Stepwise Isothermal Fast Pyrolysis (SIFP) of Biomass. Part III. SIFP of Olive Oil Industry Wastes

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Pyrolysis of olive oil industry wastes was carried out using stepwise isothermal fast pyrolysis (SIFP). SIFP consists of a succession of isothermal fast pyrolysis reactions in which the solid products obtained from the previous isothermal fast pyrolysis reaction become the substrates for subsequent reactions at higher temperatures. This article reports the results obtained from the SIFP of olive oil residue carried out between the temperatures of 300 and 500 °C using 100 °C intervals under reduced pressure (200 mm Hg). The maximum yield of liquid products occurred at 300 °C and consisted of around 35% bio-oil, which contained mainly phenols, furans, and fatty acid methyl esters (FAME). At 400 and 500 °C, FAME, which is derived from residual olive oil, was the major product.

Keywords: Fast pyrolysis; Olive oil residue; Bio-oil; Phenols; Guaiacol; Olive oil FAME

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INTRODUCTION

The fast pyrolysis of lignocellulosic biomass produces solid (char), liquid (bio-oil), and gaseous fractions. The liquid products have been reported to be of low viscosity and high chemical complexity, containing hundreds of different compounds derived from the primary and secondary reactions of lignin, cellulose, and hemicellulose (Horne and Williams 1996; Mohan *et al.* 2006; De Wild *et al.* 2011). Bio-oil is an attractive source of several interesting chemicals.

A pyrolysis technique called stepwise isothermal fast pyrolysis (SIFP) has been previously investigated by this team. This technique involves a succession of reactions whereby the solid products of each isothermal fast pyrolysis reaction become the substrates for the next reaction. Through a gradual heating of the same sample, the product composition becomes less complex at each subsequent temperature, and the separation of certain compounds from their reaction products is much easier and provides better yields. This fact has been demonstrated in previous papers in which the SIFP technique was applied to reactions of pine sawdust and peanut shell (López Rivilli *et al.* 2011, 2012).

Olive oil residue is an important biomass resource found in the province of Catamarca, Argentina, and the direct disposal of this resource has a negative environmental impact on soil and flora.

In this work, the results obtained from stepwise isothermal fast pyrolysis (SIFP) conducted between 300 and 500 °C on olive oil industry wastes, at 100 °C intervals and under low pressure (200 mmHg), are reported.

EXPERIMENTAL

Stepwise Isothermal Fast Pyrolysis

The olive oil residues were obtained from the pilot plant of the Universidad de Catamarca, Argentina *via* the two-phase centrifugal system (2PCS).

The cellulose, hemicelluloses, and lignin contents of the olive oil industry wastes were determined using the Official Methods of Analysis of AOAC (15th Edition) and are shown in Table 1.

Table 1. Composition of Olive Oil Residue

Olive Oil Residues	%
Cellulose	39.2
Hemicelluloses	19.8
Lignin	31.8
Olive Oil	6.5

The pyrolysis reactions were carried out as previously described (López Rivilli *et al.* 2011). Around 5 g of dry olive residue (dried over a period of 40 min at 105 °C) was used in each run. Even though the milling of biomass samples is a common practice in biomass pyrolysis, the crude residue, obtained after compression and centrifugation, was used in this study to minimize handling and cost, in view of a possible productive scale. Each sample was placed inside a porcelain boat that was covered with a stainless steel grid to avoid projection. Each isothermal fast reaction was run over the course of 1 h, as it had been determined that this length of time was sufficient for complete biomass decomposition at each point. The products were collected in a U-shaped trap immersed in liquid nitrogen. After the reaction had finished, this trap was allowed to reach ambient temperature, and the products were extracted with acetone and subjected to GC/MS analysis.

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

RESULTS AND DISCUSSION

Stepwise Isothermal Fast Pyrolysis

The SIFP of olive residues was studied between 300 and 500 °C at 100 °C intervals under low pressure (200 mm Hg). The maximum yield (around 35%) of bio-oil was observed at 300 °C.

The GC-MS results from the liquid products (bio-oil) obtained at 300, 400, and 500 °C are shown in Fig. 1 and summarized in Table 2.

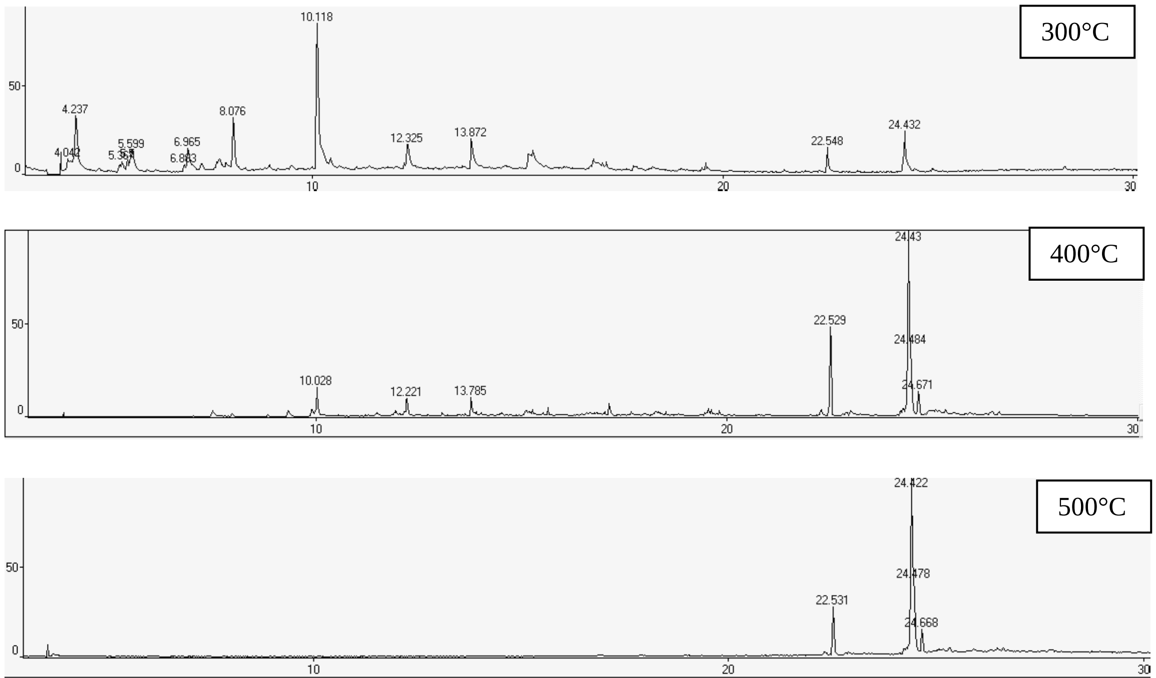

Fig. 1. GC (TIC) of crude bio-oil from SIFP of olive oil residue

Table 2. GC-MS of Bio-oil

Compound*	RT	m/z (M^+)	Peak Area (%) *T* °C (bio-oil yield %)		
			300 °C (35)	400 °C (13)	500°C (5)
2-Propanone-1-acetyloxy-	4.24	116	10.92	____	
Butyrolactone	5.60	86	6.67	____	
2-furanmethanol-tetrahydro-	8.08	102	12.98	____	
Guaiacol	10.12	124	36.74	5.46	
p-cresol-2-methoxy	12.32	138	6.16	3.25	
p-ethylguaiacol	13.87	152	11.15	3.53	
Hexadecanoic acid methyl ester	22.55	270	5.83	11.32	14.44
Octadecenoic acid methyl ester	24.43	296	11.45	36.53	78.57
Octadecanoic acid methyl ester	24.67	298	_____	3.48	6.99

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

The GC-MS results for the reaction at 300 °C showed the characteristic pattern of lignocellulosic biomass pyrolysis (Bridgwater and Peacocke 2000; Demirbas 2001; Ranzi *et al.* 2008; Yaman 2004). The bio-oil was rich in phenol and furan derivatives with a very important high yield of guaiacol. Methyl palmitate (RT ~22.5) and oleate (RT ~24.4) were also present at 300 °C. These FAME derived from olive oil became the major products at 400 and 500 °C. The peak at RT 24.48 agreed with a 9-octadecanoic acid methyl ester isomer. As far as is known, the methyl esters of fatty acids are not frequently reported on in triglyceride pyrolysis studies.

Next, the focus shifted to a study of the pyrolytic behavior of samples that had been previously enriched with pure olive oil (10% wt/wt) under the same experimental conditions. Olive oil (50 g) was dissolved in hexane and poured into 500 g of dry olive residue. Then, hexane was evaporated under reduced pressure. The results obtained from isothermal FP at 300 °C for this sample are shown in Fig. 2.

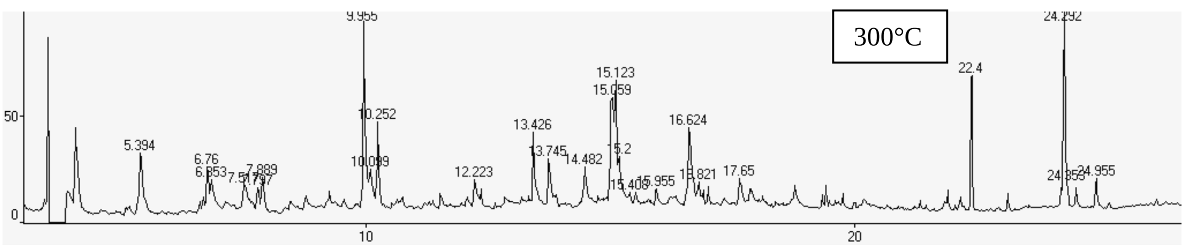

Fig. 2. GC (TIC) of bio-oil from isothermal FP of olive oil residue with 10% wt/wt of pure olive oil

A comparison of the GC shown in Fig. 2 with that shown in Fig. 1 at 300 °C clearly demonstrated the increase in FAME yield for the former. This fact reinforced the hypothesis regarding the methylating ability of lignocelluloses or their thermal derivatives. Moreover, the GC-MS of Fig. 2 displayed peaks that could be assigned to pure olive oil thermal decomposition, mainly aldehydes (RT 10.25, 13.42, and 15.12), probably because the added olive oil exceeded the methylating capability of the lignocelluloses. For this reason, it was evident that triglycerides initially present in olive oil residue interacted thermally with the other compounds within the original distribution in olives (probably lignin and/or intermediate compounds produced therein) to produce the FAME. The interaction between the lignocellulosic compounds and the triglycerides has been previously investigated. Buzetzki *et al.* (2011) reported an interesting catalytic effect of lignocellulosic residue on triglyceride cracking.

CONCLUSIONS

1. The SIFP of olive oil residue was shown to be an interesting technique for the production of less complex pyrolyzates, which makes it easier to obtain valuable chemicals from bio-oil.
2. Bio-oil obtained at 300 °C contains primarily guaiacol, an attractive compound that can be used to manufacture antioxidants as precursors to various flavors such as eugenol and vanillin. Its derivatives are used medicinally as expectorants, antiseptics, and local anesthetics.

3. Fatty acid methyl esters (FAME) derived from olive oil and present in olive oil residue were the major products obtained at 400 and 500 °C. It was apparent that olive oil reacts with lignocellulosic compounds or thermal intermediates derived from the biomass studied to produce olive oil FAME.
4. The valuable chemical products obtained from bio-oil, mainly guaiacol and biodiesel, by means of the SIFP of olive oil industry wastes are an attractive way to finance their remediation.

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