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Valorization of crude bio-oil to sustainable energy vector for applications in cars powering and on-board reformers via catalytic hydrogenation

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ABSTRACT

Crude pyrolysis bio-oil can be used as energy vector, but further upgrading is required before its utilization as transportation fuel and alternative hydrogen source. Therefore, the catalytic hydrogenation process of several model compounds (i.e. ether, alcohol, acid, olefin and guaiacol) and of crude bio-oil obtained by fast pyrolysis of nuts waste biomass has been investigated using CoMo/Al₂O₃ catalysts, pre-sulfided in flowing H₂S at 400 °C, with different textural properties under simulated industrial conditions (T, 250–300 °C; P, 10–20 bar). Depending on the chemical structure of the various compounds, a complex reaction network, involving mostly hydro-deoxygenation (HDO), hydrogenation (HYD) and hydrocracking (HCR) processes, occurs. The simultaneous proceeding of all these reactions during the hydrotreating (HDT) of the crude bio-oil implies the formation of a wide range of hydrocarbon compounds documenting the feasibility of the upgrading process to obtain liquid transportation fuels and hydrogen-source compounds.

A scale of reactivity based on the effectiveness of hydrogenation of compounds and functional groups has been proposed, also providing evidence of the effects of the texture and physico-chemical properties on the activity and selectivity of the CoMo sulfided catalysts in the HDT processes.

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Abbreviation: HDO, hydrodeoxygenation; HYD, hydrogenation; HDS, hydrodesulfurization; HDN, hydrodenitrication; HCR, hydrocracking; HDT, hydrotreating; ISR, isomerization; DHY, dehydrogenation; DHD, dehydration; HET, hydroetherification; HES, hydroesterification; HKT, hydroketonization; PCP, polycondensation and polymerization; DCO, decarbonylation; DCO₂, decarboxylation.

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Introduction

The instability of fossil fuels market and the need to limit further carbon dioxide emissions, main responsible of the “greenhouse” effect and consequent climate changes in place, urges the development of more efficient energetic technologies and the discovery of novel “energy vectors”, meeting the requirements of high thermal efficiency, low emissions and safety of use and supply. In this context, hydrogen represents the most promising energy carrier for “distributed” power generation [1] while, as indirect “solar energy” collector, biomass could play a key role as raw material for fuels production and hydrogen storage [1], especially for the automotive sector in charge of a great development of “fuel-cells” and “hybrid” configuration vehicles [2]. Then, the exploitation of biogas [3] and, mostly, of bio-oils [4] is strongly promoted by European Community because of its easy availability, insensitivity to market fluctuations, low sulphur and metal content and CO₂ neutrality [5]. However, the extensive use of bio-oils produced by pyrolysis of biomass is still hindered by several technological drawbacks [5–9]. Apart from the fact that the composition is strongly influenced by the source of biomass and pyrolysis process conditions, this generally includes a mixture of more than 300 different organic compounds deriving from the thermal decomposition of cellulose, hemicelluloses and lignin with a water content up to 30 wt% [4,10,11]. As a consequence, crude bio-oils are mostly used as boiler fuels to operate factory processes, while several upgrading strategies are under development in order to obtain value-added liquid fuels and hydrogen sources from lignin polymer [10,11].

The characteristics of bio-oils are very different from that of crude fossil oils, being characterized by low pH, chemical instability, low heating value and immiscibility with hydrocarbons [10–14]. In addition, while the sulphur content is negligible they are rich in oxygenated compounds responsible of high viscosity, low volatility, corrosiveness, thermal instability and tendency to polymerize in presence of oxygen [4,5]. In particular, large amounts of refractory compounds like guaiacyl species and unsaturated hydrocarbons, obtained by the lignin depolymerization processes, can be converted into liquid fuels or hydrogen source for mobile applications [4,5,15] by upgrading processes involving mostly a catalytic hydrogenation at high pressure [16–22]. Then, in presence of a sensible improvement in terms of hydrogen enrichment and oxygen removal, bio-oils may represent a suitable and renewable hydrogen vector [1,4,10], adequate for applications in cars powering or “on board” reformers [1,10,23]. Furthermore, pyrolysis oil could represent a suitable energy vector for the “chemical storage” of the same renewable hydrogen, in reason of its safety and easy handling [1,10].

To be employed as hydrogen vector in a reforming process, the quality of crude bio-oil must be sensibly improved in term of hydrogen enrichment and of oxygen removal, avoiding any polymerization phenomena [1,10,23]. Although several model compounds like phenols, esters, ethers and acids have been used to assess the hydrodeoxygenation (HDO) efficiency of bio-oils from wood pyrolysis [16–23], Guaiacyl species, as Guaiacol (C₇H₈O₂), Vanillin (C₈H₈O₃) and Eugenol (C₁₀H₁₂O₂)

are the most representative since their large concentration in bio-oils, a greater propensity for coking and a lower reactivity toward HDO than other model compounds [18,24].

Mochizuki et al. [18] recently analysed the effects of the reduction treatment of Ni/SiO₂, Co/SiO₂, Pt/SiO₂ and Pd/SiO₂ catalysts in the HDO of guaiacol, while Pinheiro et al. [25] investigated the hydrotreating (HDT) process of straight-run-gas-oil (SRGO) and guaiacol mixtures over sulfided CoMo/Al₂O₃ catalyst, highlighting the feasibility of a unique treatment for oxygenates and hydrocarbon mixtures. Nevertheless, the influence of the chemical composition of bio-oils in the reactivity of conventional molybdenum-based catalyst is still controversial [18].

Therefore, this work is aimed at highlighting the feasibility of the upgrading process under simulated industrial conditions of a crude bio-oil, obtained by pyrolysis of nuts waste biomass. In particular, the reactivity pattern of two CoMo/Al₂O₃ catalysts with different textural properties, *pre*-sulfided in flowing H₂S at 400 °C, in the HDT of different model compounds has been preliminarily probed to shed lights on the reaction network and factors affecting their performance in the HDT of bio-oil.

Materials and methods

Crude bio-oil characterization and model compounds

A crude bio-oil obtained by fast pyrolysis of biomass from waste of nut (i.e. wood, skin, nutshell, etc) have been employed. It was characterized in terms of elemental composition by a THERMO CHNS–O Analyser (Flash EA 1112 series), while water content, density, viscosity and cetane number were probed by ASTM procedures of (Table 1). The chemical composition of the crude bio-oil was determined by gas-chromatographic analysis and expressed as percentage of the different classes of compounds, as shown in Fig. 1. In addition, different organic species (i.e. ethers, alcohols, acids,

Table 1 – List of the chemical and physical characterizations of crude bio-oil obtained by fast pyrolysis of tailings of nuts working.

Crude BIO-OIL	Value
Colour	Dark brown/green
H ₂ O % (method ASTM D95)	2.6
pH	4.6
Density (method ASTM 1298)	1029 kg/m ³
Viscosity @ 40 °C (method ASTM 445)	6 cSt – 0.8°E
Cetano index (method ASTM 4737)	37.7
CHNS–O analysis [wt.%]	
Nitrogen	0.9
Carbon	73.0
Hydrogen	6.7
Sulfur	0.2
Oxygen	19.3
Residue by filtering:	
Filter 0.65 μm	0.2 wt.%
Filter 5.0 μm	0.3 wt.%
Main residue	0.4 wt.%

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