STEPWISE ISOTHERMAL FAST PYROLYSIS (SIFP). PART II. SIFP OF PEANUT SHELLS - ANTIFUNGAL PROPERTIES OF PHENOLIC FRACTIONS

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Pyrolysis of peanut shells was carried out using stepwise isothermal fast pyrolysis (SIFP). SIFP consists of successive isothermal fast pyrolysis reactions, where solid products obtained in the previous isothermal fast pyrolysis become the substrate of the subsequent reaction at a higher temperature. This article reports results obtained from SIFP of peanut shells between 200 and 300°C using 100°C intervals under vacuum (0.2 mm). The maximum yield of liquid products was obtained at 300°C, giving around 30% of bio-oil, which contained mainly phenols and furan derivatives. On the other hand, since previous papers have reported fungicidal activity of phenols derivatives from lingo-cellulosic biomass pyrolysis, we carried out antifungal activity tests of bio oil obtained from peanut shells SIFT at 300 °C. Results seem promising, at least on *Sclerotium rolfsii*.

Keywords: Fast pyrolysis; Peanut shells; Bio-oil; Phenols; Antifungal activity

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INTRODUCTION

Fast pyrolysis of lignocellulosic biomass produces a solid (char), liquid (bio-oil), and a gaseous fraction. The liquid products have been reported to be of low viscosity and chemically very complex, containing hundreds of different compounds derived from primary and secondary reactions of lignin, cellulose, and hemicelluloses (Horne and Williams 1996, Aguado et al. 2000, De Wild el al. 2011). Bio-oil is an attractive source of several interesting chemicals

We have previously reported a pyrolysis technique named stepwise isothermal fast pyrolysis (SIFP). This technique involves a successive set of reactions in which solid products of an isothermal fast pyrolysis become the substrate of the next one. By employing gradual heating of the same sample, it is reasonable to anticipate that the products composition at each temperature should be less complex, and in this way separation of certain compounds from reaction products could be much easier and provide better yields. This fact was shown in SIFP reactions of pine sawdust (López Rivilli et al. 2011).

Peanut shells is an important biomass available in the province of Cordoba, Argentina. Argentina is one of the most important peanut exporters worldwide, and within the country Cordoba produces more than 95% of the whole harvest. Annual production is around 700,000 metrics tonnes, so peanut shells reach near 150,000 tonnes per year.

In this work we report the results obtained in stepwise isothermal fast pyrolysis (SIFP) of milled peanut shell between 200 and 300°C at 100°C interval and vacuum (0.2 mmHg). Since a previous paper (Mohan et al. 2008) has reported interesting fungicidal activity of bio-oils from different kinds of biomass, we decided to carry out studies concerning the potential antifungal activity of phenol concentrates from peanut shells SIFP. Results are also reported in this paper.

EXPERIMENTAL

Stepwise Isothermal Fast Pyrolysis

Pyrolysis reactions were carried out in a similar way as previously described (López Rivilli et al. 2011). The contents of cellulose, hemicelluloses and lignin of peanut shell were determined using Official Methods of Analysis of AOAC (15th. Ed.), and results are shown in Table 1.

Peanut Shell	%
Cellulose	40.5
Hemicelluloses	14.7
Lignin	26.4

Around 1 g of milled peanut shells of inhomogeneous size, up to 2 mm, dried for 40 min. at 105°C, was used in each run. The sample was placed inside a porcelain boat covered with a stainless steel grid to avoid projection. Each isothermal fast reaction was run during 1 hour, since it had been checked out that this time was enough to complete biomass decomposition at each point. Products were collected in a U shaped trap immersed in liquid air. After the reaction finished, this trap was allowed to reach ambient temperature, and then products were extracted with acetone and submitted to GC/MS analysis.

These analyses were performed in a Perkin-Elmer Q-Mass 910 device, using an SE-30 column and He as carrier gas with a 1 ml/min flow and a heating ramp of: 65 °C (5 min), 65-280 °C (10 °C/min), and 280 °C (5 min).

Antifungal Activity of Bio-oil

Antifungal activity was checked out with a species of pathogenic fungi of agronomic interest, *Sclerotium rolfsii*, which was obtained from pure cultures of the pathology laboratory of the Faculty of Natural Sciences of the National University of Salta (Argentina). These fungi were kept in agar potato glucose (APG) 2 % and stored at 4 ° C. Steps used in preparation were as follows:

1 - Solutions of bio-oil were prepared at 0.5, 1, and 2 % (w/v), using DMSO 5% (v/v) as solvent.
2 - Mixtures with 20 mL of APG and 5 mL of the solution were prepared.
3 - Petri glass boxes (Ø = 6 cm) with 5 mL of the corresponding APG mix were heated to 50 °C, closed and preserved at 4 °C.
4 - Two controls were used, one with DMSO 5% (v/v) to determine the potential effect of the solvent, and the reference (*Sclerotium* in APG without any additives), to determine the normal growth of the fungus.
5 - At the centre of each box was placed a 5 mm diameter disk of fungal species that had been cultivated for not less than 7 days. The capsules were incubated at 22 ± 2 ° C for 3 days, or until the reference colony covered the full diameter of the box.

The percentage inhibition of growth was calculated for each colony according to the following formula,

$$\% \text{ Inhibition} = [(C-T)/C] \times 100 \quad (1)$$

where C is the average diameter of the colonies of control (DMSO 5%), in mm, and T is the average diameter of the colonies developed in each treatment.

The test was conducted under the framework of a design completely randomized with 5 replicas by treatment.

RESULTS AND DISCUSSION

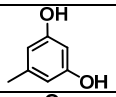
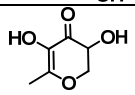
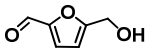
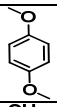
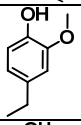
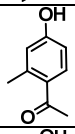
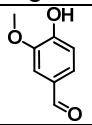
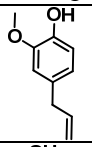
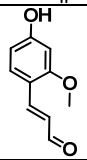
Stepwise Isothermal Fast Pyrolysis

SIFP of milled peanut shells was studied between 200 and 300°C at 100°C intervals under vacuum (0.2 mm.) using nitrogen as the carrier gas with a residence time around 0.01s. Maximum yield of bio-oil was found at 300°C (around 30 %), which is in line with values previously reported [Demirbas 2004, López Rivilli et al., 2011]. Solid char residue after reaction at 300 °C was lower than 5% compared to the original peanut shell mass.

GC-MS of liquid products (bio-oil) obtained at 200 and 300 °C are shown in Fig. 1 and summarized in Table 1.

According to reported experimental and theoretical kinetic studies on pyrolysis of several kinds of biomass, the cellulose, hemicelluloses, and lignin can be expected to react independently even in natural samples, giving a characteristic pattern of products derived from primary and secondary reactions of intermediates (Ranzi et al. 2008). For instance, phenol derivatives, i.e. phenol, guaiacols, catecols, syringols, vanillins are mainly derived from lignin, whereas levoglucosan, furfural, and furans are formed from cellulose and hemicelluloses. On the other hand, hemicelluloses react at lower temperatures than cellulose, and lignin decomposes slowly over a broad range of temperatures. The results make clear that the three decompose within the temperature range here studied; however it can be seen that furans predominated at 200 °C and phenols at 300 °C.

Table 1. GC-MS of Bio-oil

Compound*	RT	m/z (M^+)	Peak Area (%) T °C (bio-oil yield %)	
			200 °C (10)	300 °C (30)
	10.004	124	12.3	____
	11.384	144	16.6	____
	13.003	126	48.0	3.0
Hexadecane	18.340	192	5.1	____
	10.094	124		22.4
	10.342	72		27.8
	12.273	138		10.0
	13.834	152		6.6
	14.494	150		5.4
	15.948	151		4.6
	16.675	164		7.1
	17.803	178		5.2

* The identification of the peaks was based on computer matching of the mass spectra with the National Institute of Standards and Technology (NIST) library.

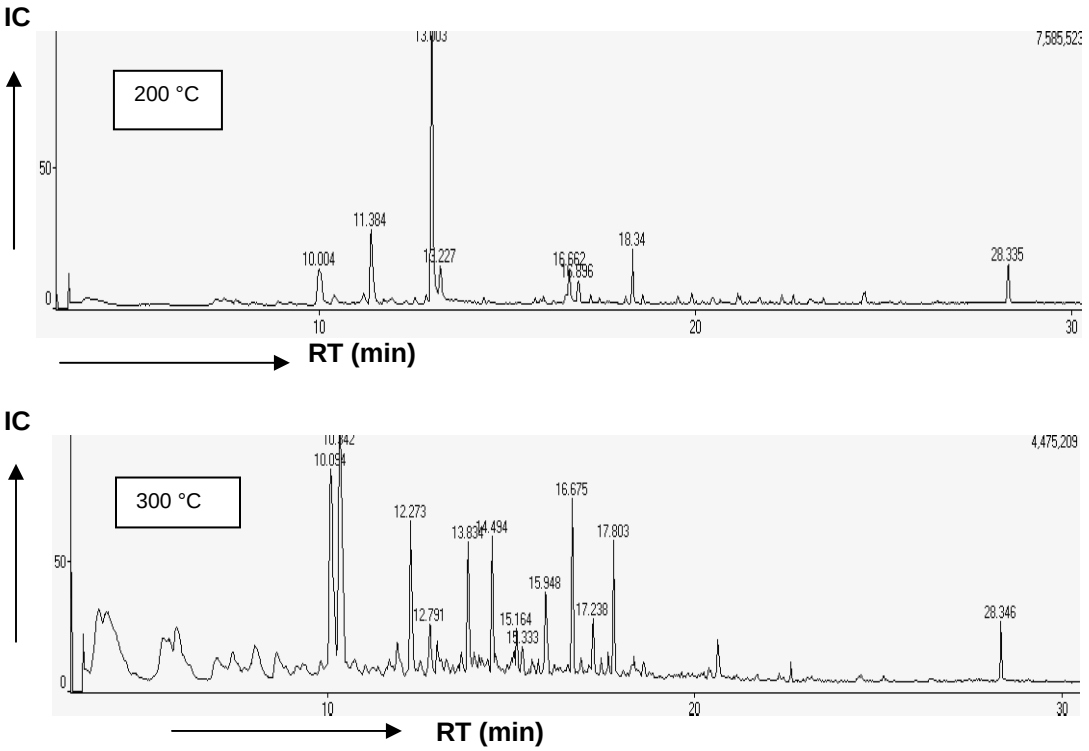


Figure 1. GC-MS of bio-oil

Antifungal Activity of Bio-oil

The antifungal activity test was carried out with *Sclerotium rolfsii*, which belongs to the genus *Sclerotium*, family *Typhulaceae*. It is a soil phytopatogen fungus with more than 500 hosts. It is distributed worldwide, with more presence in tropical and subtropical regions. Their resistance structures are called *esclerocio*, which constitute the main source of primary inoculums. This species of fungus attacks different phases of the development of their hosts, from seed to agricultural products in post-harvest. Results shown in Table 2 demonstrate that bio-oil obtained at 300 °C, constituted mainly by phenol derivatives, completely inhibited the development of *Sclerotium rolfsii* at a concentration of 2.0 % w/v.

Table. 2. Test of Antifungal Activity

Capsule Content	**Average Ø (% inhibition)**
Control (APG)	5.00 cm
Reference (APG + DMSO)	4.92 cm
0.5 % w/v	5.00 cm (0 %)
1.0 % w/v	4.14 cm (16 %)
2.0 % w/v	0.00 cm (100 %)

CONCLUSIONS

1. SIFP of peanut shells was shown to be an interesting technique to produce less complex pyrolyzates, making it easier to obtain valuable chemicals from bio-oil.
2. Reaction products were in agreement with previously reported thermal behavior of these components, with smaller energy barrier of activation for cellulose and hemicelluloses and major energy barrier for lignin. However, clearly the three decompose within the temperature range here studied.
3. Bio-oil obtained at 200 °C contained mainly 5-hyroxymethylfurfural, which is an interesting compound to be used as such, or after reduction to 2,5-dimethyl furan to replace bio-ethanol in gasoline (Zhong et al. 2010).
4. Antifungal activity of bio-oil obtained from peanut shells SIFT at 300 °C on *Sclerotium rolfsii*, seems promising, since inhibition was complete at 2% w/v.

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