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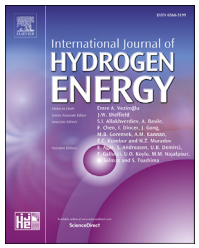

Catalytic pyrolysis of Mediterranean sea plant for bio-oil production

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ABSTRACT

The main objective of the work was to investigate about the feasibility to produce high-quality bio-oil from Mediterranean sea plant by catalytic pyrolysis process. Therefore, experiments using Posidonia Oceanica at 500 °C in a fixed bed reactor were explored taking into consideration the biomass conversion and bio-products yields. The effect of different "home-made" Ni, Ce, HZSM-5 based catalysts in pyrolysis process was analyzed mainly in terms of conversion yield, bio-oil yield and bio-oil oxygen and organic compounds content. The highest liquid yields were obtained at 500 °C. Particularly, CeO_2 (51.15 wt%), NiCe/HZSM-5 (50.66 wt%) and Ni/CeO_2 (49.74 wt%) were the most effective catalysts and these have increased the bio-oil yield compared to non-catalytic ones (47.74 wt%). The highest conversions were obtained with Ni/HZSM-5 (80.81%) and CeO_2 (79.07%) which were the most efficient catalysts. Oxygen level was decreased in bio-oils from 25.66 wt% in the starting biomass to 6–8 wt% with CeO_2, Ni/CeO_2 and NiCe/HZSM-5 catalysts. This is due to the potential of these catalysts to promote deoxygenation reactions, such as dehydration, decarboxylation and decarbonylation, that enhance the bio-oil quality. In terms of compositions zeolite and ceria based catalysts were the best. In absolute the highest content of hydrocarbons was obtained with HZSM-5 and Ni/HZSM-5, 39.56 and 34.91% respectively. Therefore, lower content of acids and oxygen in the bio-oil, higher hydrocarbons, combined with higher heating value show promise for production of high-quality bio-oil from Posidonia Oceanica via catalytic pyrolysis.

Introduction

Biomass is considered one of the most preferred alternative energy sources and its employment represents a sustainable way for solving environmental problems such as greenhouse effect and depletion of fossil fuels. Biomass can be classified in i) lignocellulosic, ii) herbaceous and iii) aquatic flora and manures materials [1]. Further, it can be converted into various forms of gaseous, liquid, and solid fuels according to the conversion process. Among alternatives proposed, pyrolysis of biomass has been indicated to obtain bio-oil which can be employed directly as fuel [2]. However, the traditional use of lignocellulosic materials promotes a large number of compounds (phenols, acidic species etc…) which show several technical difficulties [3,4]. On the other hand, algal bio-oils result stable than the corresponding to woody biomass, essentially due to proteins, lipids and carbohydrates present in the algae chemical composition [5]. Moreover, bio-oil can be up-graded in terms of oxygen content, heating value and

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acidity by in situ catalytic cracking during bio-oil production [6]. Most of investigations were focused on the deoxygenation effect promoted by the HZSM-5 zeolite. In particular, Pan et al. [7], observed that the oxygen content (30.09%) of the bio-oil produced from pyrolysis of Nannochloropsis sp. residue decreases efficiently to 19.53% in the bio-oil with HZSM-5 (catalyst/biomass ratio of 1:1). In addition HZSM-5 showed a selectivity toward the aromatic hydrocarbons formation [7–10]. Although negative aspects by using of zeolite were highlighted; such as: i) high nitrogen and oxygen content in the algal oil and ii) rapid deactivation of the catalyst [9–11]. Hence, investigations on catalysts including metals and oxides were also carried out to adjust the acidity of HZSM-5 zeolite and to increase the yield of the oil in terms of quality [6,12,13].

Low cost and availability are the main reasons that often lead to choose Ni based catalysts instead other metal phases [14]. Ni catalysts result to be active toward creaking and reforming reactions of biomass matter and tars released during pyrolysis at low temperature [15]. Bereketidou and Goula observed that $Ni/Al_2O_3–CeO_2$ catalyst has a better stability compared to Ni/Al_2O_3 catalyst due to redox properties of ceria. This behavior is due to CeO_2 properties that promote the water gas shift (WGS) reaction and the redox reversibility of active phase [16]. Among various carriers (ZrO_2, CeO_2, $MgAl_2O_4$, $Ce–ZrO_2$), the $Ni/CeO_2–ZrO_2$ system showed the highest activity as well as high stability [16]. Nevertheless, Aysu et al. [14,17], investigated on influence of ceria on based alumina and zirconia supported catalysts on pyrolysis product yields and bio-oil proprieties of algae with high and low lipid contents. Results highlighted $Ni–Ce/Al_2O_3$ catalyst as the most able system to reduce consistently acid and oxygen content in the bio-oil. In addition, the oils resulted enriched in higher aliphatic compounds and depleted in N-compounds.

Zeng et al. [18], showed that catalytic pyrolysis performed with silica-supported nickel phosphide convert the natural algae to high quality bio-oil containing long-chained alkanes (59.4%) where the oxygen content was reduced from 41.7 wt% in the algae to 8.0 wt% in the bio-oil.

Posidonia Oceanica, a seagrass widely distributed along coastlines of the Mediterranean sea, leaves residues that reaching the coasts represents a significant economical, and hygienic problem in all coastal zones [19,20]. Therefore, the conversion of this residues into value-added products could be a good opening for business of the waste recycle industry. Experimental data on pyrolysis of Posidonia Oceanica, alone and mixed with waste vegetable oils, at different temperatures (400–600 °C) confirmed the feasibility to convert Posidonia Oceanica both in bio-oil and in bio-char [20,21]. In particular, it was observed that bio-oil yields increasing with the increase of the operative temperature and the highest rate was obtained at 500 °C (>50%) [21]. Although, many papers are present in literature on catalytic biomass pyrolysis for bio-oil production, to the best of our knowledge, there are no works available in the literature on the behavior of Posidonia Oceanica using catalytic pyrolysis with Ni, ceria and HZSM-5 based catalysts. Accordingly, the aim of this work was to investigate about the feasibility to produce high quality of bio-oil as biofuels from Mediterranean sea plant by catalytic pyrolysis process. Hence, efforts were addressed in order to obtain a bio-oil with a higher quality than that produced from woody biomass or microalgae [2,22,23], mainly in terms of oxygen content (<8 wt%), carbon content (>79 wt%) and high heating value (>38 MJ/kg).

Therefore, experiments using Posidonia Oceanica at 500 °C were explored with respect to biomass conversion and bio-products (bio-char, bio-oil and syngas) yields. Bio-oil was studied also in terms of oxygen and organic compounds content. Moreover, the effect of different "home-made" Ni, Ce, HZSM-5 catalysts on pyrolysis process in terms of conversion yield, products selectivity and bio-oils deoxygenation was investigated.

Experimental section – materials and analytical methods

Biomass preparation

Posidonia Oceanica samples were collected from the costs of Sicily region (Italy). First, the samples washed with distilled water, successively, Posidonia Oceanica was air-dried (at 110 °C for 12 h), shredded and sieved into a size range of 16–25 mesh. Samples were conserved in an oven at 100 °C.

Catalyst preparation and characterization

Catalysts were prepared by impregnation (incipient wetness) using γ-Al_2O_3 AKZO-NOBEL 001-3P (SA (BET) 260 $m^2\ g^{-1}$), ZSM-5 ALFA AESAR (SA (BET) 400 $m^2\ g^{-1}$) (30:1 M ratio) and CeO_2 Sigma Aldrich (SA (BET): 27 $m^2\ g^{-1}$) as supports. Ni(5%)/CeO_2, Ni(21%)/Al_2O_3, Ni(5%)/HZSM-5 were prepared using an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich) as precursor. Ni(5%)Ce(5%)/HZSM-5 was prepared using an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich) and $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar) as precursors. Dolomite ($MgCa(CO_3)_2$) a mineral catalyst was purchased from Minerali Industriali S.r.l. All catalysts were dried at 110 °C for 3 h and then calcined at 600 °C for 3 h before use. Catalysts were pressed at 400 bar, crushed and sieved and the 16–25 mesh fraction was used for the catalytic tests. The surface area, pore volume and average pore size of the prepared catalysts were analyzed by N_2 adsorption method at −195.8 °C using Micromeritics ASAP 2020 instrument. The surface area and pore size distribution of the samples were calculated by using the standard Brunauer–Emmett–Teller (BET) equation and the Barret-Joyner-Halenda (BJH) method, respectively.

Proximate and ultimate analysis

Each sample of biomass was characterized by proximate, ultimate analyses and HHV values. Proximate analysis included measurement of moisture content, volatile matter, fixed carbon and ash. The moisture content measurement were performed on biomass samples, dried in a convection oven at 110 °C until constant weight was recorded. The volatile matter content was determined by measuring weight loss after heating biomass samples to 575 °C in an alumina crucible under N_2 atmosphere. The ash content was measured by heating samples at 575 ± 25 °C for 24 h to constant weight in a

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