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Fast pyrolysis and steam gasification of pellets prepared from olive oil mill residues

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This paper examines the fast pyrolysis coupled with the steam gasification of agropellets prepared from the olive oil industries by-products via Macro-thermogravimetry. Three pellets samples were prepared from exhausted olive mill solid waste, impregnated olive mill wastewater/exhausted olive mill solid waste and impregnated olive mill wastewater/pine sawdust. The behavior of the three pellets during the fast pyrolysis and the char gasification stages were generally comparable despite some small differences in the conversion rates or char yields. The gasification of impregnated olive mill wastewater/exhausted olive mill solid waste pellets was selected as a promising route for their valorization and the reduction of the pollution impacts of olive mill wastewater. The impregnated olive mill wastewater/exhausted olive mill solid waste pellets pyrolysis rate was affected significantly by the temperature in the range of 750 °C –950 °C. The mean char gasification rate was linearly dependent on temperature and steam molar fractions in the respective ranges of 750 °C–950 °C and 10%–30% of steam concentration. The provided data on the fast pyrolysis and char gasification of the formulated impregnated olive mill wastewater/exhausted olive mill solid waste pellets constitute new set of experimental data that can serve for the design of gasifiers working with such kind of wastes.

1. Introduction

The energy supply represents a major challenge facing our planet today. In particular, the switch from fossil resources into sustainable and renewable ones becomes an absolute necessity. Indeed, this transition is motivated by the recognized effect of greenhouse gas and other pollutants emissions on human health and climate change [1]. Among the various renewable resources, biomass feedstock has received particular attention due to their high availability worldwide [2]. Furthermore, biomass can be converted into energy or biofuels via different thermochemical processes including torrefaction/carbonization, pyrolysis, combustion and gasification [3–6].

Currently, biomass combustion is the thermochemical conversion process that is technologically advanced at large scale. In fact, electricity and district heating production from biomass is widely developed. It is based generally on grate-firing technologies such as boilers, fixed and fluidized beds. These plants are sophisticated with the implementation of flue gas cleaning systems, to improve their efficiency, and also to mitigate the pollutant effect of gaseous emissions. Nevertheless, in spite of this technological progress, many problems related to mineral contents are still embarrassing. Indeed, the corrosion and the slag formation and the bottom ash agglomeration are influencing negatively the combustion efficiency and the boilers lifetime [7,8]. Therefore, the other conversion processes should be developed in order to recover biomass with high mineral contents such as agriculture and food processing residues.

During the last decade, pyrolysis and gasification emerged as suitable paths for producing alternative solid, liquid and gaseous biofuels. Especially, alternative gaseous biofuels can be obtained through biomass gasification under water vapor and/or carbon dioxide [9,10]. Investigations on biomass gasification show that syngas composition, depending on the gasification agents, includes H_2, CO, CO_2, CH_4, N_2, H_2O and small amounts of tar. The gas concentration depends not only on the used technology and thermodynamic variables, but also on the biomass nature and the gasifier agent [11]. The H_2 and CO are the major interesting gas in the syngas composition since they could be converted to alternative

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synthetic biofuel through various processes such as Fischer-Tropsch reaction [12].

Pyro-gasification is a promising thermochemical conversion process for syngas production and particularly for hydrogen production when vapor steam is used as gasification agent. This technique could be described as a combination between pyrolysis followed by gasification. Indeed, upon heating the biomass gets dry up to 120 °C, then a devolatilisation phase of volatile organic compounds occurs up to 500 °C leaving the remained residual char [13]. Afterwards, the char can be gasified at a temperature higher than 750 °C using a gasifier agent.

Several investigations have examined the char gasification under different atmospheres [13–18]. These investigations have shown clearly that the operating condition such as temperature and gasification agent composition and concentration influence strongly the syngas composition. In addition, the biomass physico-chemical properties seem to affect strongly the gasification reactivity. Indeed, minerals such as Na, K and Mg may catalyze the gasification reaction while others such as Si, P and Al have an inhibiting effect [13,17,18]. Furthermore, char textural and structural properties are clearly correlated to gasification rate [17].

In the Mediterranean region, olive mills produce huge amounts of olive mill wastewater (OMWW) and olive mill solid waste (OMSW). The olive mill solid waste is a mixture of olive pomace and olive seeds. In Tunisia, 1525 olive-oil manufacturers use the three phases' extraction system for the olive oil production. Their average annual production of olive oil is 210.000 tons generating 1.3 million m^3 of OMWW and about 550.000 tons of OMSW. The recovery of these wastes represents a major challenge. Several investigations were performed in order to identify the suitable strategy for the recovery of these wastes. Jeguirim et al. [19] have proposed the impregnation of olive mill waste water (OMWW) on dry biomasses including pine sawdust (PS) and (OMSW). Authors found that the mineral contents present in the OMWW accelerate the thermal degradation of dry biomasses. Kraeim et al. [20] and Lajili et al. [21,22] pursued this investigation through pellets production and combustion in a domestic boiler. Authors have found a higher boiler and combustion efficiencies in agreement with the requirements of European standards. However, an increase in particulate matter (PM) emissions and residual ash content may limit their application in domestic and industrial boilers. Therefore, it seems necessary to examine their recovery through fast pyrolysis and gasification techniques.

In this context, the reactivity of these prepared pellets under pyro-gasification conditions is examined in this present work. In particular, the global reactivity of the samples, by calculating the conversion, the rate of conversion and the char reactivity, during the pyrolysis and the gasification phases, is examined. Furthermore, a particular attention is paid to the effect of operation conditions such as temperature and water vapor concentration. The obtained data during this work and the future kinetic study with the gasification yields analysis will be of a great help for the design of gasifiers fed with pellets based on olive oil residues.

2. Materials and methods

2.1. Pellets production and characterization

OMWW and exhausted olive mill solid waste (EOMSW) used in this study were collected from three-phase centrifugal olive mill located in Mahdia, Tunisia. It is to be highlighted that the EOMSW is obtained from OMSW after the second extraction of the (3–5%) of residual oil. Sawdust was provided from sawmill located in Sayada, Tunisia. The mixtures of non-impregnated samples were dried under sun then intimately mixed using hands in order to minimize their heterogeneity. During impregnation tests, 20 kg of EOMSW or sawdust were slowly added to 100 kg of OMWW while continuously agitating the mixture in a specific basin. Then, the impregnated samples were dried naturally under sun until reaching moisture content lower than 15%.

Three different agropellets were prepared through the densification in order to obtain:

- Exhausted Olive Mill Solid Waste (EOMSW),
- Impregnated Exhausted Olive Mill Solid Waste (IEOMSW) prepared from the impregnation of the olive mill wastewater on exhausted olive mill solid waste.
- Impregnated pine sawdust (IPS) prepared from the impregnation of olive mill wastewater on pine sawdust

The densification of these different pellets was carried out exactly as we realized in our previous work [20]. Indeed, a pelletizer KAHL 15/75 type (Amandus Kahl GmbH & Co, Reinbek, Germany) containing a die diameter of 6 mm and a length of 30 mm was used. the obtained pellets are cylindrical with 15–30 mm of length and 5–6 mm diameter. The mass of each pellet varies between 2.5 and 3 g depending on the type of samples.

Specifications of the used pelletizer are: Die diameter (mm): 175, Diameter/length of roller (mm): 130/29, Number of rollers: 2, Control motor (kW/min^{-1}): 3, Roller speed (m/s): 0.5–0.8. The capacity of the pelletizer depend was about 2–3 kg/h.

The characteristics of pellets were determined using different analytical techniques based on the available European standards. Moisture and ash contents were achieved by following EN 14774–2 and EN 14775 standards respectively. Nitrogen (N) determination was carried out according to EN 15104 by means of a CHONS elemental analyser. Sulphur (S) and chlorine (Cl) contents were determined following EN 15289. The major inorganic elements analysis of the produced pellets was performed according to EN 15290 using an inductively coupled plasma atomic emission spectroscopy (ICP-AES). The minor elements analysis was performed according to NF EN ISO 16968.

The high heating value (HHV) was determined using an adiabatic oxygen bomb calorimeter (IKA C200). LHV is calculated from HHV by taking into account the thermal heat losses due to water vaporization. The values corresponding to low heating values (LHV), bulk density (BD) and energy density (ED) are considered to represent the energetic characteristics of the different studied biomasses.

Concerning the porosity of the samples, it can be calculated using the following expressions:

$$p = 1 - \frac{\rho_b}{\rho_u} \quad (1)$$

Where, p is the porosity, ρ_b and ρ_u are respectively the bulk density and the unit density.

2.2. The M-TG experimental apparatus

The steam gasification of the agro-pellets is assessed using a Macro-Thermogravimetric reactor (M-TG) which is meticulously described in Ref. [23].

Grossly, the Macro-Thermogravimetric reactor (M-TG) includes three parts: (1) a heating system including a liquid water evaporator, a gas pre-heater and a cylindrical alumina reactor which are heated electrically, (2) a gas flow control system using mass flow meters/controllers, (3) a weighing system comprising an electronic scale and a stand with a platinum basket.

The alumina reactor, which is 2 m long and 0.75 m internal