



## Full Length Article

# An integrated process for the production of lignocellulosic biomass pyrolysis oils using calcined limestone as a heat carrier with catalytic properties



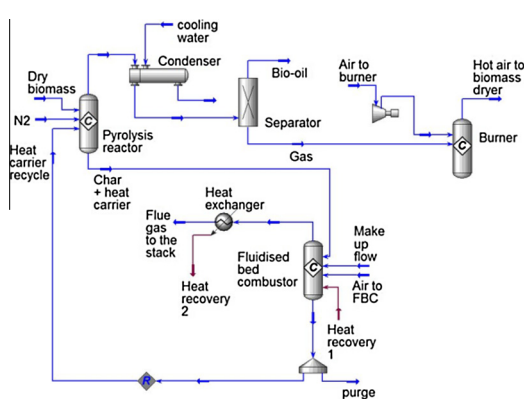
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## HIGHLIGHTS

- An integrated process for upgraded bio-oil production was assessed.
- Catalytic pyrolysis of wood biomass was studied in an Auger reactor.
- Char combustion was studied in a fluidised-bed reactor.
- Full regeneration of heat carrier catalytic properties was not accomplished.
- Char combustion was feasible from environmental and operational points of view.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The production of upgraded bio-oils by an integrated process using a mixture of calcined limestone and sand as a heat carrier with catalytic properties was experimentally studied at pilot scale. The integrated process consisted of two main steps: biomass catalytic pyrolysis in an Auger reactor for bio-oil production and char combustion in a fluidised-bed combustor for heat carrier heating and regeneration. A temperature of 450 °C was fixed as an optimum value to carry out the catalytic pyrolysis step. Temperatures ranging from 700 to 800 °C were assessed in the char combustor. Process simulation demonstrated that solid recirculation from the combustor to the pyrolysis reactor was marginally affected in this temperature range. However, an optimum char combustion temperature of 800 °C was selected from an environmental point of view, since lower polyaromatic emissions were detected whilst NO<sub>x</sub> emissions were kept under the legislation limits. Under designated conditions, several pyrolysis-combustion cycles were carried out. A moderate deactivation of the catalyst by partial carbonation was found. This fact makes necessary the incorporation of a purge and an inlet of fresh heat carrier in order to maintain the bio-oil quality in the integrated process.

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## 1. Introduction

Considering the increase on the demand of energy, new clean and renewable sources are emerging in order to minimise the environmental impact associated to the use of fossil fuels. Valorisation

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of lignocellulosic biomass from pyrolysis process is in increasing research, becoming one of the most promising thermo-chemical conversion technologies [1]. Pyrolysis allows the conversion of biomass into value-added chemicals and potential fuels in the form of gas, solid and especially in the form of liquid. This liquid, also called bio-oil, presents higher energy density than solid biomass and can be easily stored and transported, making it a good potential candidate to be used as a new sustainable energy vector [1,2]. Although there are several activities taking some steps forward in the commercialization of bio-oil for energy applications [3], its use as a fuel is limited due to its specific properties. Thus, its high oxygen content, its remarkable acidic character and its chemical instability [4] makes it difficult to be applied directly in power generation. As a result, the bio-oil needs to be upgraded in order to make it suitable for current infrastructures.

There are several technologies relying on bio-oil upgrading which are trying to eliminate the oxygen-containing molecules by increasing the H/C ratio, being in situ catalytic pyrolysis one of the most promising. It is well known that the reactor design and the proper selection of the catalysts play a fundamental role in this kind of technology. Ideally, the catalysts employed should be highly active, selective to particular products, resistant to deactivation, readily recycled and whenever possible, cheap and widely distributed. Although different and relatively high value catalysts have been tested for biomass catalytic pyrolysis, including microporous zeolites, mesoporous M41S and mesoporous aluminosilicates [5,6], some low-cost catalysts such as bulk metal oxides [7], sulphide/oxide, alumina, metals supported mainly on alumina [8], clay materials [9] or industrial wastes, such as red mud [9,10], have also been tested with relative success for biomass catalytic pyrolysis.

In order to evaluate the industrial prospects of the biomass pyrolysis, the use of Auger type reactors can be highlighted [11,12]. This type of reactors has a simple design that allows the user to work with low carrier gas flow and with large biomass particles showing an excellent reproducibility and stability [13,14]. Moreover, they are easy-scalable and can be applicable for small, medium and portable pyrolysis systems in distributed or decentralised areas. In this type of reactors, where the heat input is indirect, the use of a heat carrier at commercial scales is very recommendable in order to provide the required high rates of heat transfer [15]. Indeed, several authors [15,16] working on an Auger reactor using heat carriers without catalytic properties, have already reported liquid yields quite similar (75 wt.%) to those obtained by flash pyrolysis on fluidised-bed reactors. In this line, some of the main companies in the field, such as ABRI-tech in Canada, Lurgi-Ruhr gas process in Germany or Renewable Oil Intel in USA have already implanted large scale Auger reactors [4]. These advances at industrial scales, together with the fact that the catalytic pyrolysis of biomass in an Auger reactor has been only studied for a few researches [17], raise an attractive investigation field.

Several layouts for the pyrolysis process have also been proposed to reach a global self-sustainable performance from an energetic point of view [3,18,19]. In a previous work developed in our group, both oxygen content and acidity of bio-oils were found to decrease in woody biomass pyrolysis carried out in an Auger reactor when low-cost materials, such as CaO/sand or CaO-MgO/sand mixtures, were used as both in situ catalysts and heat carriers [20]. Moreover, the self-sustainable performance of the pyrolysis system (operating at 450 °C) followed by the char combustion process (operating at about 800 °C) was theoretically demonstrated from an energetic standpoint. The process simulation demonstrated that the circulation of solids required between the pyrolysis and the combustor reactor was the lowest using CaO/sand mixture. In that work, the pyrolysis step was also experimentally tested in a pilot-scale Auger reactor for a certain CaO to biomass ratio but the

performance of the char combustion step and its influence on the overall process was not carried out. Herein, a fluidised-bed reactor is proposed as an appropriate technology to carry out this step, since it would facilitate both the solids transport in the system and the char total combustion [21]. Besides, this type of combustor would be a suitable technology for the energetic use of biomass char because of its advantages in terms of reduction of pollutant emissions and flexibility [22].

Therefore, the initial objective of this work is to study experimentally the char combustion process in a fluidised-bed combustor at temperatures ranging from 700–800 °C, using a CaO + sand mixture as heat carrier with catalytic properties. After that, a study of the performance of the integrated system during cyclic operation was carried out.

## 2. Material and methods

### 2.1. Biomass and materials

The biomass used in the present study was forest pine woodchips (*Pinus halepensis*) containing bark, obtained from north-east area of Spain (Ansó, Huesca) and was supplied by AFPURNA S.L. The fresh biomass was first dried up to moisture levels lower than 2 wt.% and then was milled and sieved providing a maximum nominal size of 15 mm. The lower heating value (LHV) of the biomass was 18.0 MJ/kg (measured experimentally with a calorimetric bomb IKA C-2000 using the standard procedure UNE 164001 EX). Proximate analysis of the received biomass showed a moisture percentage of 4.0 wt.% (ISO-589-1981), ash proportion of 1.1 wt.% (ISO-1171-1976), volatile matter of 78.6 wt.% (ISO-5623-1974), whilst fixed carbon was 16.3 wt.% (determined by balance). Ultimate analysis of the received biomass showed a composition of C: 49.6 wt.%, H: 6.4 wt.%, N: 0.2 wt.%, S: <0.1 wt.% (by Thermo flash 1112, UNE EN 5104) and O: 43.8 wt.% (by balance). Biomass was initially dried up to <2 wt.% moisture. Silica-based sand and calcined calcite (90% CaO, Calcinor) were also used in this work. CaO was commercially available and obtained after calcination of calcite at 900 °C. Silica-based sand particle size distribution was in the range of 200–600 µm and particle size distribution for CaO was in the range of 300–600 µm. Pyrolytic char was obtained from biomass pyrolysis process at 450 °C using the Auger reactor facility previously described.

### 2.2. Simulation process

Aspen Hysys simulation software was used to simulate the process. The layout was based on the self-sustainable biomass pyrolysis system proposed in a previous work [20], where CaO/sand mixture was proposed as a heat carrier with catalytic properties. Process simulation allowed determining the different operational parameters in the char fluidised-bed reactor to carry out the combustion process at different temperatures (700 °C, 750 °C and 800 °C) whilst maintaining the biomass catalytic pyrolysis parameters at the optimal conditions [20]. Under these conditions, the overall simulation process determined the solids circulating from the pyrolysis reactor to the combustor, which can be modified by the amount of inert sand circulating in the integrated process.

### 2.3. Auger reactor experiments

Pyrolysis experiments were conducted in an Auger reactor plant of 100 kW<sub>th</sub> of nominal capacity for woody biomass. A detailed description of the reactor can be found elsewhere [9,23]. The experiments were carried out at atmospheric pressure, continuously feeding biomass and a mixture of sand and CaO as heat

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