



Cellulose slow pyrolysis products in a pressurized steam flow reactor

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HIGHLIGHTS

- Steam slow pyrolysis was studied for matter and energy recovery from biomass.
- A suitable reactor configuration with effective thermal control has been tested.
- Final temperature and pressure affect the product yields and gas composition.
- Char morphology is influenced mainly by final temperature.
- Temperature and pressure affect negligibly the calorific value of the vapor phase.

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ABSTRACT

A key strategy to achieve an acceptable degree of matter and energy recovery from vegetal waste disposal is the use of a steam-assisted pyrolysis process that operates at low heating rates and elevated pressure. This procedure, which is different from incineration and fast pyrolysis processes, is expected to reduce the production of secondary hazardous products and produce a residual char with chemical–physical properties comparable to those typical of activated carbon. However, gaseous and condensable products of the process must be demonstrated to allow for a recovery of energy to an extent that can make the process self-sustainable. To clarify these aspects and define the optimal operating conditions of the process, a multi-plate laboratory reactor was designed and constructed. This paper provides a description of the primary design criteria and operating conditions for a steam pyrolysis process. In addition, the effects of process temperature and pressure on products yields and gas and char characteristics are presented indicating the suitability of the process. In the temperature range examined, steam affects positively char and gas properties. On the other hand, pressure affects, mainly, gas yield and determines only minimal changes in char characteristics.

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1. Introduction

Biomass has gained considerable interest as a renewable, carbon-neutral resource for energy production and matter recovery. In recent years, this interest inspired an impressive number of studies aiming to determine a definition of the processes for producing suitable fuels from biomasses. Most of the literature discusses the optimization of thermochemical and biochemical conversion processes for the production of biofuels that would be used as direct substitutes of conventional fossil fuels. Regarding thermochemical processes, extensive information is available on the production of lignocellulosic char [1,2], bio-oil generated by fast pyrolysis [3,4] and syngas through gasification [2,5–7]. In terms of matter recovery and reuse, unused materials from various

agricultural activities have been exploited as a source of raw material for producing activated carbon [8].

This study evaluates the use of steam pyrolysis on biomasses as a way to recover both energy and matter. The products of this process are a vapor phase fuel, which is suitable for use directly in nonconventional combustion systems (e.g., MILD combustion), and a solid carbon-rich residue known as biochar, which has soil amending and fertilizing properties [9]. The ecological sensibility of such a process lies in not only the use of a renewable energy resource but also the possibility to reduce CO₂ emissions from soil respiration due to higher recalcitrance of biochar versus carbonized bio-fertilizers (e.g., compost) [10]. The optimization of process operating conditions is a critical step in producing a solid phase with the desired characteristics; in this framework, particular attention was given to certain physical and chemical properties of solid residue, such as the surface area, pore size distribution [11], surface and bulk chemistry [12], cation exchange capacity

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[13] and distribution of inorganic hetero-atoms in the process products, which depends on the feedstock that is selected [12].

One major challenge with biomass conversion processes is their economical sustainability related to the seasonal availability of feedstock, costs of transportation to central processing units and requirements of process heating. In this context, the proposed process must be evaluated with a distributed energy generation strategy in mind, in which the biomass, representing a residue/waste of processing plants, is processed in proximity of the production sites. In addition, energetic sustainability of biochar production has to be evaluated on the basis of vapor phase fuel yields and characteristics [14].

Previous work related to biomass pyrolysis in an inert atmosphere considered temperature, heating rate, pressure, gas residence time and feedstock as the main operating variables affecting products yield [2] and the composition of gas and condensable species [2,15,16]. Moreover, the role of the pyrolyzing agent has been evaluated for its effect on char yield and morphology [8]. Therefore, to optimize the proposed process, an overall analysis of the effects of the abovementioned variables on both the yield of the products and their chemical and physical characteristics is required. On the basis of available data from the literature, steam has been chosen as the reacting atmosphere, and appropriate ranges of pressure ($1\text{--}5 \times 10^5$ Pa), heating rate ($5\text{--}40$ K/min) and final temperature ($673\text{--}973$ K) have been selected.

The selection of the feedstock is worth a detailed discussion. In fact, the chemical and structural complexity of biomasses makes it difficult to identify how the products properties are affected by specific operating parameters or feedstock characteristics [17]. The approach proposed for the study of biomass steam pyrolysis process overcomes this problem by choosing single species that are representative of a class of a vegetal tissue in the case of single biomass analysis and that are representative of a single kind of waste in the case of the waste mixture. Accordingly this study characterizes cellulose pyrolysis. As a future development pyrolysis of single biomass components and of their mixture will be studied as suitable surrogates of real biomasses.

Another important consideration in developing the biomass steam pyrolysis system was selecting the appropriate experimental reactor. Thermogravimetric techniques are commonly used to accurately evaluate the thermal degradation of biomass. Thermogravimetric analyses allow for an effective control of the real thermal conditions that are experienced by the sample during the pyrolysis process, although the sample amount required to establish the kinetic regime conditions are too low to collect condensable products for subsequent analyses. Another approach using single-particle or packed bed reactors allows for processing a larger sample volume, but these reactors do not control the thermal conditions of the sample as well. The experimental system presented here has been designed to evaluate the steam pyrolysis of biomass under controlled thermal conditions and to enable a thorough quantitative characterization of gaseous, liquid and solid products yields. Moreover, the reaction chamber has been designed to facilitate the abovementioned approach in feedstock selection, which allows for the characterization of single biomass species and their interactions in a model biomass surrogate.

The main aim of this paper is to demonstrate the validity of the experimental setup by comparing the results obtained from a well-characterized feedstock, such as cellulose, with data from the literature. To avoid ambiguity from variable feedstock composition, cellulose, which has a well-characterized chemical formula, was chosen as a benchmark feedstock. Results on cellulose degradation in a steam atmosphere are presented as a function of reactor temperature and are compared with TGA experiments from the literature to evaluate the effectiveness of thermal control of the sample.

The effect of pressure on cellulose degradation (solid/gas and gas phase reactions) in the presence of steam was studied at two final temperatures $T_f = 873$ K and $T_f = 973$ K (the onset of char gasification reactions occurs in this temperature range), at constant heating rate ($HR = 5$ K/min) and data on product yields, gas composition and char specific surface area in the range $2\text{--}5 \times 10^5$ Pa are presented.

2. Experimental set-up

The main design steps were choosing the pyrolyzing agent, defining the operating parameters that would be varied (and their range of variation) and identifying reactor configurations that fulfill the abovementioned criteria. In the following section, a detailed description of the experimental apparatus and the design criteria are presented.

2.1. Pyrolyzing agent

Pyrolysis experiments are typically carried out in an inert environment (nitrogen or helium) while an oxygenated gas (steam or carbon dioxide) is used as a pyrolyzing or gasifying agent, depending on the established thermal conditions. Previous studies involving with the production of char-based activated carbon show the positive effect of steam as compared with nitrogen and carbon dioxide on the liquid quality and physical properties of char [18]. Using steam as a pyrolyzing agent, the yields of water-soluble liquid products increase at the expense of gaseous and solid products, given the ability of steam to perform a more efficient penetration of solid matter-enhancing desorption, distillation and removal of volatiles [19]. On the contrary, during pyrolysis in the presence of nitrogen, higher char yields are obtained with lower porosity because of the deposition of carbonaceous material inside char pores [19]. Moreover, steam seems to be the optimal diluting agent in nonconventional combustion systems that are operated in MILD conditions [20,21] that are particularly suitable for low heating value fuels, such as the vapor phase produced by biomass steam pyrolysis.

Many studies investigate the chemical mechanisms occurring during steam gasification, but only few of them deal with the effect of steam in the pyrolysis stage [22–25]. As appeared from previous literature, in the steam gasification of biomass several reactions take place simultaneously the extent of which depends on the operating conditions. In the thermal conditions (temperature and heating rate) similar to the ones established in this work steam is only weakly involved in homogeneous and heterogeneous reactions. For temperature higher than 800 K steam reforming and water-shift reactions involving primary tars take place resulting in a slight increase of H_2 and CO_2 yield. Heterogeneous reactions between steam and char occur mainly in presence of the ligninic component (not considered in the present work) at temperature higher than 873 K producing H_2 and CO_2 , while the reactions between steam and cellulosic char are less relevant, though they start at lower temperature (higher than 773 K).

These considerations have motivated the direction of this work, which focuses on characterizing pyrolysis processes that use steam as a pyrolyzing agent.

2.2. Operating variables

The primary operating parameters that influence a pyrolysis process are final temperature, sample heating rate, pressure, feedstock properties and flow rate of the pyrolyzing agent [2,26]. The flow rate is strictly linked to the residence time of the gaseous phase in the reaction environment [2].

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