

## STEPWISE ISOTHERMAL FAST PYROLYSIS (SIFP) OF BIOMASS. PART I. SIFP OF PINE SAWDUST

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Pyrolysis of pine wood sawdust was carried out using stepwise isothermal fast pyrolysis (SIFP), focusing on the search of reaction conditions to obtain chemicals in good yields from biomass. 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 by SIFP of pine sawdust between 200 and 600°C using 100°C intervals under vacuum (0.2 mm), using nitrogen as carrier gas. Both sets of reactions made it possible to obtain most of the compounds that have been previously described in conventional fast pyrolysis experiments; however this system produces a smaller number of chemical compounds in each isothermal FP, making it easier to obtain determined chemicals with industrial or research value. Maximum yield of liquid products occurred at 300°C, giving around 30% of bio-oil, which contained mainly phenols and furan derivatives. Liquid-Liquid extraction led to a rich mixture of phenol derivatives. Results showed that SIFP is an interesting technique to obtain enriched fractions of products derived from biomass pyrolysis.

*Keywords: Fast pyrolysis; Biomass; Bio- oil; Phenols*

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### INTRODUCTION

The use of biomass for different purposes such as energy production has been regarded as a significant challenge for many years. The fact that fossil fuels sources are limited, in addition to the environmental pollution caused by combustion or petrochemical uses of these fuels are among the most important reasons for this research. Much effort has been spent in this area, which is reflected in factories producing bio-oil all around the world and numerous publications and patents in this field (Bridgwater and Peacocke 2000; Demirbas 2001; Yaman 2004). Within these references, Mohan et al. (2006) reviewed the state of the art in biomass pyrolysis.

Fast pyrolysis of wood produces 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 (Horne and Williams 1996; Aguado et al. 2000).

In an attempt to quantify some of the components present in bio-oil, Branca et al. (2003) selected forty of them from the liquid fraction and carried out GC/MS of samples from different origins. The aim of the study was to establish the correspondence of yields of these compounds with reaction temperature and heating rates conditions. They proved that there is no big difference of products from the pyrolysis zone in updraft gasification and fast pyrolysis in commercial systems.

Another study reported the identification of different compounds, dividing the samples into aqueous and organic fractions, according to the condensation method. Pyrolysis reactions were carried out between 450 and 700°C. The identified compounds were almost the same as those described elsewhere in the literature (Nonier et al. (2006)).

Some other attempts were made to characterize pyrolytic lignin components from the water-insoluble fraction of bio-oil (Scholze and Meier 2001; Scholze et al. 2001), and more recently, the influence of a pre-pyrolysis step at 250°C was also studied being the reported compounds in the liquid phase analog to those previously described (Arias et al. 2006).

It has been reported that hemicelluloses thermal decomposition occurs at lower temperatures than cellulose. In slow pyrolysis of wood it begins in the temperature range of 130 to 194 °C (Ranzi et al. 2008); however this difference with the temperature required for cellulose decomposition cannot be observed when heating rate is too fast.

According to reported experimental and theoretical kinetic studies on pyrolysis of several kinds of biomass including reference studies on synthetic biomass, it has been found that cellulose, hemicelluloses, and lignin react independently even in natural samples, giving a characteristic pattern of products derived from primary and secondary reactions of intermediates. 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.

It is well known that bio-oil is an interesting source of several attractive chemicals; nevertheless most of references are directed to renewable energy sources more than experimental conditions appropriate to obtaining enriched mixtures useful for their further separation.

Conventional fast pyrolysis involves severe thermal conditions, and the energy supplied is high enough to overcome energy barriers required for several reactions routes. The great number of different reactive intermediates colliding within the reaction zone explains the complexity of products derived from primary and secondary reactions.

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.

The term stepwise fast pyrolysis has been used by Murwanashyaka (2001) to describe a technique where biomass is submitted to fast pyrolysis, increasing temperature between a lower and upper limit at different heating rates. Then, in a subsequent step, the residual solid is pyrolyzed in a new heating program, beginning at the temperature of previous upper limit.

In this paper we report results of a technique we named SIFP. We define stepwise isothermal fast pyrolysis (SIFP), as a successive set of reactions where solid products of an isothermal fast pyrolysis become the substrate of the next one.

Therefore we decided to carry out systematic efforts to find pyrolytic conditions appropriate to obtain chemicals from biomass in a practical way. In this paper we report results of stepwise isothermal fast pyrolysis (SIFP) of pine wood sawdust between 200 and 600°C with nitrogen as the carrier gas.

## EXPERIMENTAL

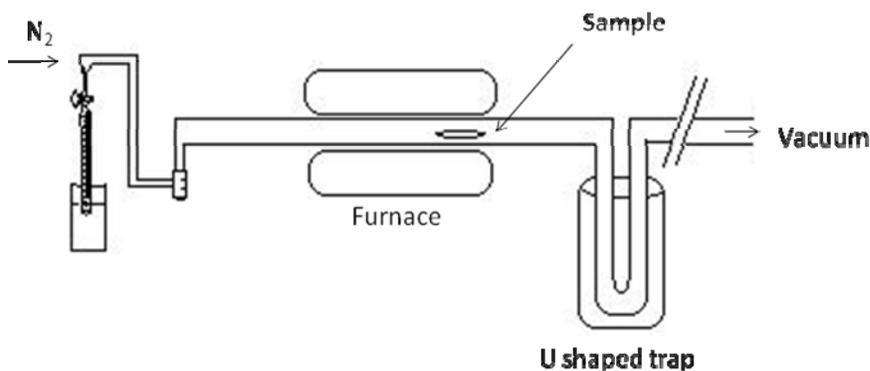
Samples of pine sawdust were of inhomogeneous size, up to 2 mm. The content of cellulose, hemicelluloses, and lignin of the sample was determined by INTA (National Institute of Agricultural Technology), using Official Methods of Analysis of AOAC (15<sup>th</sup> Ed.), and is shown in Table 1.

**Table 1.** Pine Sawdust Composition

Pine Sawdust	%
Cellulose	56.6
Hemicelluloses	18.9
Lignin	16.9

Since it has been reported that initial moisture content produces important changes on the composition of pyrolytic oils, samples were dried for 40 minutes at 105 °C (Demirbas 2004a). Around 1 g of dried sawdust was used in each run; this was placed inside a porcelain boat covered with a stainless steel grid to avoid projection.

Pyrolysis reactions were carried out in a Vycor glass reactor, 50 cm length and 2.3 cm i.d., placed inside a tubular furnace of 30 cm length (Thermolyne 21100) as shown in Fig 1.



**Figure 1.** Schematic diagram of pyrolysis system

The sample to be pyrolyzed, was placed 20 cm before the furnace inlet to maintain it cold until temperature (measured at the final sample position), pressure, and carrier gas flow had been adjusted to predetermined values. Once the system was ready, the sample

was introduced inside the hot zone, near the furnace outlet, to reduce the distance to the cold trap. Products were collected in a U-shaped trap immersed in liquid air.

After the reaction was 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 equipment, 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).

## RESULTS AND DISCUSSION

In order to be used as reference and to check whether the performance of our system was similar to those described in the literature, fast pyrolysis of 1g of pine sawdust was carried out at 300°C, 0.2 mm pressure (Hg), and nitrogen as the carrier gas with a residence time around 0.01 s. Results are shown in Fig. 2. It can be seen that the greater part of products found in the pyrolyzate agreed with those previously reported (Bridgwater and Peacocke 2000; Demirbas 2001; Yaman 2004).

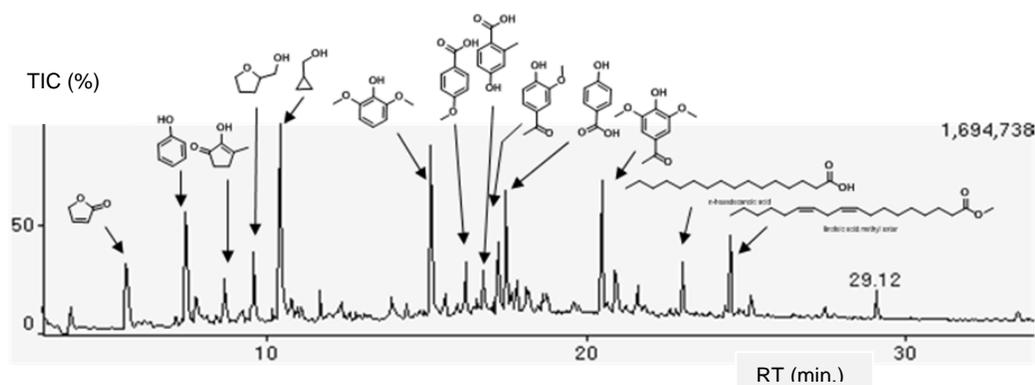


Figure 2. GC/MS of bio-oil, FP at 300°C

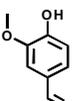
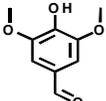
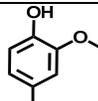
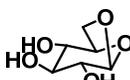
SIFP reactions of pine sawdust were carried out between 200 and 600°C at 100°C intervals, with vacuum (0.2 mm) and nitrogen as the carrier gas. Each isothermal fast reaction was run during 1 hour, since it was checked out that this time was enough to complete pine sawdust decomposition at each point.

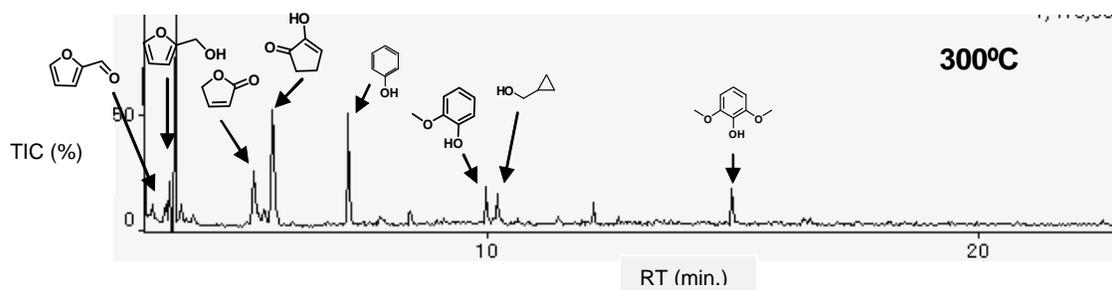
The maximum bio-oil yield was obtained at 300°C, similarly to what was reported by Demirbas (2004b). Figure 3 shows the results of GC/MS of bio-oil obtained by SIFP at 300 °C.

Clear quantitative and qualitative differences between GC/MS of bio-oil obtained from conventional FP at 300 °C, are shown in Fig. 2, in comparison with results obtained by SIFP at the same temperature (Fig. 3).

Bio-oil yields and concentration of main products obtained by SIFP at 200, 300, and 400 °C are shown in Table 2. Results at 500 and 600 °C are not reported because bio-oil yield was very low (< 1%).

**Table 2.** GC/MS of Bio-oil Obtained by SIFP at 200, 300, and 400 °C

Compound Formula	m/z	% conf.	% of Total Area		
			Temperature °C (bio-oil wt %)		
			200 (10)	300 (30)	400 (8)
	94	96	32.3	27.6	5.7
	72	91	15,8	6.6	-----
	154	95	5,8	6.5	7.6
	84	95	3.1	12.3	-----
	98	92	5.1	30.7	-----
	151	97	7,9	-----	-----
	181	94	9,4	-----	-----
	124	94	-----	9.6	9.3
	108	91	-----	-----	5.7
	138	91	-----	-----	14.2
	144(M-H <sub>2</sub> O)	94	-----	-----	31.7

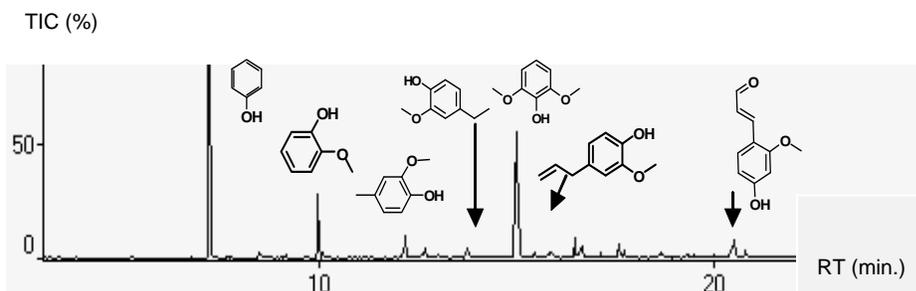


**Figure 3.** GC/MS of bio-oil obtained by SIFP at 300 °C

From the results it is apparent that three compounds, i.e. phenol, syringol, and 2-hydroxy-2-cyclopentenone represented nearly 70% of the total area of bio-oil obtained by SIFP at 300 °C. Besides, at 400 °C the levoglucosan peak represented 31.7% of the total area under the GC curve.

To prove reproducibility, and in parallel to get enough samples with preparative purposes, a set of 15 SIFP reactions at 300 °C were performed, and bio-oil was accumulated. Such accumulation afforded a GC/MS similar to that shown in Fig. 3.

It has been reported that the phenolic fraction of bio-oil has interesting anti-fungal (Mohan et al. 2008), and antioxidant activities (Dobele 2009). Besides, they may be used in synthetic resins for different targets (Nakai et al. 2007). Therefore we carried out a simple procedure to obtain a phenol derivatives-rich fraction using the accumulated bio-oil obtained at 300 °C by SIFP. Bio-oil was extracted with ethyl acetate at pH 11, then, after neutralization with hydrochloric acid, it was extracted again with ethyl acetate, which after solvent evaporation led to a mixture (> 20 % referred to bio-oil) of phenol derivatives free of products derived from cellulose and hemicelluloses. GC/MS of this mixture is shown in Fig. 4.



**Fig.4.** Phenols obtained by liquid-liquid extraction

## CONCLUSIONS

1. Stepwise isothermal fast pyrolysis (SIFP) was shown to be an interesting technique to obtain less complex pyrolyzates than those produced in conventional fast pyrolysis.

2. This technique makes it simpler to separate chemicals either in a relative pure state or as a rich fraction. Scaling up to pilot or industrial plants seems straightforward by means of available and known technologies.
3. Results from pine sawdust SIFT were in good agreement with experimental and theoretical findings previously reported.
4. Even though hemicelluloses reacts at lower temperatures than cellulose, and lignin decomposes slowly over a broad range of temperatures, clearly the three decompose within the temperature range studied in the present work.
5. Finally, it has been reported that mixtures of phenol derivatives (Fig. 4) have interesting anti-fungal (Mohan et al. 2008) and antioxidant activities (Dobele 2009). Besides, they may be used in synthetic resins for different targets (Nakai et al. 2007).

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