in EI and PCI modes. It was shown that the technique could be used to investigate the associated mechanism of the pyrolysis process.

Under the conditions employed both oils undergo a pyrolytic process to a limited extent, generating a considerable amount of carboxylic acid component from the original oils.

The process as a whole was shown to be reasonably reproducible.

Acknowledgements

References

1. Soltes, E.J.; Milne, T.A. *Pyrolysis Oils Biomass: Producing, Analyzing and Upgrading,* American Chemical Society, Division of Fuel Chemistry Abstracts, NY, 1988.

2. Carioca, J.O.B.; Arora,H. *Biomassa: Fundamentos e Aplicações Tecnológicas*; UFC, 1985.

3. Hsu, H.L.; 0sburn, J.O.; Grove, C.S.Jr. *Ind.Eng.Chem* **1950**, *42*, 2141.

4. Jurg, J.W.; Eisma, E. *Science* (Washington DC) **1964**, *144*, 151.

5. Trailer, H.; Kratzl, K. *J.Am.Oil.Chem.Soc.* **1980**, *57*, 153.

6. Craveiro, A.A.; Matos, F.J.A.; Alencar, J.W.; Silveira E.R. *Energia: Fontes Alternativas* **1981**, *3*, 44.

7. Craveiro, A.A.; Rodrigues, A.S.; Andrade, C.H.S.; Matos, F.J.A.; Alencar, J.W.; Machado, M.I.L. *J.Nat.Prod.* **1981**, *44*, 602.

8. Fortes, I.C.P. *Estudo Químico da Pirólise dos Sabões de Cálcio da Macaúba*; Universidade Federal de Minas Gerais, Belo Horizonte, 1987.

9. Williams, P.T.; Nittaya, H. Patrick A. *Biomass Gasif. Pyrolysis, [Conf]*, Bridgwater; AV. CPL Press; Newbury, UK, p. 422, 1997.

10. Williams, P.T.; Nittaya, H.; Patrick , A. *Fuel* **1995**, *74*, 1839.

11. Alencar, J.W.; Alves, P.B.; Craveiro, A.A.; *J. Agric. Food Chem.* **1983**, *31*, 1268.

12. Novaes, R.J. *Contribuição para o estudo do côco macaúba*; Escola Superior de Agricultura Luiz de Queiroz; São Paulo, 1952.

13. Markley, K. *Economic Botany* **1956**, *10*, 3.

14. Fortes, I.C.P; Baugh, P.J. *J .Anal. Appl. Py.* **1994**, *29*,153.

15. Fortes, I.C.P. *Analytical Pyrolysis and GC/MS of vegetable oils (and their calcium soaps) from Macauba palm* (*Acrocomia sclerocarpa* M); University of Salford; Salford, UK, 1994.

16. Silverstein, R.M.; Bassler, G.C.; Morril, T.C. *Spectrometric Identification of Organic Compounds;* Willey & Sons Inc, Singapore, 1991.

17. Lafferty, F.M.Mc.; Turecek, F. *Interpretation of Mass Spectra*; University Sciences Books; Mill Valley, California, 1993.

18. Fleming, I.A.M.; Williams, D.H. *Spectroscopic Methods in Organic Chemistry*; McGraw Hill; New York, 1980.

19. Jennings, W. *Qualitative Analysis of Flavour and Fragance Volatiles by Capillary Gas Chromatography;* Academic Press; New York, 1980.

20. Widmann, G.; Reisen, R. *Thermal Analysis: terms, methods and applications*; Heidelberg; Hüthig, 1987.

21. Budzikiewicz, H.; Djerassi, C.; Williams, D.H. *Mass Spectrometry of Organic Compounds*; Holden-Day Inc.; San Francisco, 1967.

22. Beynon, J.H. *Mass Spectrometry and its Applications to Organic Chemistry*; Elsevier; Amsterdan, 1960.