Upgrading of Tars from Waste Valorisation Processes by HPLC Fractionation: Scale up From Analytical to Preparative

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Pyrolysis is regarded as one of the most promising technologies for the valorization of waste materials and to obtain chemicals and alternative fuels to fossil ones. Pyrolytic oils are a very complex mixture hydrocarbons or oxygenated compounds with a wide distribution of molecular weights. High Performance Liquid Chromatography is a suitable way to analyze and separate these complex liquids. An analytical method to separate pyrolysis heavy oils into fractions has been optimized and then, this method has been scaled up to preparative chromatography. A preparative column has been chosen and operating conditions have been determined to separate high amounts of liquids into different fractions.

1. Introduction

The sustainable development demands technologic innovations to support the proposal of economically feasible processes for the valorization of waste materials in the industrial and consumer society. This requirement can also be extended to the valorization of raw materials regarded as fossil fuels alternatives and to refinery streams that previously have had a secondary interest.

Pyrolysis is considered as one of the most promising technologies for waste valorization, since it brings the possibility to obtain fuels or valuable chemicals. Generally speaking, pyrolysis yields three fractions: gas, liquid and char or solid residue, depending on the feed and operating conditions. In order to maximize liquid fraction yield, pyrolysis has to be carried out with very short volatiles residence times (typically below 1s) and fast heating rates.

The conical spouted bed reactor (CSBR) is suitable for the handling of particles of irregular texture, fine particles, sticky solids and those with a wide size distribution, due to the great versatility as far as gas flow is concerned (Olazar et al., 1992). The excellent movement of the solid in this reactor leads to high heat transfer between phases, allowing bed isothermicity. Besides, operation can be conducted with short gas residence times (as low as milliseconds) in the dilute spouted bed, which makes this reactor suitable for flash pyrolysis.

Biomass is considered one of the most promising alternatives to fossil fuels and feedstocks, since adequately used it does not contribute to a net rise in the level of CO_2. Flash pyrolysis of biomass leads to a high amount of liquid, typically between 70-80 %, and small yields of gas and char (Bridgwater et al., 1999). Bio-oil is a very complex mixture of high amounts of water and oxygenated compounds (Goyal et al., 2008). Bio-oil can be treated in numerous ways to produce hydrocarbons (Gayubo et al., 2010), hydrogen (Bimbela et al., 2008), or to improve its fuel characteristics (Oasmaa & Czernik, 1999). However, in all these processes there may be some undesirable components in the bio-oil, such as the heavy compounds called pyrolitic lignin that cause several problems in its pumping.

Waste tires are considered a hazardous waste and there are regulations that forbid their landfill, considerable attention has been paid to waste tire management. The volatile stream obtained in the tire pyrolysis process is suitable for its transformation into fuel and contains components of commercial interest, such as limonene, or chemicals, such as BTX and rubber monomers. Tire-derived residual carbon blacks have two different applications: on the one hand, reuse as carbon black, on the other hand, active carbons can be obtained from residual carbon black.

One way to remove these undesirable compounds from the pyrolysis liquids or to purify valuable products is using High Performance Liquid Chromatography (HPLC), which is a suitable technique to analyze and upgrade heavy fractions (Cela et al., 2002). The aim of this work is a first approach to optimize an analytical method to separate pyrolysis heavy oils into fractions in order to upgrade and valorize them and to scale up to preparative separation.

2. Experimental

2.1 Pyrolysis pilot plant
Pyrolysis runs have been carried out at the pilot plant shown in Figure 1.
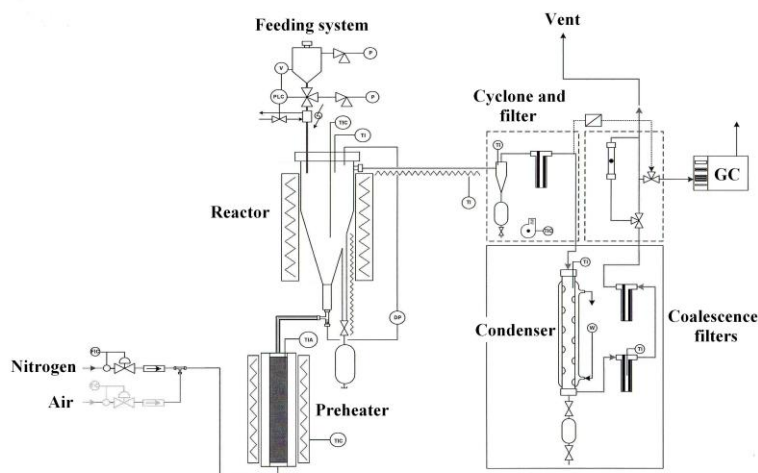

Figure 1 Schematic diagram of the pyrolysis pilot plant

This pilot plan has been used in the pyrolysis of several types of waste, such as tires (Arabiourrutia et al., 2008; Lopez et al., 2009), plastic waste (Artetxe et al., 2010; Elordi et al., 2009) and biomass (Aguado et al., 2000) and has been described in detail elsewhere.

Three heterogeneous mixtures made up by organic compounds and obtained in waste valorization processes have been studied in this work: liquid obtained at the catalytic pyrolysis of tires at 500 ºC, using a HZSM-5 catalyst (Arabiourrutia et al., 2008; Olazar et al., 2008) and light and heavy oil (tar) from flash pyrolysis of pinewood sawdust at 450ºC (Aguado et al., 2000).

2.2 Analytical to preparative scale up methodology.

The methodology follow to scale up from analytical to preparative is shown in Figure 2. When applying this methodology several considerations have to be taken into account. First, the analytical chromatography should be carried on in a similar column than the preparative one (packing material, length and particle diameter). The loading study has to be carried out overloading the column by increasing the volume or the concentration of the sample; in this way, it is possible to determinate the maximum amount of the sample that the column can separate adequately. Finally, once the maximum amount that can be adequately separated in the analytical column is known, the type and size of the preparative column have been determined using the program "Waters Preparative Calculator".
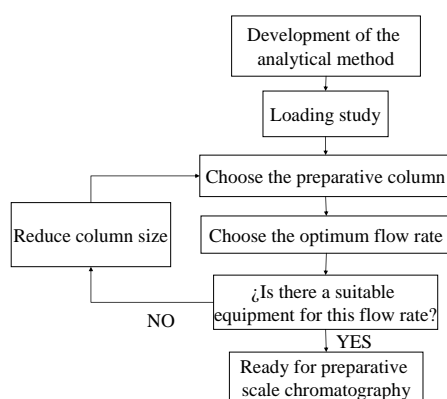

Figure 2 Methodology for the scale up from analytical to preparative.

3. Results

3.1 Analytical chromatography method development

Due to the chemical properties of the samples (PM < 3000 and soluble in polar solvents) Reversed Phase Liquid Chromatography (RPLC) is recommended (Cela et al., 2002), and so Atlantis R T3 5um (4.6 x 150 mm) column was chosen for analytical RPLC. The experiments were carried out in an Agilent HPLC 1100. Following to Snyder (1974), water (H_2O), acetonitrile (ACN) and methanol (MeOH) were selected as solvents and

samples were diluted in THF (2.5% w/w). Gradient elution has been chosen due to its better performance compared to isocratic elution, as the time required to the analysis is lower and offers the advantage of collecting fractions with higher product concentration. The optimum conditions for sample fractionation are summarized in Table 1 and the obtained chromatograms are shown in Figure 3.

Table 1 Analytical method conditions

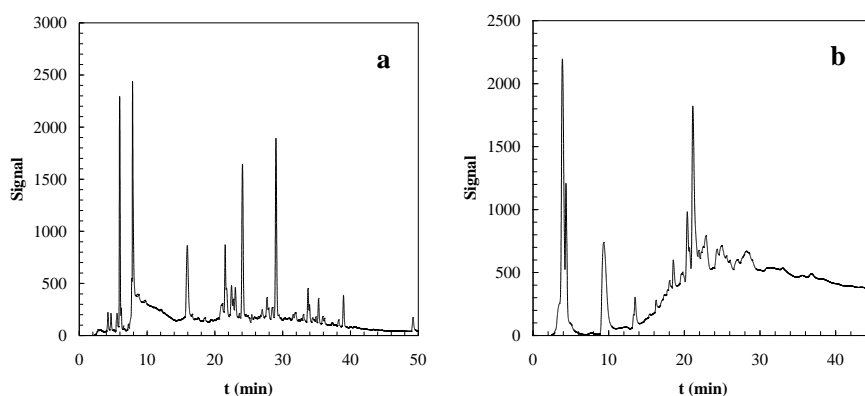| Sample	Optimum wave length	Mobil phase flowrate (mL/min)	Solvents	Mobil phase gradient (%)
Light bio-oil	202	0.5	ACN-H_2O	0-100
Heavy bio-oil	202	0.5	ACN-H_2O	0-100
Tires oil	230	0.5	MeOH-H_2O	30-85

Figure 3 Analytical chromatograms obtained for the light bio-oil (a) and tires oil (b).

3.2 Loading study
The loading study has been carried out overloading the column by increasing the injected volume until the chromatographic separation is not appropriate and peaks are completely overlapped. The maximum amounts that can be loaded in analytical scale are:

Table 2 Loading study in analytical scale.

Sample	Injected amount (mL)	Concentration (%wt)
Light bio-oil	5	35
Heavy bio-oil	5	60
Tires oil	2.5	20

3.3 Choice of the preparative column and flow rate
The results of the load study have been integrated in the "Waters Preparative Calculator" to determine the column dimensions and operating conditions of the preparative system, Table 3.

Table 3 Determination of the preparative scale column dimensions and operation conditions

	Internal diameter (mm)	Length (mm)	Load mass (mg)	Injection volume (µl)	Flowrate (mL/min)
Light bio-oil					
Analytical	4.6	150	3	5	1
Preparative	30	150	119	213	21
Preparative	50	150	330	591	59
Heavy bio-oil					
Analytical	4.6	150	0	3	1
Preparative	30	150	19	213	21
Preparative	50	150	54	295	59
Tires oil					
Analytical	4.6	150	5	5	1
Preparative	30	150	64	213	21
Preparative	50	150	178	591	59

Viewing these results, the best option would be an Atlantis R T3 column with a particle diameter of 5 µm, a length of 150 mm and an internal diameter of 30 or 50 mm. The solvent consumption, considering 1 h experiments would be 1.27 l for the 30 mm column and 3.54 l for the 50 mm column. In this case, the 50 mm column offers a lower time to purify a determined sample amount, as the ratio between the solvent consumption and the purified oil mass is the same in both cases.

On the other hand, it is noteworthy that solvent consumptions are very high, so in order to improve the efficiency of the process, a solvent purification system should be designed. Finally, if the objective is to separate a certain component, such as the pyrolitic lignin in bio-oil or the BTX fraction in tires oil, a specific gradient elution can be created to separate only this components, reducing the experiment time and therefore, the solvent consumption.

4. Conclusions

The conical spouted bed reactor is a suitable technology for both thermal and catalytic pyrolysis of different solid wastes; moreover due to it high heating rate and short residence time high yields of pyrolysis liquid are obtained.

High Performance Liquid Chromatography is an appropriate technique to characterize heavy tars produced in the pyrolysis of tires and biomass. Preparative Reversed Phase Liquid Chromatography could be a good large scale separation process to purify some interesting compounds of pyrolytic oils, and to remove undesirable products like lignin in bio-oils. Because of the high solvent consumption at preparative scale, a good solvent recovery method should be developed, in order to improve the feasibility of the process.

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