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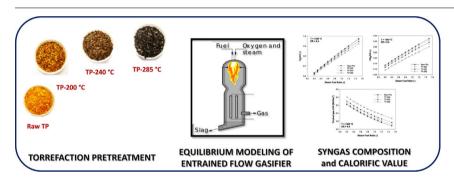
### Entrained-flow gasification of torrefied tomato peels: Combining torrefaction experiments with chemical equilibrium modeling for gasification



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### GRAPHICAL ABSTRACT



### ARTICLE INFO

# Keywords: Agro-industrial residues Fluidized bed torrefaction Entrained flow gasification Equilibrium modeling Tomato peels Oxygen-steam gasification

### ABSTRACT

The purpose of the present study is to quantify the impact of torrefaction pretreatment on the quality of the product gas arising from the gasification with steam and steam-oxygen mixtures of non-woody biomass in hightemperature entrained flow reactors. To this aim, a chemical equilibrium model for biomass gasification was adopted, which allowed predicting the product gas composition as a function of process temperature, equivalence ratio, steam-to-biomass ratio and biomass elemental composition. A global sensitivity analysis with respect to the model input parameters was performed to assess the impact of torrefaction and gasification operating conditions on the quality of the product gas in terms of heating value and composition metrics typically adopted in the process industry (H<sub>2</sub>/CO ratio, stoichiometric module, etc.). In particular, the gasification of raw tomato peels and related torrefied solids resulting from fluidized bed torrefaction tests performed under light (200 °C and 30 min), medium (240 °C and 30 min) and severe (285 °C and 30 min) conditions was investigated using ultimate analysis data in the model. Results of this analysis highlighted that the quality of product gas arising from the oxygen-steam gasification of torrefied and untreated tomato peels did not differ very much, although torrefied feedstocks produced more H2 and CO and less CO2 than the parent one. This suggests that, despite the significant benefits it determines in biomass feeding, grinding and storage, the torrefaction pretreatment provides only a marginal improvement in the product gas quality. Equilibrium simulations made available in the present study can be useful for a better understanding of the controlling variables that rule gasification processes

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### 1. Introduction

P. Brachi et al.

Biomass is an abundant, renewable, and environmentally carbonneutral energy resource. Its exploitation can contribute to reducing both the dependence on fossil fuels and the net CO<sub>2</sub> emissions. A considerable amount of research papers published in pertinent areas [1–3] describe gasification as the most promising thermochemical pathway for the above purpose due to its flexibility to convert any type of biomass, including agricultural residues, non-fermentable byproducts from biorefineries, byproducts of food industry and even organic municipal wastes, into a variety of fuels and chemicals in addition to energy [4]. Moreover, as regard heat and power generation, applied research also shows that for a given energy throughput, the amount of major air pollutants (i.e., CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, particulates) arising from an integrated gasification combined cycle (IGCC) power plant are lower than those from direct combustion systems [5].

Gasification is the conversion by partial oxidation of a carbonaceous feedstock (e.g., biomass or coal) into a gaseous energy carrier, known as "producer gas", which contains hydrogen (H2), carbon monoxide (CO), carbon dioxide (CO2), methane (CH4), water (H2O), nitrogen (if air is used as the oxidizing agent), trace amounts of light hydrocarbons and various contaminants such as small unconverted char particles, ash and tars (i.e., a complex mixture of different condensable hydrocarbons). It takes place at temperatures between 600 and 1400 °C and at a pressure in the range of 1-33 bar [6]. The partial oxidation can be carried out using air, oxygen, steam or a mixture of these as a gasifying agent. Air gasification typically produces a low heating value gas (4-7 MJ/Nm<sup>3</sup> higher heating value [7]) suitable for boiler, turbine and engine operation but not for pipeline transportation due to its low energy density arising from nitrogen dilution. Oxygen gasification produces a high to medium calorific value gas (12-28 MJ/Nm<sup>3</sup> higher heating value [7]) suitable for limited pipeline distribution and as synthesis gas for conversion into a variety of fuels (H<sub>2</sub>, Fischer-Tropsch diesels and synthetic gasoline) and chemicals (methanol, urea), even though the high capital cost for oxygen production is the main barrier to its use. Steam is another possible gasifying agent that can yield a medium heating value (10–16 MJ/Nm<sup>3</sup>, [7]) gas. However, the process would become more sophisticate, as indirect or external heating is needed for the endothermic reactions [3]. At present, gasification with air is the more widely used technology since there are neither the cost nor hazard of oxygen production and usage, nor the complexity and cost of multiple reactors. Steam-oxygen [3,4,8] and steam-oxygen enriched air [9] gasification processes have also been studied to some extent due to their many different applications. Various types of reactors have been explored for biomass gasification so far, which include fixed-bed gasifiers, operated in counter-current, co-current [8] or cross-current mode [10], fluidized bed gasifiers [4] and entrained flow gasifiers [11]. Compared with fixed-bed and fluidized bed gasification, entrained flow gasification operates at higher temperatures (> 1200 °C) and with smaller particles (< 500 µm) allowing to achieve a higher carbon conversion and to produce a high quality syngas with negligible methane and tar content [12]. However, the size reduction of biomass, typically required in entrained-flow systems, may be expensive and very difficult to achieve for some biomass feedstocks due to the inherent fibrous structure and very low grindability [13]. Accordingly, a lower number of experimental studies has been published so far on biomass gasification in entrained flow reactors compared to those concerning fossil fuels. These studies were performed at both relatively low (900-1100 °C) and high (1200-1400 °C) temperatures and investigated mostly the effects of the reaction temperature, the excess air ratio, the water addition and the biomass type on the distribution and the composition of solid (soot and char), liquid (tar) and gas products [14–16]. The influence of the particle size and residence time on the gasifier performance and the producer gas quality [17] as well as the impact of the catalytic activity of alkali metal species on the formation of soot, tar and char [18] have also received some attention. In more details, experiments by Hernández et al. [15] showed that an increase in the operating temperature can have different effects depending on the gasifying agent used. For example, air gasification mainly increases the CO and H2 concentration in the product gas via the endothermic Boudouard and steam reforming reactions, whereas gasification processes with air-steam leads to a boost in the H2 production due to the enhancement of the char-steam reforming and WGS (water-gas shift) reactions, as well as an increase in the CH<sub>4</sub> content. Again, investigations by Qin et al. [16] showed that the carbon conversion during biomass gasification is higher than 90 wt% at the optimal conditions of 1400 °C with steam addition and that the syngas contained nearly no tar. In addition, they also found that, during the entrained flow gasification processes, the carbon in biomass not converted to gas only appeared as soot particles, except for experiments performed at lower temperatures (around 1000 °C), where a very small amount of char was also left. To enable and facilitate the biomass gasification in entrained-flow reactors, a variety of pretreatment methods for improving the properties of raw biomass have been developed, including hydrothermal carbonization [19], pyrolysis [20] and torrefaction [21,22]; among them torrefaction seems to be the most promising one [13].

Torrefaction is a mild thermal treatment where raw biomass is heated in an inert environment to a temperature ranging between 200 and 300 °C. It is traditionally characterized by low particle heating rate (typically less than 50 °C/min) and by a relatively long reactor residence time that ranges from 15 to 120 min depending on the specific feedstock, technology and temperature. After torrefaction, the fuel properties of biomass are deeply improved [23,24]. In particular, torrefied solids have lower moisture content, higher hydrophobicity, intensified energy density and improved storability in comparison to their parent feedstocks. Moreover, the fibrous structure of fresh biomass is partially destroyed by torrefaction thus making easier its size reduction. Finally, pulverized particles obtained from torrefied biomass are more spherical and this makes them more easily fluidizable or flowable [25] and less prone to agglomeration in pneumatic dense flow feeding systems [23,26]. Due to these benefits, there has been much interest in torrefaction and several studies have been done to understand this process [13,24,27]. However, the application of torrefied biomass in gasification remains largely unexplored. To the best of our knowledge, no works can be found in literature on the impact of torrefaction on the behavior of non-woody biomass (e.g., low-value agro-industrial residues) during gasification with steam and oxygen-steam mixtures at high temperature in an entrained flow reactor, in terms of neither syngas quality nor solid gasification kinetics. Therefore, a systematic study on torrefied non-woody biomass gasification in entrained flow reactor is of great practical and scientific interest.

As a continuation of a previous study aimed at assessing the potential of fluidized bed torrefaction treatment in improving the fuel properties of low value agro-industrial residues (i.e., tomato peels) [24], the idea behind this work was that of considering the addition of a torrefaction stage prior to gasification. Therefore, the first objective of the present paper was to investigate the influence of torrefaction on the quality of the product gas arising from the oxygen-steam gasification in high temperature entrained flow reactors; the second one was to determine operating conditions beneficial for obtaining a product gas

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