



## Exploitation of hemicellulose, cellulose and lignin from *Hesperaloe funifera*

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### ABSTRACT

This work seeks the integral use of all major components of *Hesperaloe funifera*, separating hemicellulose by hydrothermal treatments; cellulose by pulping processes; and exploitation of lignin of pulping liquor by pyrolysis and gasification processes.

By using sulfuric acid in the hydrothermal treatment (150–190 °C, 0–20 min after reaching operating temperature, 6–10 liquid/solid ratio, 0.1–0.5% sulfuric acid), the glucose and xylose of liquid fraction increase from 1.5% to 5.9%, and 4.0% to 12.4%, respectively; the yields of solid fraction decrease from 91.6% to 79.5%, and the lignin content increase from 23% to 32%.

Pulps and paper sheets obtained from solid fractions hydrothermal treatments and from raw material pulped with diethanolamine, are worse than those obtained with soda–anthraquinone (Yield 57.8%; kappa number 24.9; Viscosity 711 mL/g; Brightness 54.8%; Tensile index 73.6 Nm/g; Stretch 2.84%; Burst index 6.13 kN/g and Tear index 1.69 mNm<sup>2</sup>/g).

By acidification (pH 6) of soda pulping liquor it separate lignin-rich solids, which by pyrolysis gave a gas containing 1.13% H<sub>2</sub>, 31.79% CO and 1.86% CH<sub>4</sub> by weight. Gasification of the same sample provided a gas containing 0.18% H<sub>2</sub>, 24.50% CO and 17.75% CH<sub>4</sub>.

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### 1. Introduction

More than 30% of the paper types used at present did (*e.g.* filter, chromatographic, interleaving, electrotechnical paper) not even exist only 10 years ago and have emerged in response to new social needs (ASPAPPEL, 2010). The increasing variety of paper types and uses has resulted in a pulp production from wood species over this period has grown by 3.1%; by contrast, the use of non-wood species for this purpose has risen much more markedly (18.1%) (FAO, 2010), which testifies to the growing significance of the latter as cellulose raw materials. This phenomenon can be ascribed to non-wood plants providing an effective alternative to wood, paper and cellulose pulp imports for developing countries with scant forest resources; also to the added value acquired by agrifood residues used for pulping; and also to the special chemical composition and morphological characteristics of non-wood raw materials (*e.g.* their less compact, more porous structure, more readily accessible tissues and weaker fibril–fibril bonds) reduce energy requirements and reagent consumption in cooking and bleaching processes.

A promising non-wood raw material is *Hesperaloe funifera*. Although the fiber morphology of *H. funifera* plants is especially suitable for making cellulose pulp (McLaughlin, 2003), little research in this direction appears to have been conducted. In the few exceptions, the material was subjected to alkaline sulfite–anthraquinone or soda–anthraquinone pulping (Wong and McLaughlin, 2000; Fairbank and Detrick, 2000) and the resulting paper sheets found to have very high tensile, burst and tear indices, and hence to be highly suitable for making special paper.

Interest in exploiting plant raw materials in full rather than specific fractions such as those used to obtain cellulose for papermaking purposes has grown considerably in recent years. In fact, researchers have sought methods to additionally obtain hemicellulose and lignin, which are usually burnt instead. This has led to the development of biorefining, which is concerned with the separation of plant components (lignin, hemicellulose and cellulose, mainly) with a view to obtaining various products from them (Pan et al., 2005; Towers et al., 2007; Kadam et al., 2008).

Hydrolyzing polysaccharides in plant raw materials with water at a high temperature provides a liquid fraction containing oligomers (Caparrós et al., 2007, 2008a,b; Garrote et al., 2003; Alfaro et al., 2009; Yáñez et al., 2009) which can be further hydrolyzed and fermented to obtain food additives or sugar substrates (Boussarsar et al., 2009; Dogaris et al., 2009). The fractionation method used causes structural alterations in some compounds

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and detracts from quality in the final pulp; the problem, however, can be overcome by using an appropriate hydrothermal treatment for the plant material and improving the strength-related properties of the pulp by beating (Caparrós et al., 2007, 2008a,b).

One other use of biorefining is for isolating lignin from residual cooking liquor. Lignin removed by organic solvents is of a much higher value than if used as a fuel in the kraft process. In fact, lignin can be used to obtain phenol–formaldehyde resins, polyurethanes, acrylates, epoxides and composites (González et al., 2009; García et al., 2009). One special use of lignin is for the production of gases synthesis by pyrolysis (Mani et al., 2009; Murugan et al., 2008) or fuel gases by gasification (Osada et al., 2007; Furusawa et al., 2007; Yamaguchi et al., 2008).

This paper seeks the integral use of all major components of *H. funifera*. It was studied the influence of operating variables of a hydrothermal treatment (temperature, time, liquid/solid ratio and concentration of sulfuric acid used as catalyst) on the composition of the liquid (glucose, xylose, arabinose and acetic acid) and solid fractions (lignin content and yield of solid) resulting. Then the solid fractions obtained from two hydrothermal treatments (with and without acid catalyst) were submitted to two different processes of pulping (soda–anthraquinone pulping and diethanolamine pulping), in order to compare the properties of pulp and paper obtained, with properties having of the pulp and paper directly obtained from raw material without prior hydrothermal treatment. Finally, the cooking liquors were acidified to separate solid fractions (lignin-rich) that were subjected to pyrolysis and gasification in order to obtain synthesis and fuel gases.

Soda and soda–anthraquinone processes have been used to pulp non-wood raw materials with good results (Labidi et al., 2008; Jiménez et al., 2009). These processes have some advantages such as the following: a high production resulting from the use of relatively short pulping times; good yields; applicability to both wood and non-wood raw materials; reusability of the cooking liquors; and increased yields, more expeditious cooking and reduced kappa numbers by effect of the joint use of soda and anthraquinone.

Organosolv processes have been widely used at the laboratory scale (López et al., 2006; Rodríguez and Jiménez, 2008) and applied to various alternative raw materials including *Cynara cardunculus*, wheat straw, *Paulownia fortunei*, vine shoots, cotton stalks, *Leucaena leucocephala* and *Chamaecytisus proliferus* (Ligero et al., 2008; Ziaie-Shirkolaee et al., 2008; Caparrós et al., 2008a; Jiménez et al., 2007). The most salient advantages of these processes are as follows: economy at the small and medium scale, and efficient recovery of solvents and by-products, in relation to Kraft processes; reduced water, energy and reagent consumption; reduced pollution and easy recovery of bleaching effluents; applicability to wood and non-wood raw materials; production of pulp with properties on a par with those of Kraft pulp in addition to higher yields, lower lignin contents, higher brightness, and easier bleaching and refining; and the need for no additional investments if Kraft pulping facilities are available as it suffices to use high-boiling solvents (glycols, ethanolamines) to exploit them.

## 2. Methods

### 2.1. *H. funifera*

*H. funifera* is a plant with very modest irrigation requirements. Based on these properties, *Hesperaloe* might be an effective cellulose raw material in arid zones precluding cultivation of other species (McLaughlin, 2003) or in areas with scant water resources. High-density plantations (27,000 per hectare) can yield approximately 20 tons of dry biomass per hectare and year (Wong and McLaughlin, 2000).

The contents in holocellulose, lignin,  $\alpha$ -cellulose, ethanol–benzene extractives, hot water solubles, 1% NaOH solubles and ash of the raw material (determined in accordance with the Wise method (Wise et al., 1946) and the following Tappi standards: T-222, T-203 0S-61, T-204, T-257, T-212 and T-211) are: 76.5%, 7.3%, 40.9%, 4.0%, 13.5%, 29.5% and 5.9%, respectively.

The fiber length of *H. funifera* was determined by using a projection microscope Visopan, proved to be of 4.19 mm.

### 2.2. Hydrothermal treatment and pulping

The raw material was subjected to hydrothermal treatment and to pulping process in a 15 L batch reactor that was heated by means of an outer jacket and stirred by rotating the vessel via a motor connected through a rotary axle to a control unit including the required instruments for measurement and control of pressure and temperature.

After hydrothermal treatment, the material was separated into two fractions (solid and liquid) through a filter of 0.40 mm pore size. In the various experiments being carried out, the operating variables vary in the ranges: temperature (155–180 °C), time (0–30 min after reaching operating temperature) and liquid/solid ratio (6–8).

The pulping processes were operated at a temperature of 180 °C, with a soda–anthraquinone or diethanolamine concentration of 10% or 70%, respectively, while maintaining a liquid/solid ratio of 6, for 30 min after reaching operating temperature. After each pulping process was completed, cooked material was unloaded from the reactor, washed to remove residual cooking liquor and fiberized in a disintegrator at 1200 rpm for 30 min, which was followed by beating in a Sprout–Bauer refiner. Finally, the fiberized material was passed through a filter of 0.16 mm pore size to remove uncooked particles.

### 2.3. Analysis of liquid and solid fractions of hydrothermal treatment

To determine the glucose, xylose, arabinose and acetic acid contents weighed 10–20 g of the liquid fraction to be analyzed and taken to an ISO bottle of 100 mL. Sulfuric acid was added until the concentration of 4% by weight and the ISO bottle was introduced in an autoclave for 20 min at 2 atmospheres (121 °C). Then the ISO bottle was cooled with water to room temperature and analyzed by HPLC (Garrote et al., 2003).

The yield of the solid fraction is determined by gravimetry. The lignin content was determined using Klason method. A solid sample with sulfuric acid was placed in the autoclave for one hour at 2 atm (121 °C). Then the ISO bottle was cooled with water to room temperature. Finally filter the contents of the bottle in a Goosch crisol (pore size 3) by introducing the solid fraction retained in the crisol in an oven at 105 °C for 24 h (Garrote et al., 2003).

### 2.4. Pulp and paper sheets characterization

The pulp samples obtained were characterized in terms of yield (gravimetrically), and also for kappa number and viscosity according to the UNE standards 57-034 and 57-039, respectively.

Paper sheets were obtained with an Enjo-F39-71 former and analyzed for tensile index, stretch, burst index, tear index and brightness in accordance with the following UNE standards: 57-054, 57-028, 57-08, 57-033 and 57-062, respectively.

### 2.5. Processing of residual liquor

It considers only the liquors of the pulping process of the original raw material, using soda and diethanolamine. These liquors were treated with sulfuric acid at pH 6, 4 and 2 to obtain various

solid fractions which were then dried at room temperature and subjected to pyrolysis in a helium atmosphere and gasification with a 9:1 mixture of helium and oxygen.

The experimental system (Conesa et al., 2009) consists in a quartz tube, 10 mm wide, where the sample is introduced uniformly occupying an appreciable length of the tube (approx. 350–400 mm). A horizontal actuator (servomechanism that supplies and transmits a measured amount of energy for the operation of another mechanism or system) introduces with a constant linear velocity the tube with the lignocellulosic material inside a furnace maintained at the desired temperature (850 °C). The operating conditions used for gasification have been selected among commonly used for similar lignocellulosic material experiments.

The gas obtained from lignocellulosic material gasification was analyzed by GC-TCD (Shimadzu GC-14A Gas Chromatograph) and GC-FID (Shimadzu GC-17A) (Conesa et al., 2009).

Furthermore, experiments were performed in a thermobalance with TG-DTA analyzer (Mettler Toledo, model TGA/SDTA851e/LF/1600) coupled to a mass spectrometer (Pfeiffer Vacuum, model Thermostar GSD301T) to monitor the signal of the volatile compounds evolved. The initial sample weight was around 5 mg. Dynamic experiments were carried out at 10 K/min from 25 to 900 °C.

### 3. Results and discussion

#### 3.1. Hydrothermal treatment without catalyst

Table 1 shows the operating conditions of the 15 experiments in the considered experimental factorial design (Montgomery, 1991), for the *H. funifera* hydrothermal treatment without catalyst. The choice of the values of operating variables was done considering the values used for similar materials: *Paulownia* (Caparrós et al., 2008a), vine shoots (Jiménez et al., 2006), *Arundo donax* (Caparrós et al., 2007), sunflower stalks (Caparrós et al., 2008b), legumes (Alfaro et al., 2009) *Sabastian grandiflora* (Yáñez et al., 2009) and bagasse from sugar cane (Boussarsar et al., 2009).

In the same Table 1 shows the results of characterization of the resulting liquid and solid fractions. As shown, the results for liquid fractions (glucose, xylose, arabinose and acetic acid concentrations) vary little from one test to another, which together with the low values found have resulted in failure to find equations satisfactorily reproduce the experimental results in terms of operating variables, whether considered polynomial and neural fuzzy models (Jiménez et al., 2006).

As regards the influence that temperature has on the composition of the liquid fraction can be observed (Table 1), by comparison the values of experiments performed under identical conditions of

time and liquid/solid but a different temperature, that the concentrations of glucose and xylose of liquid fractions and lignin content of the solid fraction increase with increasing temperature. Also note in Table 1, comparing experiments to the temperature and liquid/solid identical, but at different times, that the concentrations of glucose and xylose and lignin content not clearly depend on time of the operating range considered. When comparing experiments performed under identical conditions of temperature and time but with different liquid/solid ratio, it was found that the glucose concentration decreases with increasing liquid/solid ratio, while the concentration of xylose and lignin content do not depend on clearly the values of the liquid/solid ratio. Finally, the solid yield of the solid fraction decreases when increasing the three operating variables considered.

#### 3.2. Hydrothermal treatment with acid catalyst

Table 2 shows the operating conditions of the 15 experiments in experimental factorial design (Montgomery, 1991) applied to *H. funifera* hydrothermal treatment using sulfuric acid as catalyst, and with a value of 8 for the liquid/solid. Also shown in Table 2 the experimental results obtained in the characterization of solid and liquid fractions resulting from the application of hydrothermal treatments. As happened in the study of *H. funifera* hydrothermal treatment without catalyst, in this case the polynomial and neural fuzzy models do not provide adequate equations to reproduce the experimental values of the dependent variable in terms of operating variables.

By a similar procedure for the experiments performed before the hydrothermal treatment without catalyst, in the case of hydrothermal treatment with acid catalyst can be observed when comparing the values of the experiments of Table 2, that the concentrations of glucose and xylose and content lignin clearly do not vary by increasing or decreasing the operating temperature and the processing time. Referring to the concentration of acid catalyst can be concluded that the concentrations of glucose and xylose increase and the lignin content decreases with increasing the concentration of acid. Finally the yield of the solid fraction decreases with increasing temperature and time, not being so clear the influence of acid concentration.

Comparing Tables 1 and 2, corresponding to the results of composition of liquid and solid fractions of hydrothermal treatment with and without catalyst, respectively, one can deduce that by using sulfuric acid as catalyst:

- a) The maximum level of glucose increase in the order of up to 4 times: from 1.5% to 5.9%.

**Table 1**  
Characterization of solid and liquid fractions resulting from hydrothermal treatment without catalyst.

Experiment	Operation conditions (°C; min; L/S ratio)	Liquid fraction				Solid fraction	
		Glucose, %	Xylose, %	Arabinose, %	Acetic acid, %	Solid yield, %	Lignin, %
1	170; 10; 8	1.06	1.99	0.84	0.36	84.5	18.44
2	190; 20; 10	1.01	2.24	0.54	0.80	69.2	23.08
3	150; 20; 10	0.75	1.65	0.70	0.28	86.4	17.98
4	190; 20; 6	1.24	2.53	0.61	0.97	77.6	23.11
5	150; 20; 6	0.64	1.40	0.45	0.25	87.3	14.67
6	190; 0; 10	0.93	2.01	0.46	0.38	77.3	19.16
7	150; 0; 10	0.87	1.53	0.54	0.22	87.9	18.17
8	190; 0; 6	1.50	2.75	0.24	0.24	86.9	19.57
9	150; 0; 6	1.28	2.59	0.46	0.16	91.6	18.61
10	170; 20; 8	0.93	1.76	0.76	0.38	79.9	20.52
11	170; 0; 8	0.79	1.88	0.72	0.26	86.3	19.28
12	170; 10; 10	0.81	2.12	0.64	0.30	80.1	20.72
13	170; 10; 6	1.37	4.01	0.39	0.46	84.5	17.41
14	190; 10; 8	1.42	2.38	0.86	0.66	77.2	22.44
15	150; 10; 8	0.82	1.62	0.71	0.24	87.9	20.16

**Table 2**

Characterization of solid and liquid fractions resulting from hydrothermal treatment with acid catalyst.

Experiment	Operation conditions (°C; min; %H <sub>2</sub> SO <sub>4</sub> )	Liquid fraction				Solid fraction	
		Glucose, %	Xylose, %	Arabinose, %	Acetic acid, %	Solid yield, %	Lignin, %
1	170; 10; 0.3	4.62	10.56	1.28	0.35	57.0	17.96
2	190; 20; 0.5	1.38	6.90	0.83	0.94	50.6	24.84
3	150; 20; 0.5	3.36	8.28	1.14	0.23	64.8	11.63
4	190; 20; 0.1	1.29	7.13	0.78	0.89	50.1	27.22
5	150; 20; 0.1	3.57	7.79	0.99	0.18	73.2	17.48
6	190; 0; 0.5	3.09	10.33	1.50	0.62	52.7	26.62
7	150; 0; 0.5	3.04	6.12	0.51	0.11	76.5	22.42
8	190; 0; 0.1	1.41	3.13	0.53	0.17	61.1	34.88
9	150; 0; 0.1	1.46	3.78	0.94	0.68	79.5	26.30
10	170; 20; 0.3	1.34	3.26	0.87	0.53	64.7	23.48
11	170; 0; 0.3	4.74	10.09	1.56	0.30	72.2	23.36
12	170; 10; 0.5	5.92	12.35	1.57	0.31	58.3	20.75
13	170; 10; 0.1	1.77	3.96	1.14	0.45	72.0	31.19
14	190; 10; 0.3	1.49	4.36	1.05	1.09	58.7	25.93
15	150; 10; 0.3	1.21	3.00	0.89	0.21	82.7	31.72

- b) The maximum levels of xylose increased to 3 times: from 4.0% to 12.4%.  
 c) The maximum yields decreased from 91.6% to 79.5%.  
 d) The minimum yields decreased from 69.2% to 50.1%.  
 e) The maximum lignin content increased from 23% to 32%.

Moreover, with regard to the contents of arabinose and acetic acid liquid fractions of hydrothermal treatments can be observed that the values of those concentrations are very small in all cases.

### 3.3. Comparison of pulp and paper sheets obtained from solid fraction of the hydrothermal treatment and from original raw material

For this study *H. funifera* undergoes hydrothermal treatments with and without acid catalyst under operating conditions that are presented in Table 3. In the same table shows the results of the characterization of cellulose pulp obtained from solid fractions considered hydrothermal treatments (with and without a catalyst), using soda–anthraquinone and diethanolamine; in this table also specifies the conditions of operation pulping.

On the other hand, Table 3 also shows the values found in the characterization of cellulose pulp derived from the original material under the same pulping conditions what the solid fractions of hydrothermal treatment (see Table 3), using soda–anthraquinone and diethanolamine.

**Table 3**Characteristics of pulp and paper sheets of *H. funifera* and solid fractions from hydrothermal treatments.

Characteristic	Types of pulping					
	H + S	HA + S	S	H + D	HA + D	D
Yield hydrothermal treatment, %	67.2	78.5	–	65.4	70.7	–
Pulping yield, %	50.7	52.3	57.8	51.5	54.0	57.7
Kappa number	27.2	22.3	24.9	29.1	28.6	23.7
Viscosity, mL/g	511	373	711	383	397	765
Brightness, %	57.4	64.9	54.8	53.2	54.1	60.5
Tensile index, Nm/g	46.7	44.7	73.6	46.5	52.1	87.1
Stretch, %	2.92	3.03	2.84	2.93	3.23	3.16
Burst index, kN/g	3.67	3.61	6.13	3.85	4.23	7.59
Tear index, mNm <sup>2</sup> /g	6.08	6.51	1.69	6.08	6.09	3.32

Operating conditions: H = Hydrothermal treatment without acid: 170 °C, 10 min, liquid/solid relationship = 8.

HA = Hydrothermal treatment with acid: 170 °C, 0, 3% H<sub>2</sub>SO<sub>4</sub>, 10 min, liquid/solid relationship = 8.

S = Soda–AQ pulping: 155 °C, 20 min, 5% NaOH, 1% AQ, liquid/solid relationship = 8.

D = Diethanolamine pulping: 155 °C, 30 min, 50% Diethanolamine, liquid/solid relationship = 8.

The yields obtained after pulping processes of the solid fraction hydrothermal treatments are slightly lower than those obtained in the pulping of the original raw material, no significant difference between them (soda and diethanolamine pulps).

The kappa number is lower in pulp raw material and the obtained solid fraction catalyzed hydrothermal treatment by soda process.

In the case of the viscosity of the pulps, it is possible to see significant differences when performing a hydrothermal treatment prior pulping, on the original raw material: the viscosity of the former is about half of those obtained in the case of the raw material.

The physical and mechanical properties (except tear index) of the paper sheets of the cellulosic pulps obtained after a previous hydrothermal treatment, with and without catalyst, are lower than the values found for sheets of cellulose pulp obtained from the original raw material.

Finally, the maximum brightness of the paper sheets corresponds to the diethanolamine pulp of the raw material, and the minimum to soda–anthraquinone pulps of the raw material and the diethanolamine pulps of the solid fraction hydrothermal treatment with and without catalyst.

### 3.4. Exploitation of residual liquors of pulping processes

The residual liquors from pulping of raw material by soda–anthraquinone and diethanolamine processes, which proved the most efficient methods for pulping *H. funifera* (see Table 3), were acidified in order to isolate lignin-rich fractions. Table 4 shows the results obtained at different pH values.

Soda cooking an amount of 500 g of *H. funifera* provided pulp in a 48.3% yield. Based on the lignin contents of the raw material (7.3%) and pulp (3.07%), the cooking liquor should have contained 29.09 g of lignin. This amount, however, was much greater than the combination of the three individual fractions: 15.27 g. Since the solid fractions contain additional components such as hemicellulose and ash, only part of the lignin in the liquors was recovered by acidification. The diethanolamine pulping process provided similar results: the amount of lignin obtained from the cooking liquor was 18.15 g (pulp yield was 55.1% and the pulp contained 6.66% lignin), but the solid fractions in combination only contained 12.66 g.

As can be seen from Table 4, acidification of the soda pulping liquor at pH 6 extracted the highest proportion of solid fraction (91.0%). Therefore, using lower pH values to obtain other solid fractions may be counterproductive as they will add little to the previous one and unnecessarily raise the cost of neutralizing the effluent. The main solid fraction in the liquor from the diethanola-

**Table 4**  
Solid fractions extracted by acidification of the cooking liquor and overall proportions of gases obtained by their pyrolysis and gasification.

Liquor	pH for extraction of solid fraction	Amounts of solids extracted (g) and proportion with respect to the body of fractions	Total amount of gases obtained (% with respect to the extracted fraction)	
			Pyrolysis	Gasification
Soda-AQ pulping	pH = 2	0.23 (1.5%)	–	–
	pH = 4 (sample A)	1.14 (7.5%)	82.6	98.0
	pH = 6 (sample B)	13.90 (91.0%)	91.0	96.1
Diethanolamine pulping	pH = 2 (sample C)	1.81 (14.3%)	74.1	99.6
	pH = 4 (sample D)	8.01 (63.3%)	75.1	97.3
	pH = 6 (sample E)	2.84 (22.4%)	77.9	87.5

mine process, which accounted for 63.3% by weight, was obtained at pH 4; by contrast, only 14.3% was extracted at pH 2. Using a pH

below 4 may be counterproductive for the same reasons as with the soda pulping liquor.

Thermal decomposition of the previous solid fractions in an inert atmosphere (He) and an oxidizing atmosphere (9:1 He/O<sub>2</sub>) resulted in the weight losses shown in Figs. 1 and 2.

As can be seen from Fig. 1, approximately until 700 K the weight loss curves for the solid fraction in the soda pulping liquor treated in the absence of oxygen, are higher than those obtained for diethanolamine pulping liquor, whereas above 700 K the opposite happens. This suggests that pyrolysis of the solid fractions obtained from the soda pulping liquor produce smaller amounts of carbonaceous residues and ash, and hence greater amounts of evolved gases (see fourth column in Table 4).

As can be seen from Fig. 2, mass losses during the gasification process decreased with increasing temperature up to 800–850 K; also, the solid fractions extracted at the lower pH values provided smaller amounts of gases (see last column in Table 4).

Samples of the different solid fractions (A–E in column 2 of Table 4) were pyrolyzed and gasified in a horizontal tubular reactor and the resulting gases analyzed by GC/FID and GC/TCD. The results are shown in Table 5, and the concentration

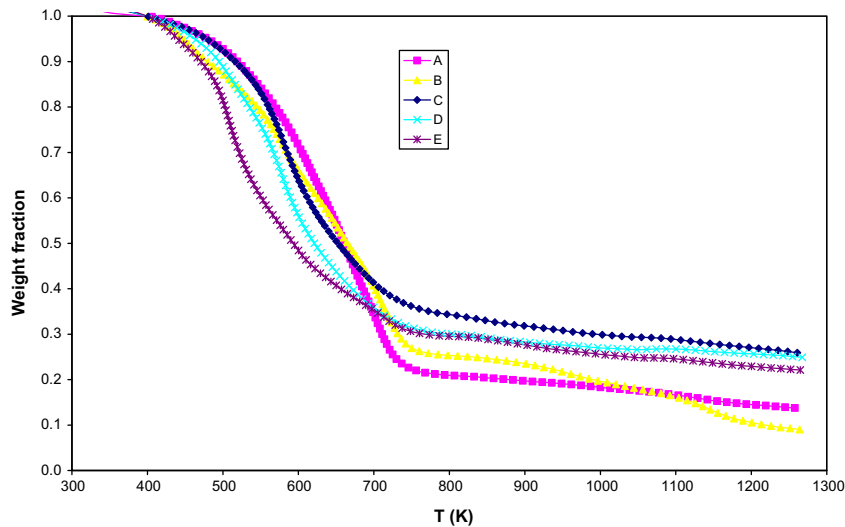


Fig. 1. Mass loss of the solid fractions from *H. funifera* in the absence of oxygen.

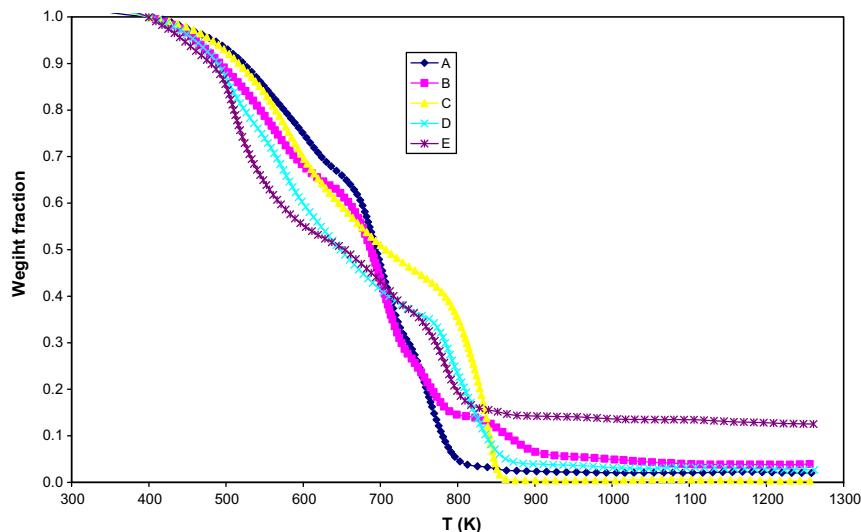


Fig. 2. Mass loss of the solid fractions from *H. funifera* in an oxidizing atmosphere.

**Table 5**

Composition of evolved gases generated by pyrolysis and gasification of the solid fractions.

Process	Samples	Composition, g/100 g sample			
		H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>
Pyrolysis	Sample A	1.54	16.30	19.00	1.81
	Sample B	1.13	31.70	22.40	1.86
	Sample C	0.97	13.60	16.80	3.70
	Sample D	0.74	10.50	12.80	2.37
	Sample E	0.64	13.00	14.80	1.55
	Sample (D + E)	0.71	11.16	13.33	2.16
Gasification	Sample A	0.17	32.40	67.20	17.66
	Sample B	0.18	24.50	52.90	17.76
	Sample C	0.15	53.40	51.60	16.01
	Sample D	0.26	23.00	48.60	23.26
	Sample E	4.92	20.40	38.40	14.01
	Sample (D + E)	1.48	22.32	45.94	20.84

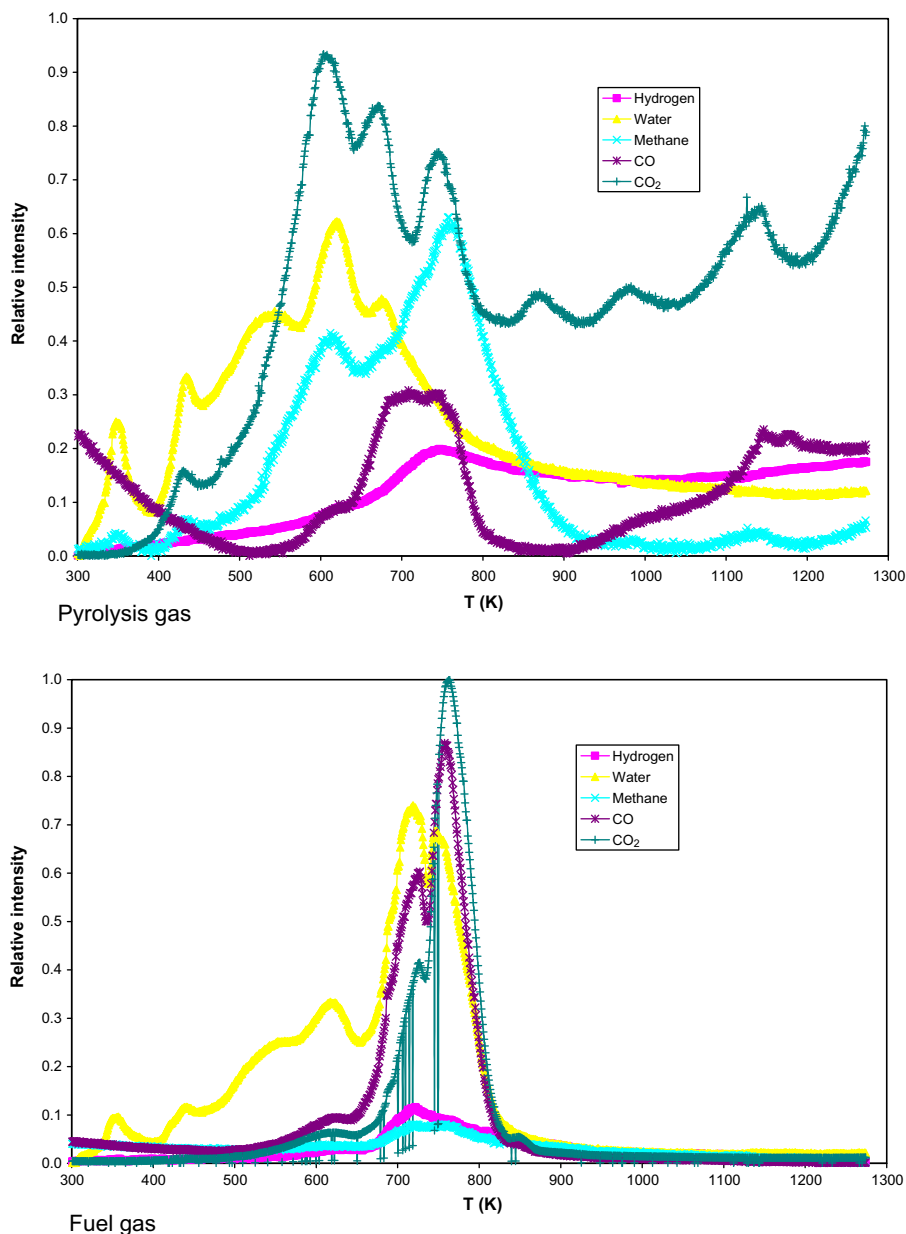
profiles for the synthesis and fuel gases in Figs. 3 and 4, and similar others.

A comparison of Figs. 3 and 4, and the data in Table 5, reveals that pyrolysis of the solid fraction extracted by acidifying the soda cooking liquor at pH 6 produced less H<sub>2</sub> but more CO than that extracted at pH 4. Also, gasification of the solids extracted at pH 6 from the same liquor produced slightly more H<sub>2</sub> but less CO.

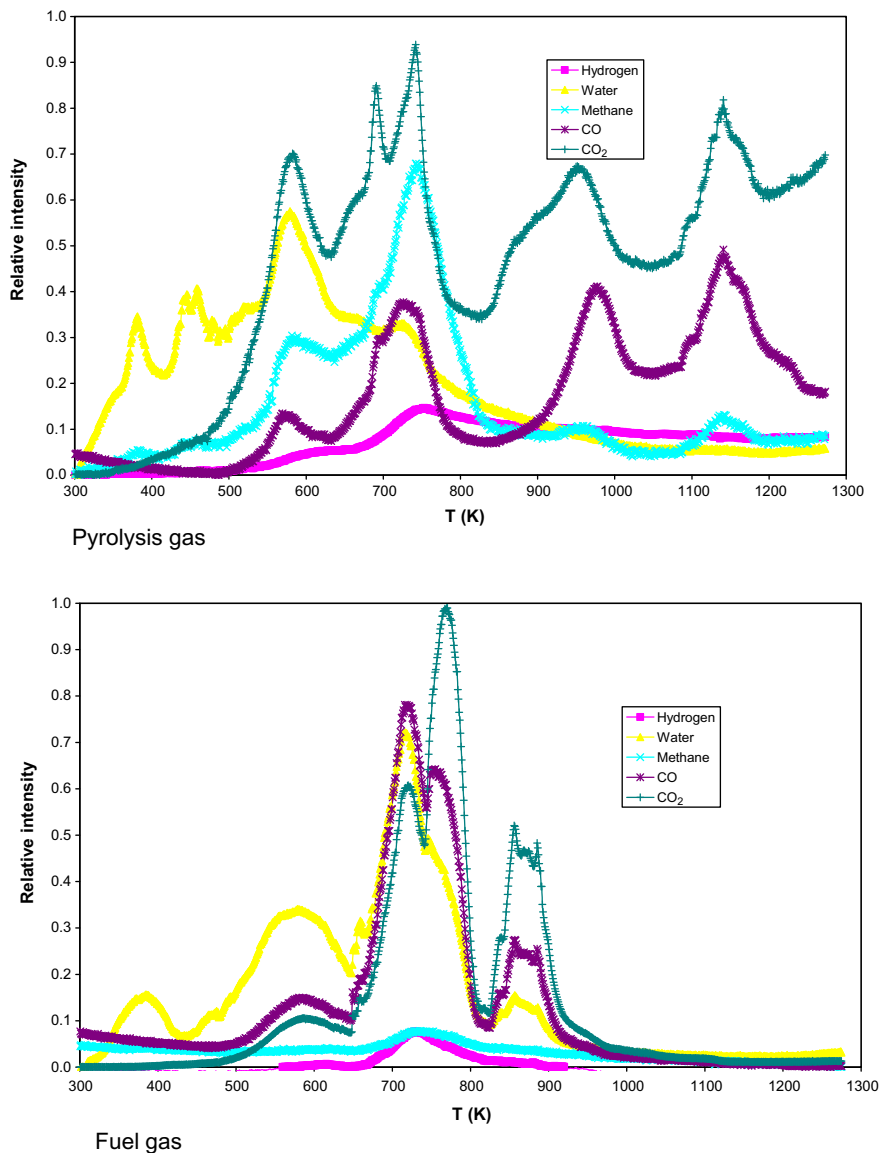
The amounts of H<sub>2</sub> and CO obtained by gasifying the fraction extracted from the soda cooking liquor at pH 6 were smaller than those obtained by gasification. The opposite was true of CH<sub>4</sub> and CO<sub>2</sub>.

On the other hand, from the graphs of Figs. 3 and 4 it is deduced that is not appropriate to operate at temperatures above 800–900 K, because that range produce larger quantities of H<sub>2</sub>, CO and CH<sub>4</sub>, both pyrolysis and gasification.

A comparison similar Figs. 3 and 4, and the data in Table 5, reveals that pyrolysis of the solid fraction obtained by acidification of



**Fig. 3.** Concentration profiles for the synthesis and fuel gases obtained from the solid fraction extracted from the soda–anthraquinone pulping liquor at pH 4 (sample A).



**Fig. 4.** Concentration profiles for the synthesis and fuel gases obtained from the solid fraction extracted from the soda–anthraquinone pulping liquor at pH 6 (sample B).

the diethanolamine cooking liquor at pH 6 produced decreased amounts of H<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub> relative to pH 2; and decreased amounts of H<sub>2</sub> and CH<sub>4</sub> and increased amounts of CO and CO<sub>2</sub> relative to pH 4.

On the other hand, gasification of fraction extracted at pH 6 produced increased amounts of H<sub>2</sub>, but decreased amounts of CH<sub>4</sub>, CO and CO<sub>2</sub>, relative to pH 4 and 2.

A comparison of the amounts of gases obtained by gasification and pyrolysis of the solid fraction extracted from the diethanolamine cooking liquor at pH 4 reveals that gasification produced less H<sub>2</sub> but more CO, CO<sub>2</sub> and CH<sub>4</sub> than pyrolysis.

As can clearly be seen from similar Figs. 3 and 4, using temperatures above 750–850 K resulted in no further increase in the amounts of H<sub>2</sub>, CO and CO<sub>2</sub> obtained by pyrolysis or gasification.

As can be seen from Table 5, pyrolysis of the solids from the soda cooking liquor provided increased amounts of H<sub>2</sub>, CO and CO<sub>2</sub> relative to the diethanolamine liquor. However, pyrolysis of the soda liquor fractions extracted at pH 4 and 2 provided decreased amounts of CH<sub>4</sub> relative to diethanolamine.

Gasification provided very small amounts of H<sub>2</sub> with all fractions except that extracted from diethanolamine liquor at pH 6.

The fractions extracted at the lower pH values (samples A and C) gave greater amounts of CO and CO<sub>2</sub>. Finally, the largest amounts of CH<sub>4</sub> were obtained from the diethanolamine liquor extracted at the intermediate pH.

Based on the foregoing, the solid fraction extracted from soda liquor at pH 6 is the best source for producing synthesis gases (H<sub>2</sub> + CO) by pyrolysis, and so is the fraction extracted from diethanolamine liquor (sample C) for obtaining fuel gases (H<sub>2</sub> + CO + CH<sub>4</sub>) by gasification.

Table 5 shows the composition of the synthesis and fuel gases obtained from the combination of the two fractions extracted at pH 4 (samples D and E). As can be seen, pyrolysis of sample B produced greater amounts of synthesis and fuel gases than did the combination of D + E; the actual difference was even more marked than suggested by the results if one considers that the amounts of B and C + D obtained from 500 g of pulp were 13.90 and 10.85 g, respectively. On the other hand, gasification of samples B and D + E produced similar amounts of synthesis and fuel gases; however, since the amount of B extracted exceeded that of D + E, the former fraction is to be preferred as it provides greater amounts of gases and requires less acid for extraction.

#### 4. Conclusions

In the hydrothermal treatments performed with acid catalyst, it follows that it should operate with low values for temperature and time and a high acid concentration to achieve good glucose and xylose concentration, resulting in savings of energy for heating and assets required for industrial plant.

The better pulps are obtained by pulping of original raw material.

A comparison of the amounts of synthesis gases ( $H_2 + CO$ ) and fuel gases ( $H_2 + CO + CH_4$ ) generated by pyrolysis and gasification of the solid fractions obtained by acidifying the pulping liquors revealed that the best results were those for the soda-anthraquinone liquor extracted at pH 6.

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