



Biocrude oil Production Upgrading by Catalytic Assisted Hydrothermal Liquefaction of Underutilized non-edible seed Biomass

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Abstract

Thermal and catalytic aqueous hydrothermal liquefaction of *Ricinus communis* and *Jatropha curcas* L. seeds, after mechanical defatting, was conducted at 260 °C for 40 min under subcritical water conditions with a biomass-to-water ratio of 1:5 (expressed in wt.). For catalytic aqueous hydrothermal liquefaction, Ni-Pt/Al₂O₃ was used as heterogeneous catalyst besides a solution of glycerol as in situ hydrogen donor agent. It was noticed that the combination of heterogeneous catalytic aqueous phase glycerol reforming and hydrothermal liquefaction favours and increases the biocrude yield, without external H₂ supply. Indeed, a maximum biocrude yield of 59 wt% was registered when *Ricinus communis* defatted seed was used as starting biomass, which represents an increase of 28 wt% compared to the yield obtained by the non-catalytic HTL process. The biocrudes analysis by GC/MS confirmed that approximately 60% were C16 and C18 hydrocarbon compounds, indicating that the catalyst linked with aqueous glycerol reforming has a marked effect on distribution and upgraded fuel-biocrude stability and quality respect to direct hydrothermal liquefaction (HTL-D). The bimetallic Ni-Pt/Al₂O₃ conformed catalyst (with a Ni: Pt=100:1 expressed as an atomic ratio) was effective in the coupled reactions of aqueous reforming of glycerine as well as hydrodeoxygenation and hydrocracking. It upgrades the biocrude with a lower O/C ratio and a higher H/C ratio, which is directly reflected in the HHV of the biocrude that reaches the value of 37 MJ·kg⁻¹ and can be used as direct fuel. The heterogeneous catalytic process technology, by coupling the glycerol APR and the assisted hydrolysis-depolymerisation of wet-biomass in water subcritical conditions yield to a biomass-derived biocrude with liquid fuel quality.

Keywords Underutilized biomass · Hydrothermal liquefaction · Biocrude · Catalytic upgrading · Biofuel

1 Introduction

Global interest in the progress of technologies to harness renewable energy is constantly increasing motivated both by environmental, economic and social concerns [1], and the decrease in the availability of fossil fuels due to the high demand caused by the increasing population and

industrialization [2]. Currently, biomass plays a fundamental role as an alternative source of energy focused on the biofuels for transport sector [3, 4]. Due to the absence of competition for land use and water resources, together with the integrated valorisation of food chain waste, the use of value feedstocks such as forest residues, agricultural residues, sewage sludge, and municipal solid waste is a promising alternative in the transition to a sustainable bioeconomy, being the only sustainable carbon source for a production well-suited to the existing transport infrastructure.

Combustion, gasification, pyrolysis, and hydrothermal liquefaction (HTL) are the most developed thermochemical technologies of biomass transformation, which can mainly produce heat, syngas or flue gas and biocrude oil. Combustion, gasification, and pyrolysis are energetic intensive processes and, therefore, the hydrothermal liquefaction has gained more attraction as compared to other processes due

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to its advantages like feedstock flexibility, energetic efficiency and, probably, the bioproduct quality [5]. HTL of biomass can be considered as one of the leading technologies for the conversion of high-water content feedstocks into drop-in biofuels and renewable chemicals. Besides, several catalytic strategies were proposed for this process to increase the yields of the product (biocrude) and/or to obtain a product with better properties considering the final utilization.

HTL utilises the unique properties of subcritical or supercritical water conditions, $T_c = 374\text{ }^\circ\text{C}$, $P_c = 22.1\text{ MPa}$, and $\rho_c = 320\text{ kg}\cdot\text{m}^{-3}$. Both near-critical and supercritical water conditions behave as solvents and do not require bases or acids and can use any type of biomass to produce a crude oil-like product [6]. In the HTL process, wet biomass is processed at high temperature and high pressure in water subcritical conditions and the water as a solvent presents several advantages close to its critical point, such as lower viscosity, ionic character, and dielectric constant, favouring the solubility of organic compounds. The oxygen content is partly removed to form CO_2 , CO , and H_2O with an enhanced biocrude quality. However, the oxygen content can be high and result in a viscous and unstable biocrude. Many research efforts were dedicated to the production of biocrude by HTL process, analysing the characteristics feedstock, process variables and biomass-water initial ratio on HTL crude-oil product.

The biocrude produced via HTL generally has a higher heating value (HHV) of $30\text{--}36\text{ MJ}\cdot\text{kg}^{-1}$ and a lower oxygen content of $10\text{--}20\%$ than the biomass feedstocks, normally possessing a HHV of $10\text{--}20\text{ MJ}\cdot\text{kg}^{-1}$ and an oxygen content of $30\text{--}50\%$ [5]. The reported oil yield, however, varies broadly from 12 to 75% depending on the feedstock tested and HTL operating conditions. Yield of biocrude from HTL can be affected by several factors. As a thermal process, temperature has been recognized as the most important variable impacting the final oil production. Temperature for HTL of biomass materials has been recommended in the range of $300\text{--}350\text{ }^\circ\text{C}$ [6]. Besides temperature, the nature and composition of biomass is also crucial. So, for lignocellulosic biomass, hydrolysis of carbohydrates produces monosaccharides, furfural, 5-hydroxymethyl furfural (5-HMF), levulinic acid (LA), etc., while HTL of algal biomass produces bio-crude with oil as the main product [7]. Additionally, it is important to note that biocrude produced via HTL under standard conditions may contain other hetero-atomic elements, as sulphur (S) or nitrogen (N), which can impact its suitability as a direct drop-in replacement for conventional fuels.

Different catalysts, homogeneous or heterogeneous, such as organic acid, alkaline and metals were tested for different biomass feedstocks. So, for catalytic HTL of *Chlorella*

vulgaris or *Spirulina* sp, two algal biomasses with high lipidic content, the addition of organic acids has a beneficial effect on oil yield and boiling point distribution of the biocrude products. Another study claimed that a maximum bio-oil yield of 25.8% is obtained at a reaction temperature of $360\text{ }^\circ\text{C}$ and a reaction time of 50 min , using 5% Na_2CO_3 as a catalyst and *Dunaliella tertiolecta* residue left after lipid extraction [8]. Regarding *Dunaliella salina*, the addition of a solid catalyst of Ni/REHY results in a significant increase of the biocrude yield [6].

Some reports have discussed the role of heterogeneous catalysts in the improvement of yield and the properties of biocrude; several categories such as redox, noble and transition metals (e.g., CeO_2 , ZrO_2 , Al_2O_3 ; Pd, Pt, Ru based and Ni.) were employed for catalytic assisted HTL biomass conversion. R. Kaur et al. [9] studied the homogeneous catalytic hydrothermal liquefaction of *Ricinus communis*, which can be considered a lignocellulosic biomass residue, performed at $260\text{--}300\text{ }^\circ\text{C}$ for 60 min in the presence of alkali catalysts (KOH and K_2CO_3). It was observed that the use of catalyst enhanced the total biocrude yield and a maximum total bio-oil yield of ca. $21.20\text{ wt}\%$ was found at $300\text{ }^\circ\text{C}$ in the presence of $0.5\text{M}\text{-K}_2\text{CO}_3$. Phenols and its derivatives, aromatics, N-contained compounds, acids were observed in bio-oil using GC-MS. An increase in the carbon and decrease in oxygen content leads to enhance the heating value of the product.

As reported by Xu et al. [10], the performance of several metal oxides on the biocrude yield as MgO , CaO , Al_2O_3 , ZrO_2 , and CeO_2 and metal salts (MgCl_2 , FeCl_3 , and CuCl_2) at different temperatures ($260\text{--}300\text{ }^\circ\text{C}$) using water, methanol, and ethanol as solvents employing the micro-alga *Ulva prolifera* as biomass source were tested. They reported that the biocrude yield close to $51\text{ wt}\%$, containing a high amount of ester groups, was achieved using the MgO catalyst and ethanol as solvent. Some Fe-based catalysts enhanced the formation and hydrogenation of light organic compounds content in water-soluble fraction [11]. Noble metal-based catalysts seem to favour high activity on reduction of oxygen-containing compounds to hydrocarbons present in the microalgae biomass as reported by Duan et al. [12]. The heterogeneous catalysts containing transition metals are efficient to improve the quality of the bio-oil through the deoxygenation and denitrification of oxygen and nitrogen respectively of the biomass components as reported by Nagappan et al. [13].

So far, several investigations were conducted on the HTL process in batch reactors using zeolites [14–16]. Duan and Savage [12] studied the production of crude bio-oils from the *Nannochloropsis* sp. microalgae at $350\text{ }^\circ\text{C}$ in the presence of six different heterogeneous catalysts (Pd/C, Pt/C, Ru/C, Ni/ $\text{SiO}_2\text{--Al}_2\text{O}_3$, CoMo/ $\gamma\text{-Al}_2\text{O}_3$ (sulphide) and

zeolite) under inert (helium) and high-pressure reducing conditions (hydrogen), obtaining a biocrude with typical atomic ratios of 1.7 and 0.09 for H/C and O/C, respectively. In the absence of added H₂, all tested catalysts produced higher yields of crude bio-oil from the liquefaction of *Nannochloropsis sp.* As reported by Biller et al. [17], the use of heterogeneous catalysts in the HTL process at 350 °C and pressures of 150 to 200 bar in water using microalgae biomass and lipids extracted from oilseeds leads to an increase in deoxygenation. Catalysts such as Co-Mo/Al₂O₃ and Pt/Al₂O₃ appear to selectively deoxygenate carbohydrate and protein fractions, while Ni/Al₂O₃ deoxygenates the lipid fraction. Many efforts continue to be made to improve conversion efficiency and promote the technology application. The nature of the biomass feedstock influences the catalytic action of heterogeneous catalysts, generally affecting the yield and quality of the bio-oil due to different operating conditions and starting biomass compositions.

This work is focused on establishing the efficiency of the advanced strategy identified as *Catalytic Assisted Hydrolysis* (HTL-AC) using a developed and conformed bimetallic supported catalyst, 9Ni-0.09Pt/γ-Al₂O₃, for the tandem combination of HTL and APR (Aqueous Phase Reforming) process of a short chain alcohol (glycerol) comparing two types of mechanically defatted oilseed biomass, as *Ricinus communis* and *Jatropha curcas l.*

2 Materials and Methods

2.1 Raw Materials Composition and Characterization

Underutilized biomass of non-edible oilseed energy crops with high lipid content was evaluated, specifically *Ricinus communis* (RC) and *Jatropha curcas L.* (JC) seeds, collected in Portoviejo, Manabí province, Ecuador. The shelled seeds were partially defatted by mechanical pressing. Compositional analysis and some physical-chemical properties were evaluated. The elemental analysis of C, H, O, N and S were conducted at the SCAI-Central Research Support Services-of the University of Málaga using a TruSpec micro CHNSO instrument from Leco. Higher Heating Values of biomass and of bio-oil were determined from elemental composition and using a Parr 6050 calorimeter following ASTM D240-19 protocol [18]. Calculation and correlation between elemental composition and approximate analysis: volatile matter, ash, and fixed carbon, was carried out for the biomass feedstocks employed with a SDT Q600 Thermobalance from TA Instruments, in accordance with ASTM E1756-08 protocol. The determination of total lipids was carried out using the method proposed by Folch et al. [19],

employing a chloroform-methanol mixture 2:1 v/v as the extraction solvent in stream of nitrogen. The protein total content was estimated considering the N-content determined from the elemental analysis by multiplying the nitrogen content by conversion factor of 6.25 [20].

2.2 Hydrothermal Liquefaction (HTL) Activity: Evaluation of Biocrude Production

Hydrothermal liquefaction (HTL) is an effective medium-temperature, high-pressure thermochemical process to reduce biomass to a liquid biocrude as main product, minimizing the solid and gas phases volume. The *Direct HTL* experiments (HTL-D) were conducted in a pressure, mechanical stirred reactor, Anton Parr 4842, with a 600 cm³ stainless steel vessel work-operation under water subcritical conditions. A stirring speed of 600 rpm and a temperature of 260 °C were maintained, with an autogenous pressure of 7 MPa with a biomass: water mass ratio fed was 1:5. For assisted *Catalytic Assisted Hydrothermal Liquefaction* reaction, HTL-AC, the H-donor agent 3% w/w of aqueous glycerine solution was added to the total volume of 100 cm³ with the presence of 3wt.% of 9Ni-0.09Pt/γ-Al₂O₃ catalyst in pellets form, placed in a basket attached to the stirring axis of rotation between two helices to ensure the contact with the fluid phase. The catalyst was externally pre-activated in a flow of H₂ (15 mL·min⁻¹ total flow 20% v/v of H₂ in He) at 700 °C for 2 h and previously, the reactor was purged with a stream of N₂ at atmospheric pressure to remove residual gas phase at room temperature. Gas phase was extracted of reactor by purge and its composition was analyzed by a gas chromatograph (Agilent 7820 A GC) provided with TCD and FID detectors although data are not reported. The reaction products were first filtered to separate the solid phase from the liquid phase, then 100 ml of dichloromethane -DCM- was used as a solvent for biocrude extraction [21, 22]. DCM-biocrude mixture was separated by filtration and decantation. To separate the DCM from the bio-crude, a Heidolph rotary evaporator was used, operating at 45 °C, reduced pressure and 80 rpm for 20 min, resulting in a solvent-free bio-crude.

The conversion to reaction products, i.e. biocrude, bio-solid or biochar and the aqueous and gaseous phases, being the contribution of the latter minimum, was calculated using the following equations:

$$\% \text{ Biocrude Yield} = \frac{\text{biocrude weight}}{\text{initial biomass weight}} \times 100 \quad (1)$$

$$\% \text{ Biochar} = \frac{\text{biochar weight}}{\text{initial biomass weight}} \times 100 \quad (2)$$

$$\begin{aligned} & \% (\text{Aqueous} + \text{Gaseous}) \\ & = 100 - (\% \text{ Biocrude Yield} + \% \text{ Biochar}) \end{aligned} \quad (3)$$

2.3 Crude Bio-Oil Analysis

The composition of the biocrude was analyzed using gas chromatography coupled with mass spectrometry, GC/MS Triplus RSH Autosampler Trace 1300. The Gas Chromatograph was equipped with a TR-5ms SQC column and the Mass Spectrometer, an Exploris GC 240, with Orbitrap detector from ThermoFisher Scientific. Electron impact ionization (EI) mode at 70 eV was utilized and full scan monitoring mode with mass range of 50–400 m/z. Due to the characteristics of the obtained biocrude, the samples were diluted in acetone, then filtered through a 0.2 μm PTFE filter into a transparent chromatography vial. Compound identification was achieved by comparing mass spectra with the NIST MS Search 2.0 mass spectra library.

2.4 Catalyst development, Synthesis, and Characterization

Ni-Pt/ Al_2O_3 , with 9-Ni atoms and 0.09 Pt -atoms per nm^2 of support optimized formulation, expressed as formal surface atomic density ($\text{at}\cdot\text{nm}^{-2}$) in terms of surface coverage, was synthesized. A conformed bimodal $\gamma\text{-Al}_2\text{O}_3$, $S_{\text{BET}}=246 \text{ m}^2\cdot\text{g}^{-1}$ and $V_p=0.76 \text{ cm}^3\cdot\text{g}^{-1}$ from *Alfa Aesar* was used as the support in the form of $6\times 4 \text{ mm}$ cylindrical-pellets [23], and the impregnation of 20 wt% Ni and 1wt.% Pt was carried out via incipient wetness method using precursor solutions of $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{Pt}(\text{NH}_3)_2(\text{NO})_2$ (3.4 wt%, Aldrich Chemical) for Ni and Pt, respectively. After drying in static air for 12 h at 80 $^\circ\text{C}$, calcination was carried out at 500 $^\circ\text{C}$ with a ramp of 5 $^\circ\text{C}\cdot\text{min}^{-1}$ for two hours in air. The catalyst was *ex situ* activated in hydrogen at 700 $^\circ\text{C}$ for 2 hours prior to its use in the reaction and was placed on a support ensuring good contact without altering the shape of the extrudate during the process.

X-ray powder diffraction data of the catalyst were recorded using an X'Pert MPD Pro diffractometer (PANalytical) equipped with $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) and a primary Ge (111) monochromator. The X-ray tube operated at 45 kV and 35 mA in the Bragg angle range between 5 and 80 $^\circ$ (2 θ). X-ray photoelectron spectra (XPS) were obtained using a Physical Electronic spectrometer (model PHI 04-584) employing Al $\text{K}\alpha$ radiation (1486.6 eV, 100 μm , 100 W, and 20 kV) as the excitation source and a dual-beam charge neutralizer to analyze the nickel (Ni 2p $_{3/2}$) and platinum (Pt 4d $_{5/2}$) bands at different binding energy ranges. Nitrogen adsorption-desorption isotherms for the supports were recorded at -196 $^\circ\text{C}$ using a Brunauer-Emmet-Teller

(BET) surface area analyzer on a Micromeritics ASAP 2020 Analyzer. Prior to analysis, the samples were degassed under vacuum ($1\cdot 10^{-3} \text{ Pa}$) for 5 h at 180 $^\circ\text{C}$. The specific surface area was obtained using the BET equation and the pore volume was determined using the BJH method. TEM images were acquired using a TalosTM F200x equipment from FEI equipped with an energy dispersive X-ray (EDX) analyzer.

3 Results

3.1 Biomass Characterization

Ricinus communis -RC-, commonly known as castor oil plant or castor bean, is a species from *Euphorbiaceae* family. Native of tropical Africa and Asia, this plant is widely cultivated worldwide for its industrial, medicinal, and ornamental uses. On the other hand, *Jatropha curcas L* -JC- is a medium-sized shrub that can thrive in various climatic and soil conditions. It is drought-resistant and can adapt to marginal soils, making it an attractive option for production in arid or semi-arid areas. Among the main lipid components of the RC-oilseeds, palmitic (2.2%), stearic (2.4%), oleic (6.7%), linoleic (8.8%), and ricinoleic (77.1%) fatty acids are found [24], whereas for JC-oilseeds, oleic acid represents more than 50% of the fatty acid composition besides, linoleic (29.7–34.1%) and other saturated fatty acids are reported [25].

Defatted residual cake after oil extraction from *Ricinus communis* and *Jatropha curcas L* is byproduct composed of organic matter, proteins, fibres, and other non-fat compounds. Due to their high protein, carbohydrates, and residual lipids content, they possess certain nutritional value as feed for livestock or as organic fertilizer, but also a considerable energetic added value.

In Table 1, elemental CHONS and proximal analyses, lipids and protein content and HHV values registered for RC and JC residual cakes are summarized. CHONS values indicated that elemental analysis is very similar, where the carbon weight percentage represented approximately 50% of total weight, varying between 50.89% and 49.58%. A content close to 39% of O (39.17 and 39.97%) and 7.44 and 6.78% of H-content were registered for RC and JC, respectively. There was higher variation in N content: 2.45 and 3.40% associated with the different protein fraction, 14 vs. 21% and, an appreciable sulphur content varying between 0.15 and 0.30% was also detected. The measured and estimated HHV values for the RC and JC residue were 24.1 and 21.0 $\text{MJ}\cdot\text{kg}^{-1}$, respectively. These are high values and are in accordance with a residual oleaginous defatted biomass [26]. The moisture and ash content in defatted cake were

Table 1 Characterization analysis of defatted residue of *Ricinus Communis* (RC) and *Jatropha curcas l.* (JC)

	Ricinus communis	Jatropha curcas l
Lipid content (%wt)	27.5	16.2
Protein content (%wt)	14.5	21.3
Proximate analysis (%wt) Moisture	4.6	4.0
Volatile material	70.7	66.1
Fixed carbon	20.7	23.9
Ash	4.0	6.0
Ultimate analysis (%wt)	50.89	49.58
C	7.44	6.78
H	2.45	3.40
N	0.15	0.27
S	39.17	39.97
O		
HHV MJ·kg⁻¹	24.1	21.0

found to be 4.3 and 4.0% for RC and, 9.3 and 6.0 wt% for JC, respectively.

3.2 Catalyst Characterization

XRD profile and TEM images of the Ni-Pt/Al₂O₃ catalyst activated under reducing atmosphere at 700 °C are shown in Fig. 1. It can be seen that the catalyst showed diffraction peaks at 37.8, 39.5, 45.8, 49, 61.0 and 66.7 (2θ), characteristic of a γ-alumina (JCPDS 75–0921) [27], used as a support. Furthermore, the diffraction peaks at 44.4, 51.8, 75.9 (2θ) were attributed to Ni⁰ (JCPDS 040850) [28, 29] phase formation. Signals superimposed on γ-Al₂O₃, associated with Pt⁰ (JCPDS 01-1190), were also detected. The diffraction peaks centered at 39.8, 46.1 and 67.5 (2θ) were attributed

Table 2 BEs and surface atomic ratios of reduced Ni-Pt/Al₂O₃ powder catalyst

		BE (eV) ^a			M/Al ^b
		eV	Species	%	
Ni-Pt/Al ₂ O ₃	Ni 2p _{3/2}	852.9	Ni ⁰	85	Ni/Al
		856.1	NiO	15	0.08
	Pt 4d _{5/2}	317.0	PtO	49	Pt/Al
		314.2	Pt ⁰	51	0.00136

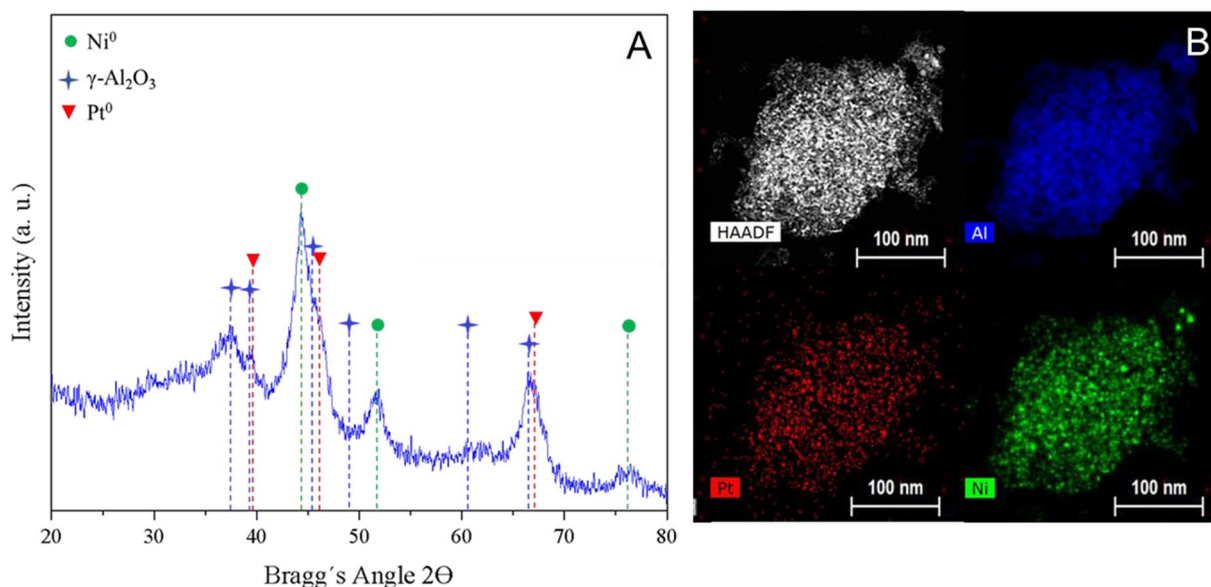
^aBinding Energy (±0.2 eV) and relative population of the species expressed in %.

^bSurface atomic ratio between the metal, Ni or Pt, and Al

to the fact that Pt⁰ was formed during the reduction procedure of the catalysts at high temperature. The TEM mapping of the elements showed a homogeneous morphology with a well distribution of Ni and Pt particles onto the support, with few nanometres of particle size.

N₂ adsorption-desorption results revealed that Ni-Pt/Al₂O₃ catalyst had a decrease in surface development up to 170 m²g⁻¹ and pore volume to 0.54 cm³·g⁻¹ respect to alumina pellets support (1/8" A_s = 246 m²·g⁻¹; V_p = 0.76 cm³·g⁻¹) caused by the incorporation of the bimetallic phase on the support.

In Table 2, the surface atomic ratios and the Binding Energies (BEs) obtained with the deconvolution of the signals of Ni2p_{3/2} and Pt4d_{5/2} regions are presented for the Ni-Pt/Al₂O₃ catalyst. Two Ni-signals at 856.1 and 852.9 eV were recorded and associated with NiO and Ni⁰, respectively, according to the BE-values reported by Pavwelec et al. [30]. In spite of the low platinum content and the noisy signal in Pt4d_{5/2} region, two signals for Pt were also detected after the deconvolution, located at 317.0 and 314.2 eV and related to Pt⁰ and Pt²⁺ as PtO. A good adjust of the deconvolution

**Fig. 1** (A) XRD pattern and (B) HR-TEM mapping of Ni, Pt and Al of the shell in powder form of the Ni-Pt/Al₂O₃ conformed catalyst

was observed obtaining a χ^2 near to 1. From the comparison of the calculated surface atomic ratio of Pt/Ni from XPS (0.017) and the theoretical Pt/Ni ratio of 1:100 used in the catalyst formulation, it is assumed that there is a higher surface concentration of platinum, associated with the presence of stabilized bimetallic reduced centers in the form of Ni particles enriched with Pt [31], as was early reported.

3.3 Hydrothermal and Catalytic Assisted Hydrothermal Liquefaction Results

In the HTL process under subcritical pressure conditions, the proteins, carbohydrates, and lipids, and others main components biomass are transformed by hydrolysis, depolymerization, decomposition and/or recombination processes. The depolymerized molecules are highly reactive resulting in the formation of different fractions that can be separated. The HTL process produces biochar, a liquid fraction consisting of biocrude and aqueous phase, and gas fraction. Conversion of biomass into biocrude is highly dependent on the composition; it is well known that lipids are easily transformed into biocrude, but it was also reported that between 5 and 10% of carbohydrates from biomass are transformed into biocrude, and near 20% of proteins are also converted [32]. The operating conditions of HTL process are also decisive, i.e. temperature, reaction time, even the agitation, and

solid loading [33]. A preliminary study was carried out for direct hydroliquefaction (HTL-D) using defatted *Ricinus communis* cake as starting biomass, varying between 20 and 60 min of reaction time and a temperature range between 240 to 300°C, without appreciable modifications in the conversion and biocrude yield recorded values. Therefore, the reaction conditions were established at 260°C and 40 min of reaction, keeping the biomass/water ratio constant at 1:5; reaching an autogenous pressure of 7 MPa.

Solid residue and biochar. The solid residue after HTL tests of both biomasses consisted of inorganics and remaining organic matter. Solid residue mainly contain ash, which approximated composition identified by SEM-EDX analysis was 0.8% Na, 3% Mg, 7% Si, 9% P, 0.95% Cl, 0.4% K, 6% Ca, 0.39% Fe and 2.5% Cu, rich in inorganics and the yield highly depends on ash content in the feedstock and biochar produced depending on the conversion raised.

Gas Fraction. The gaseous products represent less than 1% (in weight) of raw material and contain CO_x (mainly CO₂); other small quantities of hydrocarbons, such as CH₄ and C₂ and even H₂ were occasionally detected. Nitrogen and sulphur compounds were not detected in the gas phase and, therefore, they should be part of the liquid phase.

Aqueous Fraction. In HTL processes, aqueous extracted products are generated because water participates in all conversions. Main constituents of the aqueous phase include salts and metal ions, such as K, Na, and Mg. The remaining soluble organic compounds in the aqueous phase are O-compounds such as sugars, short chain and free fatty acids, alcohols, and N-compounds such as amines and amides and even sulphates and soluble S-compounds.

The product distribution, biochar, biocrude and A+G (gas+aqueous fractions), for direct-HTL and catalytic assisted-HTL is represented in Fig. 2. It is well known that the effects on the composition showed that biomass enriched in lipids and proteins have a positive impact on the biocrude quality, while carbohydrates and lignin have negative effects, leading to an increase in the solid residue. A biocrude yield of 46% for RC and 36% for JC were observed for D-HTL; with a biochar fraction of 36% for RC and 40% for JC, respectively. As was previously reported [32], a general trend was identified for the efficiency in the conversion of biocrude based on the content of Lipids > Proteins > Carbohydrates; although the volatile matter content was similar for both biomasses, the highest biocrude yield for CR was mainly associated with its higher lipidic content.

Catalytic assisted HTL, using Ni-Pt/Al₂O₃, results in an increase from 46 to 59% in the biocrude fraction obtained and a reduction of the biochar fraction from 36 to 29% for the residue of the RC-*Ricinus* biomass. This same trend was also observed for JC-*Jatropha Curcas* as starting biomass, reaching 48% biocrude fraction and 31% biochar, which

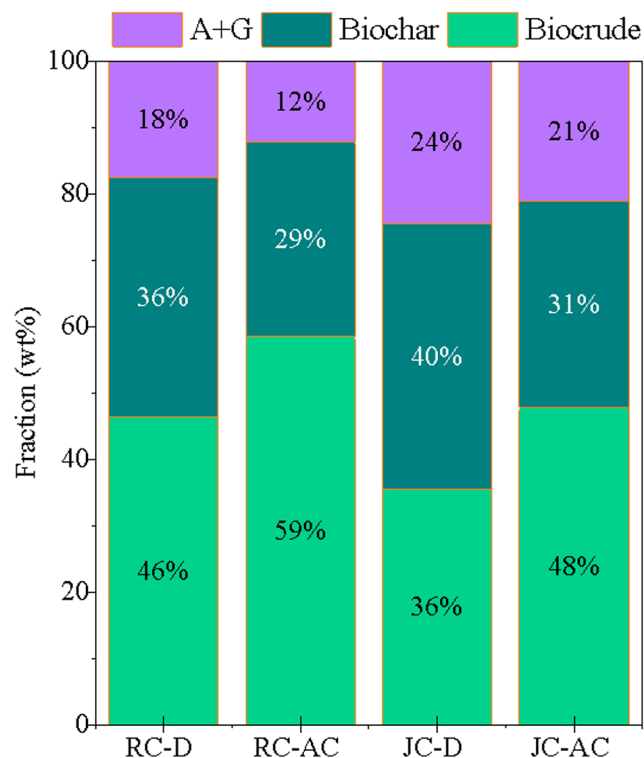


Fig. 2 Product distribution fractions for HTL-D and HTL-AC of *Ricinus communis* (RC) and *Jatropha curcas* L (JC). T=260°C, P=7 MPa and biomass/water ratio=1:5

means an overall increase in biocrude yield of almost 30% compared to direct HTL. In agreement to Yang et al. [34], that reported an increase up to 20% in the biocrude production using Ni/REHY catalyst compared to the processes without catalysts.

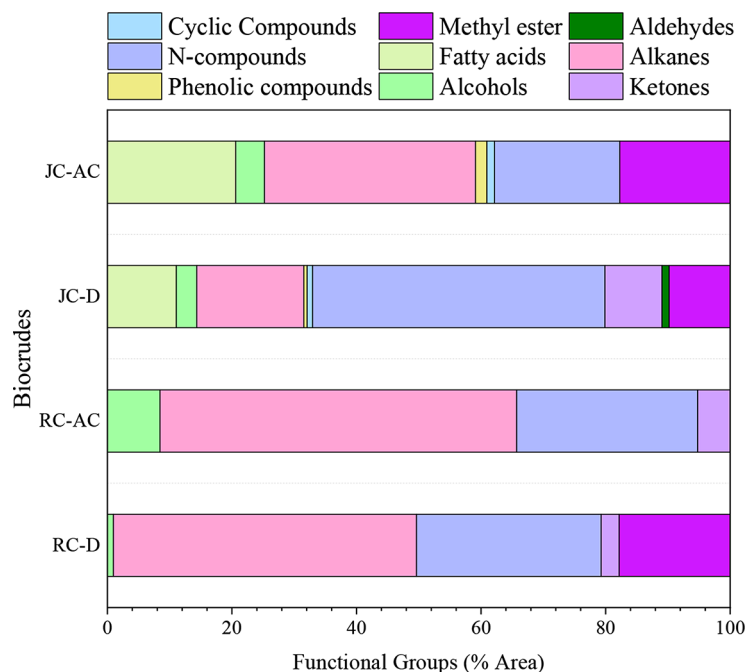
HTL-AC process considerably reduces the biochar content, which represented around 30% for both biomasses. The catalyst must also reduce the number of organic compounds soluble in water, because there was a decrease in the aqueous fraction, thus, it benefited the generation of intermediates and reduced the gas product yield, leading to a significant increase of biocrude yield.

This contribution points out the existence of a synergetic effect of Ni-Pt compared to monometallic catalysts. The bifunctional nature of the Ni-Pt pair of the catalyst makes it efficient in the reforming of glycerol in the liquid phase and in the hydrogenation-deoxygenation reactions by internal transfer through the Lewis acid metal centres. The residual acid character of catalyst also favours the hydrolysis-depolymerization process of wet-biomass in subcritical water conditions, that cause stabilization and improvement of the energy properties of the biocrude fraction produced. Ni-Pt/ Al_2O_3 catalyst promoted tandem combination between biomass hydrolysis, H_2 -in situ generation and the hydrodeoxygenation of fatty acids, under the reaction conditions, favoured the generation of intermediates reducing the gas product fraction, leading to the significant increasing of biocrude yield. Ni-Pt-pairs promotes glycerol aqueous phase reforming that can be act as a hydrogen donor [35]. This serves to stabilise the intermediated compounds for biomass cracking of liquefaction [36], inhibiting reactions such as condensation, cyclization or repolymerization of free

radicals, thus reducing carbonization [37]. The formation of H_2 by in situ reforming of glycerol coupled with other intermolecular reactions leads to promote saturation reactions and increased biocrude yield.

Bio-crude composition. The complexity of families of compounds and C, H, O, N and S atoms are distributed between gas, liquid and solid phases during the process, and the effect of the heterogeneous catalyst on biocrude composition from the different feedstocks was analyzed. The compounds of the bio-oil obtained by HTL were characterized by using gas chromatography coupled with mass spectrometry (GC/MS). In Fig. 3, the compounds distribution of the biocrude obtained by HTL-D and HTL-AC is depicted, calculated based on the percentage of area obtained from GC-MS. The identification was made using MS spectra and the aid of NIST libraries as was included in the experimental section. The major compounds were identified combining the chromatogram by relative content and the MS-spectra match-file with the NIST mass spectra library. It has been grouped by relative weight according to functional groups and heteroatoms and by the length of the hydrocarbon chain. Biocrude yields for HTL-D was of 46% and 36% for RC and JC respectively and represented approximately two times higher than the lipidic content in the partially defatted seed biomass residue, indicating that other components such as carbohydrates or proteins were also converted into compounds contained in the organic phase during HTL reaction. This fact was confirmed in the analysis by GC/MS chromatogram, where compounds such as phenols, pyrroles, indoles, carbazoles, and its alkyl-substituted homologues formed from the decomposition of carbohydrates and proteins, for example by Maillard reaction,

Fig. 3 Average compounds distribution for Direct Hydrothermal Liquefaction (HTL-D) and Catalytic Assisted (HTL-AC) of the biocrudes obtained using RC and JC. Operation conditions: 40 min at 260 °C, 3% (wt.) glycerol and Ni-Pt/ Al_2O_3 catalyst



were found, in agreement with Da Costa et al. [38]. C16 and C18 carboxylic acids formed from the hydrolysis of di- and triglycerides represented 60% of HTL biocrude. Fatty amides were also formed from the reaction between fatty acids and ammonia coming from protein degradation. A family of compounds with polarity close to C16 and C18 carboxylic acids and amides, but with a higher boiling point, was also observed in the GC chromatogram. However, their identification was not possible with MS detector due to the fragmentation of the molecule and low probability using the NIST MS data base.

Protein hydrolysis may generate nitrogenous compounds such as amino acids, short-chain peptides, amines, and amides derived from the deamination of certain amino acids, which can include primary, secondary, and tertiary amines as well as fatty acid amide [39]. The presence of ester and phenolic compounds is generated by the hydrolysis of carbohydrates; complex carbohydrates can be thermally hydrolysed to release monosaccharides such as glucose, fructose, and galactose. This process occurs under high temperature conditions; carbohydrates can be broken down to form phenols and aromatic aldehydes [4]. However, when the HTL-AC process is applied, it is evident that the catalyst acts mainly to convert carbohydrates, leading to the formation of esters, alcohols, aldehydes, ketones and hydrocarbons. Meanwhile, the conversion to nitrogen products generated by catalytic thermal hydrolysis of proteins is reduced by up to 50%.

On the other hand, hydrogen and carbon contents of the bio-crudes obtained by HTL-AC were higher, which is likely due to the greater hydrodeoxygenation, and hydrogenation attributed to functionality of Ni-Pt pairs. It is known that Pt plays a significant role in the decarboxylation process of fatty acids and the hydroprocessing of fast pyrolysis oil [40], while Ni is effective in the deoxygenation of biocrudes [35]. There is evidence of partial denitrogenation and desulphuration although there are non-large differences in the nitrogen and sulphur contents between the bio-crudes obtained by HTL-D and HTL-AC.

In addition to residual acidity, the effectiveness of Ni-Pt catalysts is attributed to their ability to promote thermal decomposition of biomass compounds, increase the formation of liquid hydrocarbons and improve the selectivity toward desired products. Furthermore, Ni catalysts can facilitate the breaking of carbon-oxygen and carbon-carbon

bonds [41, 42] thus promoting the formation of lower molecular weight compounds and higher quality products for further processing.

Compared with the elemental composition of initial biomasses, the biocrude obtained by direct HTL and catalytic-assisted HTL-AC, presented much higher contents of carbon (72.50 and 74.16%), hydrogen (11.01 and 10.50%) and nitrogen (1.40 and 2.35%), as listed in Table 3. N, S, and O contents in final bio-crudes are lower than those of the starting biomasses, demonstrating that partial reactions of denitrogenation and deoxygenation occurred under tested pressure and temperature conditions and in the presence of the catalyst. HHV registered values for the bio-crudes were in the range of 32.08 for biocrude of RC and 34.02 MJ·kg⁻¹ for JC, higher than those correspond of initial biomass used, which was 24.1 and 21.0 MJ·kg⁻¹ for RC and JC, respectively. Hydrogen and carbon contents of bio-oils obtained with HTL-AC were the highest, which was likely due to the further hydrogenation reactions promoted by the catalyst. The oxygen content and O/C ratio of biocrude decreased, leading to the significant increase of HHV. Meanwhile, the sulphur content and S/O ratio were also reduced. These results show that the deoxygenation and desulfurization of biocrudes occur in the presence of Ni-Pt catalyst. Besides, the estimated molecular weights of HTL-AC-biocrude by empirical formula result lower than that estimated for the initial biomass and the D-HTL-biocrude, i.e., the properties of the biocrude obtained significantly improved.

In Fig. 4(A), Van Krevelen diagram, depicting the O/C vs. H/C ratio of biomass and biocrudes, is presented, while in Fig. 4(B), the HHV values are shown, with the aim of standing out the trend. Biomass samples have similar characteristic with very close O/C and H/C ratios, meanwhile, biocrude obtained by HTL-D and HTL-AC presented several deviations in comparison with the starting biomass. The HTL-AC process caused an important stabilization and improvement of the quality of the biocrude with a significant decrease in the oxygenate content, which reduces the O/C ratio and increases the H/C ratio, increasing the character of the biocrude as of a saturated hydrocarbon-based fuel. The oxygen content in the RC and JC biocrudes was also much lower than that of bio-oils from pyrolysis of terrestrial biomass. Also, it is important to indicate that the sulphur content and therefore the S/O ratio also decreased. The heating values are around 37 MJ·kg⁻¹, which exceed those of

Table 3 Elemental analysis data and HHV of biocrudes

	Elemental Analysis (wt%)					HHV, MJ·kg ⁻¹
	C	H	N	S	O	
RC-D	65.53	9.43	1.59	0.03	23.21	32.08
RC-AC	72.50	11.01	1.40	0.02	13.8	37.61
JC-D	67.25	8.74	2.61	0.14	22.56	34.02
JC-AC	74.16	10.50	2.35	0.08	12.29	37.32

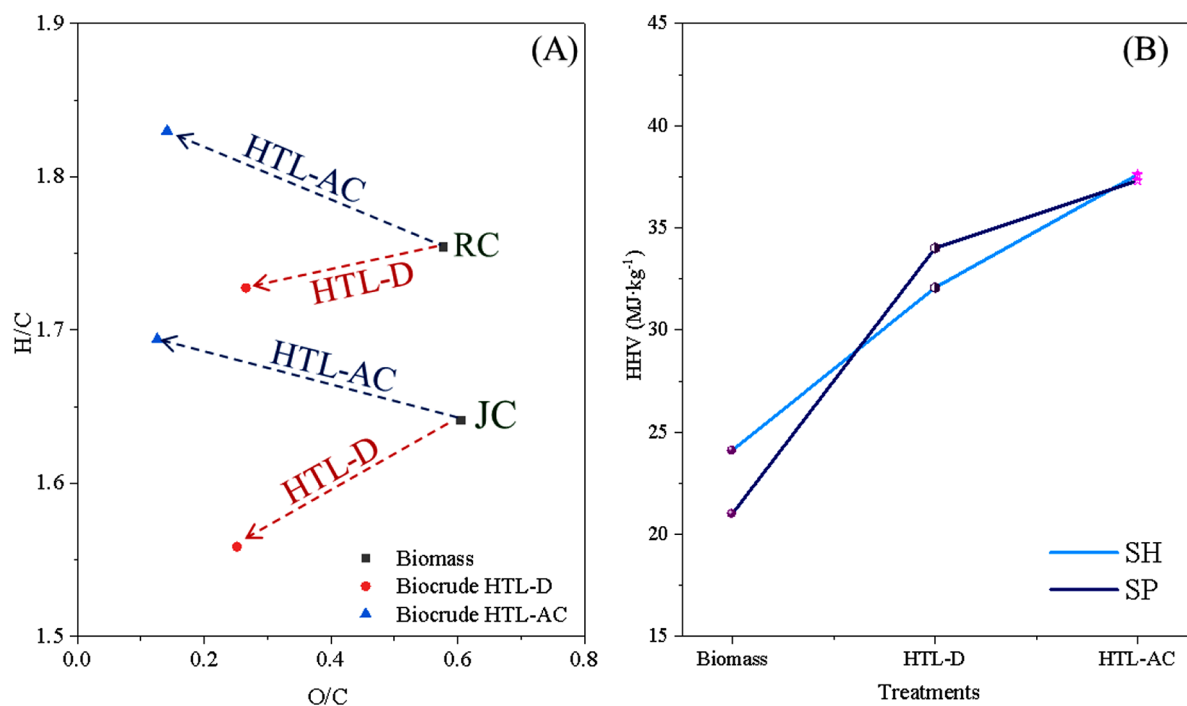


Fig. 4 Van Krevelen diagram (A) and HHV ($\text{MJ}\cdot\text{kg}^{-1}$) (B) of the biomasses and biocrudes obtained by HTL-D and HTL-AC

biocrudes obtained from pyrolysis of 3D biomass (as microalgae) and are very close to those of petroleum-derived fuels ($\sim 42 \text{ MJ}\cdot\text{kg}^{-1}$).

These results demonstrated that in situ deoxygenation and desulfurization of the biocrude is feasible through the assisted catalytic strategy, combining the aqueous reforming of glycerine and hydrothermal liquefaction in the presence of the efficient Ni-Pt catalyst, reaching a lower oxygen content in the biocrude close to 12% ($\text{O}/\text{C} = 0.12$) and a considerable increase in the biocrude HHV.

This result reports on the enhancement of biocrude production through catalytically assisted hydrothermal liquefaction of underutilized non-edible seed biomass. In the experiments, it was evident that the biocrude was mainly composed of hydrocarbons, 60–70% mol including n-paraffins and aliphatic, whose compositions do not differ much from biodiesel where about 90% are hydrocarbons including n-paraffins and aliphatic components. It is suggested that catalytic hydrothermal liquefaction of partially defatted biomass coupled to internal hydrodeoxygenation occurred mainly through decarboxylation and decarbonylation reactions and, to a lesser extent, ketonization. The conformed bimetallic catalyst Ni-Pt/ Al_2O_3 , with a ratio Ni: Pt = 100:1 expressed as atomic ratio, was effective in the coupled reactions of hydrolysis, aqueous reforming of glycerine and in situ hydrodeoxygenation and hydrocracking. An improvement in the biocrude is achieved with a lower O/C ratio and a higher H/C ratio, which is directly reflected in the HHV of the biocrude, which reaches the value of $37 \text{ MJ}\cdot\text{kg}^{-1}$ and can

be used as direct fuel. Heterogeneous catalytic liquefaction process of wet biomass under subcritical water conditions is a technology for the boosted production of a biomass-derived biocrude with liquid fuel quality. Therefore, *Catalytic-Assisted HTL* Technology is an innovative, short-term strategy for the energy sector, offering the sustainable production of liquid fuels, capable of managing underutilized wet biomass of different origins and overcome the presence of heteroatoms in the biomass.

4 Conclusions

The *Catalytic Assisted Hydrothermal Liquefaction* -HTL-AC- is a cutting-edge technology for improving biocrude production applicable to a wide variety of wet biomass feedstocks. An efficient and well-characterized Ni-Pt/ Al_2O_3 bimetallic conformed catalyst was developed by single-step impregnation. The coupling of the catalyst together with an aqueous glycerol solution, as a hydrogen-donor agent avoiding external hydrogen supply, operating in a batch reactor under subcritical water conditions results in a biomass-derived biocrude with liquid fuel quality ($37 \text{ MJ}\cdot\text{kg}^{-1}$), due to the occurrence of tandem glycerol APR, hydrogenation-deoxygenation and hydrolysis-depolymerization reactions. The result is greater performance in the production of biocrude and can be capable of being applied to wide variety of underutilized feedstocks. Furthermore, HTL does not

require prior drying of the biomass, thus reducing costs and energy required for processing.

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Declarations

Competing interests The authors declare that they have no significant competing financial, professional, or personal interests that might have influenced the performance or presentation of the work described in this manuscript.

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