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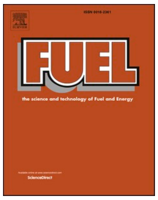

Full Length Article

Influence of catalysts on the hydrothermal liquefaction of municipal primary sludge: Upgrading to a higher quality biocrude

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A B S T R A C T

Effect of homogeneous and heterogeneous catalysts on hydrothermal liquefaction of primary sludge was studied. Biocrude, biochar, aqueous phase and biogas were all affected, in terms of quantity and quality. HTL without any catalyst attained a biocrude yield of 37.7 % (w/w_{VS}). The best improvements in biocrude yield are observed with $CuSO_4$ (10 %), 42.20 % (w/w_{VS}) and TiO_2 (20 %), 41.90 % (w/w_{VS}). All experiments with catalyst produced a biocrude with HHV higher than 30 MJ/kg and with carbon content higher than 60 %. The analysis demonstrated that the major fraction of biocrude were asphaltenes, the heavier phase. While, the light phase, oils, in most of the cases, contained more saturates than polars. Biochar and aqueous phase were recuperated with high organic contents, that enables their usages in further applications. Even though gas fractions were small, their compositions varied between CO, CO_2 and hydrocarbons. Catalysts were normally recuperated with the solid phase, except some cases due to their particle sizes. Most of the ashes of primary sludge were transferred to biochar. Some parts of them went to the aqueous phase and biocrude during separation process.

1. Introduction

Municipal waste sludge is a nutrient-rich by-product generated from the wastewater treatment process. The composition of sludge is complex and difficult to treat as it contains organic contaminants. Conventional treatments of sewage sludge include incineration, landfarming, biological composting and oxidations. However, they have changing degrees of limitations in processing cost, efficiency and effectiveness [6]. Hydrothermal liquefaction (HTL), performed at high temperature and high pressure, represents a promising route to convert a wet organic feedstock (municipal sludge) into an intermediate fuel (Biocrude) by means of a solvent, usually water, without high-cost drying steps. It is accomplished by the hydrolysis of bio-constituents of the wet biomass and by the improvement of the depolymerization products to simple organic molecules [23]. Solid phase noted as Biochar, gaseous phase and aqueous phase containing water-soluble products are co-products [7]. Biocrude yield from HTL of municipal sewage sludge changes from 10 to 48 % (w/w) in the previous studies [24]. Lately, the researchers have considered different strategies to improve the quality and production of biocrude from municipal sewage sludge. The effect of temperature (260–350 °C) on the products distribution was studied by Xu et al. in the HTL of secondary municipal sludge. It was found that high temperature improved the quality of biocrude and the yield of gas and lowered the yield of solid phase and the total organic carbon in the aqueous phase [31]. Hao et al. investigated the influence of time (10–50 mins) on the HTL process. The results showed that long reaction time increased the yield of biocrude and decreased the yield of solid phase [14]. However, Biocrude obtained in HTL is generally very viscous at room temperature and has a very high heteroatom content (mainly oxygen and nitrogen) and has low heating value to be used directly as fuel, so it needs important upgrading [13,11]. At present, some studies have introduced the catalyst in HTL process for helping the extraction efficiency of biocrude [6]. The acquisition of catalysts in HTL of wet biomass could improve biocrude yield and decreases its O, N and S concentrations [23]. Homogeneous catalysts like organic acids or alkali catalysts and heterogeneous catalysts such as supported metal catalysts or zeolite have been considered, respectively [15]. Significant studies proved that homogeneous alkaline catalysts (like K_2CO_3, and KOH) were able to effectively improve the quality and yield of biocrude by restraining repolymerization reactions [27]. The optimum conditions 300 °C with 5 % $FeSO_4$ were reported for maximum biocrude yield (47.79 %) [20]. The highest yield of biocrude (47.45 %) from municipal sewage sludge was attained with $CuSO_4$ catalyst and ethanol: water (1:1) at 270 °C for 30 min [28,29]. Whereas, heterogeneous catalysts are seen to be a very

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attracting option as they assist the upgrading of biocrude during its production and, generally, they can be separated from the reaction products [23]. For example, Ru/C was selected as the best catalyst to remove heteroatoms from biocrude elsewhere [5]. 34.2 % (w/w) was the highest biocrude yield obtained from dewatered sewage sludge with 10 % (w/w) Co-Mo/ATP catalysts at 320 °C for 15 min reaction time [36]. Primary sludge, containing high moisture and volatile content, was considered as a convenient feedstock for the HTL process. The effects of temperature and reaction time on the products distribution and the quality of biocrude were completed as well. Yet, biocrude produced contained a critical amount of oxygen, diminishing its use in further applications. To the best of our knowledge, there is only limited information available on catalytic hydrothermal liquefaction of sewage sludge. Different catalysts reported above have shown positive effect on the optimization of biocrude yield derived from HTL of sewage sludge. However, they were used either at high temperature or with an organic solvent. Therefore, a hypothesis using different type of catalysts in HTL of PS to improve biocrude yield, energy efficiency and quality was proposed. The purpose of this work is to utilize various catalysts (homogeneous and heterogeneous) for improvement of biocrude production. The elemental and chemical composition of biocrude and other co-products were analysed.

2. Materials and methods

2.1. Materials

2.1.1. Reagents

Dichloromethane 99.9 % (ref.: 32222) was obtained from Honeywell. n-Hexane 95 % (ref.: 363242), high performance chromatography grade, and phenol crystalline (ref: 144852.1211) were supplied by PanReacAppliChem. Sulfuric acid reagent (ref: 34632), orange reagent (ref: 131130.1612), sulfuric acid 95.0–97.0 % (ref: 30743), bovine serum albumin (BSA) (ref: A9647), sodium hydroxide 98 % (ref: 30620), sodium carbonate (ref: 222321), potassium sodium tartrate tetrahydrate (ref: 217255), copper (II) sulphate pentahydrate (ref: 209198), Folin & Ciocalteu's phenol reagent (ref: F9252), magnesium sulphate monohydrate (ref: 434183), anhydrous sodium sulphate (ref: 239313), and fuming hydrochloric acid (ref: 84418), high analytical reagent grade, were purchased from Sigma-Aldrich. ASTM® D2887 Reference Gas Oil (ref: 48873) and chloroform-d (ref: 225789) were provided also by Sigma Aldrich.

2.1.2. Commercial catalysts

Homogeneous catalysts including sodium carbonate, ACS reagent, anhydrous granular 99.5 % (ref: 22231), potassium carbonate GR for analysis 100 % (ref: 1066830500) and cupric sulfate anhydrous 99 % (C-1297) and heterogeneous catalysts comprising Titanium (IV) oxide 99.0–100.5 % (ref:14027), platinum on alumina 0.5 % (w/w) loading, pellets (ref: 206016), palladium on alumina 0.5 % (w/w) loading, pellets (ref: 205745), Molybdenum (IV) sulphide 98 % (ref:234842), Tungsten (IV) sulphide 99 % (ref:243639) and Nickel on silica/alumina (ref:208779) were all purchased from Sigma-Aldrich.

2.2. Primary sludge

2.2.1. Collection and management

The municipal wastewater treatment plant of Reus in Tarragona, Spain provided samples of primary sludge. 500 mL bottles of sludge were sampled after partial gravity thickening of the primary treatment. They were deposit in a freezer at −15 °C and defrosted in an oven at 60 °C for 5 h. The bottles of sludge were utilized directly as received, without any pre-treatment.

2.2.2. Characterization

A full characterization of primary sludge was repeated at least three times. Total solids (TS), volatile solids (VS) and ash content were analysed according to standard methods 2540B and 2540E respectively [26]. Extraction of lipids was completed in a Soxhlet apparatus using hexane as a solvent, according to standard method 5520E [26]. Total carbohydrate percentage was measured by phenol–sulfuric acid Dubois method [8]. Shortly, 0.05 mL of 80 % phenol solution was added to 2 mL of diluted sludge sample in a glass tube. Then, 5 mL concentrated sulfuric acid was quickly added. The tubes were kept under room temperature for 10 min and then placed into a thermostatic bath at 30 °C another 15 min. The absorbance was measured at 480 nm. Protein content was detected with Lowry method [18]. The protein solubilization in the sludge samples was completed by heating the samples with 2 M sodium hydroxide at 100 °C for 10 min in a digester. The absorbance was measured at 750 nm. Finally, elemental analysis was acquired by Serveis Técnics de Recerca at Universitat de Girona. Analysis was carried out using an elemental analyzer (Perkin Elmer model EA2400). C, H and N were determined, and O was calculated by difference. Heavy metals were observed through environmental scanning electron microscopy (ESEM) with X-ray microanalysis by using the Quanta 600 from FEI company at conductive and high vacuum (20 kV) mode.

2.3. Catalytic hydrothermal liquefaction of primary sludge

The experiments were accomplished in a 1 L Stainless Steel Autoclave (Autoclave Engineers model EZE Seal) surrounded by a movable heating shell, a fixed MagneDrive® stirrer (magnetically coupled, packless rotary impeller system) and an operating condition controller. The reactor is connected to a gas line through an inlet valve allowing the purging of nitrogen. The outlet valve is connected to a gas flow meter and a Tedlar bag push lock valve 0.6 L (Superlco 30289-U) for gas collection. A bottle containing approximately 500 g of primary sludge was unloaded in the reactor. Pure nitrogen gas was introduced three times to create an atmosphere free of oxygen and then pressurized up to 1 bar as an initial pressure. HTL experiments were always completed at a temperature of 300 °C (∼86.9 bar), a reaction time of 30 min and an agitation rate of 100 rpm. Catalysts (homogeneous and heterogeneous) were added at 5 wt%, 10 wt% and 20 wt% with respect to dry feedstock. The pressure of the reaction was not controlled and retained as auto generated with respect to its reaction temperature. The heating up time was recorded as 2 h, based on the condition chosen. After achievement of each batch experiment, the reactor was cooled down in a room temperature water bath (∼25 °C) until going back to its initial condition.

2.4. Products separation

Fig. 1 presents the schematic diagram of the experimental separation procedures after hydrothermal liquefaction of primary sludge. The products obtained from the hydrothermal liquefaction of primary sludge are distributed into 4 different phases: gas, organic, aqueous and solid.

When the reactor was returned to laboratory ambient temperature and atmospheric pressure, the gas phase was vented. The output gas was passed through a flow meter, indicating the volume of the gas mixture, and collected in the gas bag. Then, the reactor was opened, and the mixture was poured into a large beaker. The solid phase was separated from the liquid phase through vacuum filtration. The filtrate, mainly containing the aqueous phase and a small part of the organic phase, was moved into a bottle.

Simultaneously, the reactor was washed with dichloromethane several times until being totally clean to recover the organic remaining part, deposited on the walls, on the cover of the reactor and, in the agitation module. After that, the mixture, where a part of solids was captured by the organics, was separated via vacuum filtration. The liquid part (organic phase and dichloromethane) was transferred into another bottle. The solid retained on the filter paper, biochar and ashes, was washed with dichloromethane repeatedly. The biochar was dried in the oven for 24 h at 105 °C. In the scenarios where heterogeneous

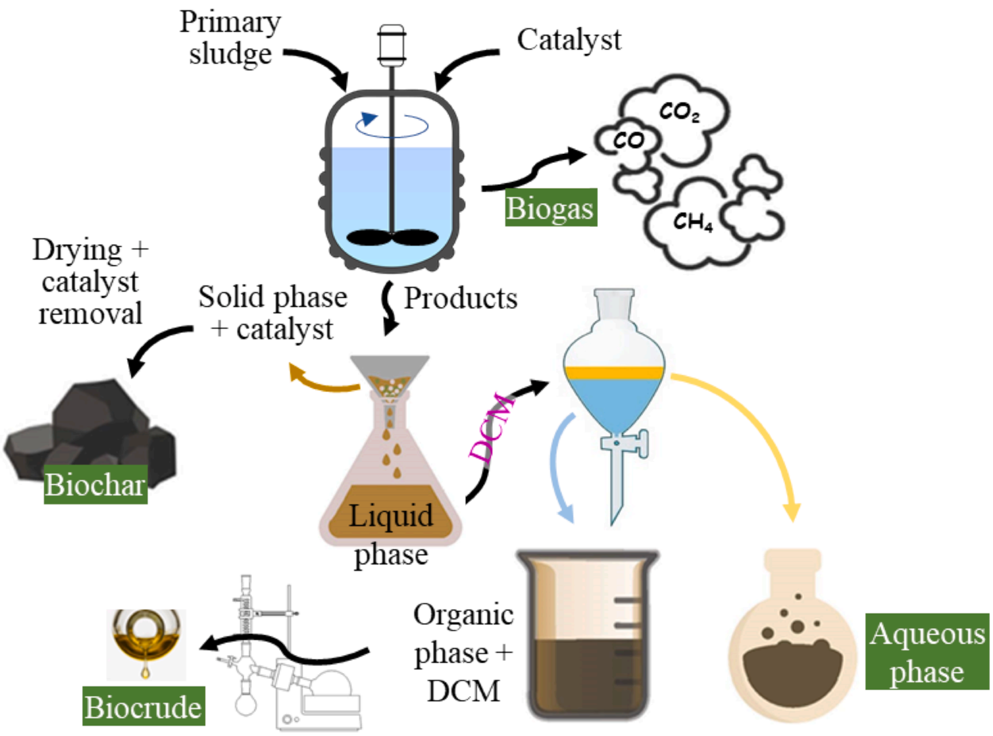

Fig. 1. Process overview of catalysed HTL of primary sludge.

catalysts were used in the form of pellets, they were collected with the solid phase, dried in the oven and recuperated separately. The quantification of biochar was done by taking into account the amount of catalyst used.

A small amount of dichloromethane was added to the aqueous phase. Then, the mixture was centrifuged at 8000 rpm for 5 min. The upper phase containing the dichloromethane and organics was added to the organic phase previously separated. The lower phase is the aqueous phase containing soluble organic molecules.

Dichloromethane was separated from the organic phase by the rotary evaporation, at 65 °C and atmospheric pressure. The viscous organic liquid obtained is the biocrude, that it was further weighted for quantification. Finally, biocrude was divided into oils and asphaltenes by Soxhlet extraction using 200 mL of hexane. Hexane was evaporated from oils by rotary evaporation at 65 °C and vacuum pressure of 273 bar. Asphaltenes were calculated by the difference between biocrude and oils.

2.5. *Analytical characterisation of biocrude*

The characterization of biocrude was very wide. The weight and ash content were done. Gas chromatography/mass spectrometry (GC/MS), thermogravimetric analysis (TGA), elemental (ultimate) analysis, determination of higher heating value (HHV), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) and simulated distillation (SimDis) were achieved. Finally, saturated, aromatics, resins and asphaltenes (SARA) fractions of biocrude were considered.

2.5.1. *Gas chromatography/mass spectrometry spectroscopy of biocrude*

The samples of biocrude with all catalysts were characterized by gas chromatography-mass spectroscopy (GC/MS) using a Perkin Elmer Turbo Mass Gold GC/MS, equipped with a Supelco SLB®-5ms capillary GC column (L × I.D. 30 m × 0.25 mm, d_f 0.25 μm). Solvent used was dichloromethane. The GC oven was maintained at 70 °C for 1 min, heated to 180 °C at a rate of 7 °C/min, then heated to 240 °C at a rate of 12 °C/min and finally 7 min hold at 330 °C.

2.5.2. *Thermogravimetric analysis of biocrude*

The weight loss properties of biocrudes were studied by thermogravimetric analysis (TGA). In each test, about 3 to 4 mg of sample was heated from 30 °C to 800 °C at a nitrogen flow of 60 mL/min and a 10 K/min heating rate [36].

2.5.3. *Ultimate analysis and HHV of biocrude*

Ultimate analysis of biocrude samples was also realized by Serveis Técnics de Recerca at Universitat de Girona as commented in section 2.4. C, H and N were quantified, and O calculated by difference. Then, the higher heating values of (HHVs) of biocrude were calculated [38].

2.5.4. *FTIR of biocrude*

FTIR spectra were collected using a Thermo Nicolet Nexus 670 Fourier Transform Infrared Spectrophotometer equipped with a single-bounce diamond attenuated total reflectance (ATR) accessory (Specac Golden Gate) and KBr beam splitter. Spectra were collected from 4000 to 500 cm^{-1} with 0.98 cm^{-1} resolution and averaged over 50 replicate scans using Omnic software. Background scans were conducted of the dry accessory at ambient temperature. The spectra were then collected after smearing about 30 mg of sample directly on the ATR crystal surface.

2.5.5. *^{1}H NMR of biocrude*

^{1}H NMR spectra were collected using a Varian Unity 400-MHz spectrometer outfitted with a 5-mm broadband probe. 50–75 mg of biocrude were dissolved in deuterated chloroform containing 0.03 % tetramethylsilane (TMS) as an internal reference. Samples were then filtered (0.22-lm PTFE) to remove any suspended particulates before loading into 5 mm diameter NMR tubes. ^{1}H spectra were acquired with a 90° pulse angle, spinner frequency of 20 Hz, sweep width of 8000 Hz across 32 transients.

2.5.6. Simulated distillation of biocrude

Simulated distillations were modeled after ASTM-D2887 method and performed using a HP 5890 Series II FID gas chromato-graph and a Durabond DB-HT-SimDis GC column by Agilent-J&WScientific (5 m 0.53 mm id, 0.15 µm film). Helium (56.4 mL/min) was used as the carrier gas. The oven temperature was initially set to 36 °C, and raised to 400 °C at 10 °C/min and then held constant for 10 min. The injector volume was set to 0.5 µL and the injector temperature was set to 350 °C. Detector temperature was set to 375 °C, hydrogen gas set to 40 ml/min, airflow set to 400 mL/min, and helium makeup set to 24 mL/min. Samples (1 % w/w) and reference standards (0.5 % w/w) were dissolved in dichloromethane. Samples were filtered (0.22 µm PTFE) to remove any suspended particulates. Boiling points were determined in accordance to a D2887 calibration mix and a D2887 Reference Gas Oil standard, both purchased from sigma Aldrich. Data (retention time and areas) were collected. Each sample was distributed between fractions (% wt) and boiling points were calculated accordingly.

2.5.7. Quantification of SARA fractions of biocrude

SARA fractions of biocrude were analysed. The separation of light phase and heavy phase was repeated as mentioned above, but with n-heptane. Maltenes were separated into saturated hydrocarbons with 20 mL of n-heptane using activated alumina in a glass chromatographic column. Then, aromatics were extracted by mean of 20 mL of toluene. Finally, polars were removed from the adsorbent using 20 mL of a mixture of toluene and 2-propanol (1:1). Remaining resins were also removed using 20 mL of methanol. Each eluted fraction was recovered by solvent removal using a rotary evaporator.

2.6. Biochar

Total solids, moisture content, volatile solids and ash content were determined in biochar according to standard methods 2540B and 2540E respectively [26]. Also, ultimate analysis and heavy metals detection were done by following the same procedures described above.

2.7. Aqueous phase characterization

Chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen (TN), proteins, and carbohydrates were measured or analysed for the aqueous phase. COD analysis was performed according to standard method 5220D [26]. TOC was analysed by using a TOC analyser TOC-L Series based on a specific standard calibration curve. Total organic carbon (TOC) was measured by ASI-L auto sampler Shimadzu into a Shimadzu TOC-L CSN TOC analyser provided with a NDIR detector and calibrated with standard solutions of hydrogen potassium phthalate. Total dissolved nitrogen was measured in the same TOC analyser coupled with TNM-L ROHS unit [40]. Protein amount was measured according to Lowry method [18] and carbohydrates were quantified following Dubois method [8] as described in the previous section (2.3). Total solid (TS), volatile solid (VS) and ash content were measured in the aqueous phase as well. A specific volume of aqueous phase was dried in a weighted crucible for 24 h in the oven at 100 °C then burned in the furnace at 550 °C for 1 h, as detailed by the standard methods 2540B and 2540E respectively [26]. Measurement of pH value in the HTL aqueous phase was performed by pH meter. Heavy metals were analysed in the ash of the solid dissolved in the aqueous phase by following the same procedure mentioned before.

2.8. Biogas

Identification and quantification of biogas were realised by a gas chromatograph (micro-GC, Agilent, 990) equipped with a thermal conductivity detector (TCD). A MS5A SS 10MX0.25MMX30UM BF RTS, CP-PORABOND Q 5MX0.25MMX3UM column (column 1) was used to separate the light gases using Argon as a carrier gas and a PORAPLOT Q UM 10MX0.25MMX8UM BF, CP-PORABOND Q 1MX0.25MMX3UM column (column 2) was used to separate heavy gases using helium as a carrier gas. Column 1 was maintained at injector temperature 100 °C, injection time 40 ms, column temperature 100 °C and initial pressure 200 kPa. Column 2 was maintained at injector temperature 100 °C, injection time 40 ms, column temperature 60 °C and initial pressure 150 kPa. The run time was 120 s. The mole percentage of each gas was determined with respect to gas standards prepared by Carburos Metálicos, S.A.

2.9. Calculations

The biocrude yield was calculated from Eq. (1):

$$Biocrudeyield(\%) = \frac{Massofbiocrude}{Massofvolatilesolids} \times 100 \tag{1}$$

The aqueous phase yield was calculated from Eq. (2):

$$Aqueousphaseyield(\%) = \frac{Massofsolidsdissolvedinaqueousphase}{Massofvolatilesolids} \times 100 \tag{2}$$

The solid yield was calculated from Eq. (3):

$$Biocharyield(\%) = \frac{Massofsolidresidue}{Massofvolatilesolids} \times 100 \tag{3}$$

In some cases, the amount of catalyst should be subtracted from the total amount of solid phase obtained after drying.

The gas yield was calculated from Eq. (4):

$$Gasyield(\%) = \frac{Massofgas}{Massofvolatilesolids} \times 100 \tag{4}$$

In all the equations, mass of volatile solids is referred to that of primary sludge.

HHV is calculated through Dulong formula and expressed in MJ/kg.

$$\mathrm{HHV}\ (\%) = 0.3383 \cdot \mathrm{C} + 1.443 \cdot \left(\mathrm{H} - \frac{\mathrm{O}}{8}\right) \tag{5}$$

C, H and O are the mass percentages of carbon, hydrogen, and oxygen from the ultimate analysis of the samples, respectively.

3. Results and discussion

3.1. Characterization of primary sludge

Table 1 presents the full characterisation of primary sludge from WWTP of Reus (Tarragona, Spain). The wet primary sludge had 4.3 % of total solids, then by difference, 95.70 % were moisture. Total solids had

Table 1
Physiochemical characterisation of primary sludge.

Characteristic		Value
Total solids*		4.3 % ± 0.1 (w/$w_{\text{wet sludge}}$)
Moisture content**		95.7 % ± 0.1 (w/$w_{\text{wet sludge}}$)
Ash content*		22.9 % ± 0.3 (w/$w_{\text{total solids}}$)
Volatile solids**		77.1 % ± 0.3 (w/$w_{\text{total solids}}$)
Proteins*		21.2 % ± 1.7 (w/$w_{\text{total solids}}$)
Carbohydrates*		29.8 % ± 1.2 (w/$w_{\text{total solids}}$)
Lipids*		23.4 % ± 0.8 (w/$w_{\text{total solids}}$)
TOC*		6290 mg/L
COD*		35180 mg/L
Density*		1.01 g/mL
Ultimate composition	C	47.81 %
	H	6.93 %
	N	4.81 %
	O**	40.45 %
HHV		18.83 MJ/kg

* Average of at least three assays.
** Calculated by difference.

22.9 % of ashes, then by difference, 77.1 % were volatile solids. These, are composed by carbohydrates, 29.84 % (w/w_{TS}), lipids (oil, greases, fats and long fatty acids), 23.41 % (w/w_{TS}) and proteins, 21.15 % (w/w_{TS}).

It is common for the primary sludge from the Reus WWTP to have a very similar composition of the four species of the total solids (ashes, lipids, carbohydrates and proteins), always between 20 and 30 % [22]. More or less 50 % of lipids plus carbohydrates make this primary sludge very attractive when developing thermochemical processes to valorise it.

In terms of energy source, primary sludge covered low nitrogen content (3.71 %), low hydrogen content (5.34 %), but high carbon content (36.86 %) and high oxygen content (54.12 %), resulting in a higher heating value (HHV) of 10.37 MJ/kg. The total solid percentage was very low, less than 5 %. The initial concentration of the primary sludge used in the HTL conversion of wastewater solids to fuels was 4.5 wt% [39]. The density of primary sludge was 1.01 g/ml, similar to that of water. HTL process is a convenient alternative for handling high moisture content solids as water is used as medium to hydrolyse the organic matter into nearly simpler chemicals at high temperatures and pressures [17]. Lipids in primary sludge are produced from free fatty acids in the range of C10 to C18 which are precursors for esters production. Also, proteins are confirmed to be supporters for biocrude production through HTL. Maillard reactions represent a significant part in the distribution of biocrude and composition, originated from the reaction of amine groups present in proteins with carbonyl groups present in reducing carbohydrates [9]. Primary sludge, including a high moisture content, is rich in lipids, proteins and carbohydrates. Therefore, HTL is supposed to be an ideal option for thermally hydrolysing the macromolecules into valuable chemicals and primary sludge helps in validating an economically viable and energy-efficient sludge biorefinery approach.

3.2. The effect of catalyst on products distribution

Series of HTL experiments were performed using different catalysts, either homogeneous or heterogeneous, either powder or pellets, to understand the product distribution profiles obtained (biocrude, biochar, biogas and aqueous phase). In all the scenarios, the parameters were set to 300 °C for temperature, 30 min for reaction time and 100 rpm for agitation rate.

An experiment at the same conditions without any catalyst was used as a control. The Table 2 presents the yields of biocrude, asphaltenes and oils after SARA fractionation of biocrude. Biocrude yield without any added catalyst was 37.7 % (w/w_{VS}) with 23.96 % (w/w_{VS}) of oils and 13.74 % (w/w_{VS}) of asphaltenes. Based on the results obtained, itś clear that the addition of catalyst has an influence not only on the biocrude yield, but also on the quality of biocrude (yields of oils and asphaltenes). In some scenarios, the yield of biocrude has been improved. In some others, the introduction of catalyst has worsened the production process. A more detailed explanation is provided below.

3.2.1. Effect of homogeneous catalysts

All the homogeneous catalysts were added at the same ratio, 10 % of the total solid of primary sludge. With $CuSO_4$, the highest yield of biocrude was reached, 42.20 %, with 27.93 % of oils and 14.26 % of asphaltenes. The results from the HTL of sewage sludge with $CuSO_4$ displayed as well better yield of biocrude (47.45 %) than that without any catalyst [28,29]. $CuSO_4$ encourage the production of esters and suppress the decarboxylation of fatty acid, resulting a better quality of biocrude [10]. K_2CO_3 has contributed to the increase of yield by almost 2 % with 21.95 % of oils and 17.38 %. Runs of HTL of corn stover with K_2CO_3 have showed significant effects on biocrude yield [4]. However, the K_2CO_3 showed a less improvement than $CuSO_4$ on biocrude yield, but this improvement verified that K_2CO_3 could promote the liquefaction process. It was not the case with Na_2CO_3. The yield of biocrude was shifted into lower value (31.03 %). It has been reported that alkali catalysts ameliorate the degradation of biomass polymer, which induce hydrolysed intermediate products in the aqueous phase [16]. However, high quantity of alkali catalyst can promote the repolymerization [4]. In our study, the concentration of Na_2CO_3 could have been enough high to support the repolymerization, demonstrated by the results obtained.

3.2.2. Effect of heterogeneous catalysts

Heterogeneous catalysts were distributed between two categories: powder and pellets. The powder ones were used in three different ratios: 5, 10 and 20 %. Whereas, the pellet ones were added in three different amounts: 4, 8 and 12 g. When HTL was achieved with powder heterogeneous catalysts, yield of biocrude was affected obviously. The presence of MoS_2 didńt promote the production of biocrude until itś added in

Table 2
Yields of biocrude, oils and asphaltenes after SARA fractionation, effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

Catalyst	Yields% (w/w_{VS})			Oils% (w/w_{oils})		
	Biocrude	Asphaltenes	Oils	Saturates	Aromatics	Resins
None	37.7 ± 0.66	13.7 ± 1.63	24.0 ± 0.71	68.4	11.2	20.5
Na_2CO_3 10 % (w/w_{TS})	31.1	17.6	13.5	54.2	35.7	10.1
K_2CO_3 10 % (w/w_{TS})	39.4	17.4	22.0	45.0	31.3	23.7
$CuSO_4$ 10 % (w/w_{TS})	42.2	14.3	27.9	48.7	7.9	43.5
Ni over SiO_2/Al_2O_3 5 % (w/w_{TS})	26.1	7.1	19.0	26.2	36.9	36.9
Ni over SiO_2/Al_2O_3 10 % (w/w_{TS})	25.6	6.9	18.7	63.9	8.0	28.1
TgS_2 5 % (w/w_{TS})	34.4	11.6	22.8	43.6	5.3	51.2
TgS_2 10 % (w/w_{TS})	39.2	12.4	26.8	9.3	80.5	10.2
TgS_2 20 % (w/w_{TS})	40.4	16.4	24.0	72.9	19.6	7.5
MoS_2 5 % (w/w_{TS})	32.5	11.5	21.0	42.3	7.9	49.8
MoS_2 10 % (w/w_{TS})	32.5	7.0	25.5	63.5	23.4	13.1
MoS_2 20 % (w/w_{TS})	35.6	10.1	25.5	67.8	13.6	18.7
TiO_2 65 mg	41.6	28.7	12.9	42.7	50.0	7.4
TiO_2 125 mg	37.5	20.9	16.6	53.3	19.2	27.5
TiO_2 5 % (w/w_{TS})	41.6	19.0	22.6	39.2	12.2	48.7
TiO_2 10 % (w/w_{TS})	40.8	16.7	24.1	61.4	2.5	36.1
TiO_2 20 % (w/w_{TS})	41.9	14.1	27.8	52.0	21.0	27.0
Pt/Al_2O_3 4 g pellets	38.6	18.6	20.0	60.4	4.8	34.9
Pt/Al_2O_3 8 g pellets	40.1	14.4	25.7	75.0	3.9	21.1
Pt/Al_2O_3 12 g pellets	36.1	21.7	14.4	25.4	14.1	60.5
Pd/Al_2O_3 4 g pellets	29.3	7.6	21.7	39.8	55.3	4.9
Pd/Al_2O_3 8 g pellets	29.2	9.5	19.7	32.7	42.0	25.2
Pd/Al_2O_3 12 g pellets	22.7	12.2	10.5	33.9	1.6	64.6

a high fraction. With 20 %, the yield of biocrude became 35.58 % with 25.45 % of oils and 10.13 % of asphaltenes. When used in small quantities, that yield turned into a lower value (≈32.50 %). In the case of TgS_2, a fraction of 10 % was enough to increase the percentage of biocrude to 39.23 % with 26.81 % of oils and 12.41 % of asphaltenes. HTL experiments performed with Ni over SiO_2/Al_2O_3 catalysts produced very low yield of biocrude, 25.85 % approximately. The use of TiO_2, regardless its amount, showed a positive effect on HTL process. Biocrude yield was increased to a percentage higher than 40 % with around 24.8 % of oils and 16.59 % of asphaltenes.

The addition of catalyst in pellet form also has altered the biocrude yield. With Pt/Al_2O_3, when added in small (4 g) and moderate (8 g) amounts, the biocrude yield has increased to 38.64 % and 40.13 %. However, when the dosage was exceeded (12 g), that percentage has been dropped slightly to 36.06 %. With Pd/Al_2O_3, the biocrude yield was always in decrement to less than 30 %, despite the quantity added.

Regarding all the results obtained, it´s clear that the introduction of catalyst did influence the biocrude yield and its quality. Among all the catalysts used, the optimum yield of biocrude was achieved when TiO_2 was applied with 20 % dosage. TiO_2 has clearly promoted the hydrolysis of macromolecules in primary sludge. This is confirmed also by the high percentage of oils present (27.78 %). Titanium Oxide (TiO_2) is a proper catalyst for HTL process optimization. It is an extensively accepted promoter for technical research and industrial production as it is characterized by high thermal stability and activity in oxidation–reduction catalysis [28,29]. Even though 10 % of $CuSO_4$ resulted high biocrude yield, it´s a homogeneous catalyst. The use of heterogeneous catalyst is more favourable as it´s easy to handle, separate, recover and can be recycled [25].

3.3. *Characterisation of biocrude*

3.3.1. *Gas chromatography/mass spectrometry spectroscopy (GC/MS)*

GC/MS reports the molecular composition of the biocrude. Fig. 2 presents an example of GC–MS chromatogram of biocrude, in this case, using $CuSO_4$ as catalyst.

Generally, many substances could be detected by GC/MS in the biocrude. However, the identification of substances was not exhaustive due to limitations on the column temperature. The detailed substances identified from the biocrude samples chromatograms can be found in Table SI1 (Supporting information). The main composition of biocrude included hydrocarbons, esters, acids, ketones, alcohols, phenols and nitrogen-rich compounds. During the high-pressure conversion, the reformation and depolymerization reactions of biomass components, mainly carbohydrates, promoted the production of phenols [3]. The hydrolysis of carbohydrates produces phenols. N-compounds and O-compounds could be synthesized in Maillard reaction between the hydrolysis product of carbohydrates and proteins [32]. The presence of

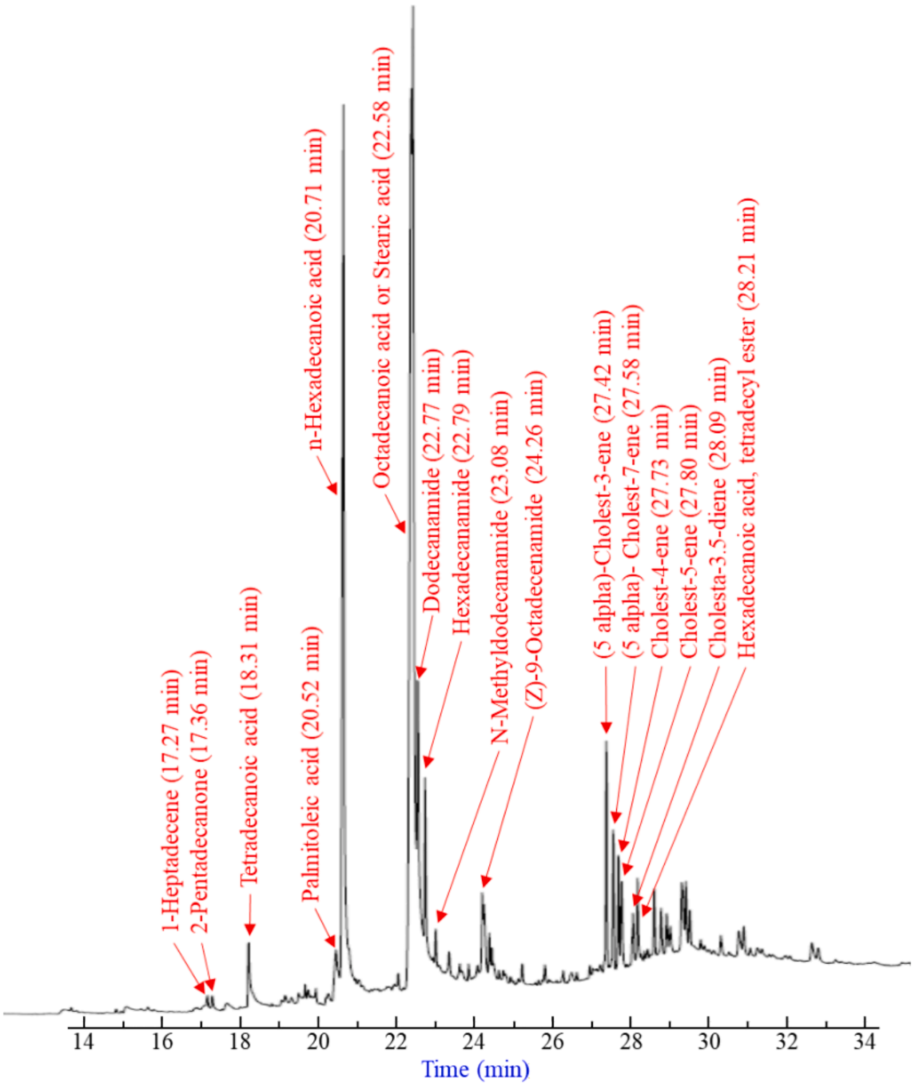

Fig. 2. Example of GC–MS chromatogram of biocrude. Catalyst: $CuSO_4$; Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

catalysts, either homogeneous or heterogeneous, promoted the production of more acids and esters. n-hexadecanoic acid, dodecanoic acid, octadecanoic acid and tetradecanoic acid were observed in all the biocrudes, which was attributed to the hydrolysis of lipids [11]. The N-containing compounds, amides and N-containing heterocycle compounds like hexadecamide, octadecanamide, dodecanamide came from the proteins present in primary sludge. Amide compounds were products of the reaction between fatty acids and amines formed from the cracking of amin acids [19]. Esters including hexadecenoic acid, methyl ester, hexadecenoic acid, dodecyl ester and hexadecenoic acid, tetradecyl ester were predominant. Ketones were mainly observed in the form of 2-heptadecanone and 2-pentadecanone. Cyclic hydrocarbons like cholest-3-ene, cholest-4-ene, cholest-5-ene were products of the recombination reactions between the hydrophilic molecules in sludge [30].

3.3.2. Thermogravimetry analysis (TGA)

TGA analysis was performed to study the weight loss stages of the biocrude. The TGA curves of the samples of biocrude from HTL of primary sludge are shown in Fig. 3. For comparisons, thermograms of the same category of catalyst are plotted in the same figure. In Fig. 3, biocrudes produced from HTL using homogeneous catalysts presented similar decomposition process.

A relatively significant weight loss took place at 210 °C in HTL-Na_2CO_3 with 66.91 % of weight loss, 200 °C in HTL-K_2CO_3 with 73.18 % of weight loss and 243.80 °C in HTL-$CuSO_4$ with 90.19 % of weight loss. Considering the samples of biocrude produced from HTL using powder heterogeneous catalysts, an important weight loss took place near 230 °C in HTL-TiO_2 with around 75 % of weight loss, near 230 °C in TgS_2 with around 80 % of weight loss, near 235 °C in HTL-MoS_2 with around 80 % of weight loss and near 170 °C in HTL-Ni over SiO_2/Al_2O_3 with around 71 % of weight loss. While in the case of heterogeneous pellet catalyst, biocrude samples faced an important weight loss near 220 °C in HTL-Pd/Al_2O_3 with around 75 % of weight loss and near 240 °C in HTL-Pt/Al_2O_3 with around 75 % of weight loss.

3.3.3. Ultimate analysis, HHV and energy recovered by the biocrude

The ultimate composition C, H, N and O, higher heating values HHV and the energy recovery ER of biocrude are presented in Table 3. Generally, through the HTL process, primary sludge was converted into a product with higher energetic value. However, the optimization of the process by adding a catalyst was not that convenient. Based on the results obtained, it́s clear that none of the catalysts was able to boost the energetic property of biocrude.

While the HHV of biocrude produced from HTL without using any catalyst reached 39.99 MJ/kg, the HHV of biocrude produced from HTL using catalyst, either homogeneous or heterogeneous, didńt pass that value. Very close attaints were observed in the HTL-$CuSO_4$ where HHV of biocrude was 39.2 MJ/kg with 75.0 % of carbon, 11.0 % of hydrogen, 3.1 % of nitrogen and 10.9 % of oxygen. Also, the quality of biocrude produced from HTL without using any catalyst was very close to that of petroleum, 42.7 MJ/kg [27]. Regarding the results of energy recovery, the increase noticed in the HTL-$CuSO_4$ from 80.1 % to 87.9 % is due to the improvement of biocrude yield (see Table 3). Among the alkali-based catalysts, K_2CO_3 showed better results than Na_2CO_3 in terms of yield as in terms of quality. HHV of biocrude produced from HTL- K_2CO_3 reached 30 MJ/kg with 63.8 % of carbon, 8.8 % of hydrogen, 3.7 % of nitrogen and 23.7 % of oxygen, resulting in an ER% of 62.7. As potassium salt improves the re-polymerization of biocrude products, it increases the non-polarity of biocrude, helping in the separation of biocrude from water [42]. The effect of Nickel on silica/alumina on the quality of biocrude was independent from the amount added. In both cases, an averaged HHV of 30.5 KJ/kg was attained with very similar

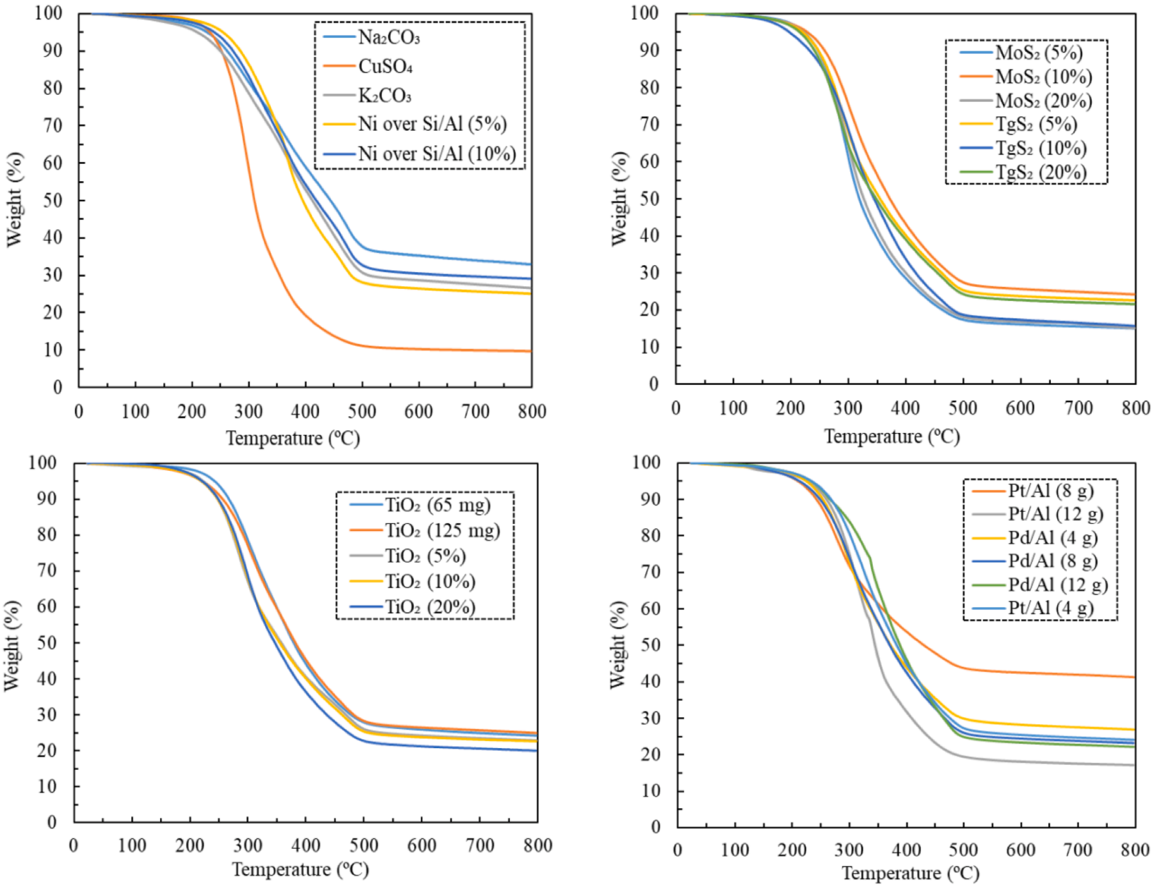

Fig. 3. TGA curves of biocrude samples, effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

Table 3
Ultimate analysis, HHV and energy recovery of biocrude, effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

Catalyst	Elemental composition% (w/w)				HHV (MJ/kg)	ER %
	C	H	N	O*		
None	75.1	11.3	4.1	9.6	40.0	80.1
Na_2CO_3 10 % (w/w_{TS})	59.7	8.3	2.9	29.2	26.9	44.1
K_2CO_3 10 % (w/w_{TS})	63.9	8.8	3.7	23.7	30.0	62.7
$CuSO_4$ 10 % (w/w_{TS})	75.0	11.0	3.1	10.9	39.2	87.9
Ni over SiO_2/Al_2O_3 5 % (w/w_{TS})	65.5	9.0	2.9	22.7	31.0	43.0
Ni over SiO_2/Al_2O_3 10 % (w/w_{TS})	64.2	8.7	3.1	23.9	30.0	40.9
TgS_2 5 % (w/w_{TS})	69.0	9.6	3.0	18.5	33.8	61.6
TgS_2 10 % (w/w_{TS})	71.2	10.2	3.2	15.5	36.0	74.9
TgS_2 20 % (w/w_{TS})	69.4	9.7	3.3	17.6	34.3	73.6
MoS_2 5 % (w/w_{TS})	73.3	10.6	3.1	13.1	37.7	65.2
MoS_2 10 % (w/w_{TS})	71.2	9.7	3.8	15.4	35.3	60.9
MoS_2 20 % (w/w_{TS})	72.5	10.4	3.1	13.9	37.1	78.3
TiO_2 65 mg	68.1	9.4	3.6	18.9	33.2	73.4
TiO_2 125 mg	66.8	9.1	3.3	20.8	31.9	63.6
TiO_2 5 % (w/w_{TS})	64.2	9.2	3.0	23.6	30.8	67.9
TiO_2 10 % (w/w_{TS})	70.6	9.8	3.4	16.1	35.1	76.0
TiO_2 20 % (w/w_{TS})	69.6	9.7	3.3	17.4	34.4	77.7
Pt/Al_2O_3 4 g pellets	67.9	9.5	3.6	19.0	33.2	68.2
Pt/Al_2O_3 8 g pellets	63.7	9.2	3.8	23.4	30.6	65.1
Pt/Al_2O_3 12 g pellets	70.3	10.4	3.3	16.0	35.9	68.8
Pd/Al_2O_3 4 g pellets	67.9	9.4	3.7	19.0	33.1	51.5
Pd/Al_2O_3 8 g pellets	67.6	9.5	3.7	19.2	33.1	51.4
Pd/Al_2O_3 12 g pellets	69.1	9.8	3.6	17.5	34.4	41.5

* O is calculated by difference, considering that the biocrude is ash-free.

elemental compositions. With TgS_2, the highest HHV (36.0 %) was reached with TgS_2 10 %, which is close enough to the value obtained with $CuSO_4$. In HTL-MoS_2, all the biocrude samples obtained had a significant HHV (higher than 35 MJ/kg) with high carbon (higher than 71 %) and hydrogen content (higher than 9 %). Regarding the results obtained from HTL-TiO_2, better quality of biocrude was observed when more amount of TiO_2 was added (10 and 20 %). The behaviour of Pt/Al_2O_3 and Pd/Al_2O_3 was the same on the quality of biocrude. HHV was in increment with the amount of catalyst added. The ability of biomass to provide heat, electricity and fuel can be distinguished by the different energy vectors produced. To do this, the Van Krevelen diagram allows us to compare fossil fuels, biomass and biocrude products produced by their transformation. The comparison is made by calculating the atomic ratios O/C and H/C. In fact, these ratios allow us to know the energy content of the substance, and the lower the ratios, the greater the amount of chemical energy of the substance [1]. Fig. 4 presents the Van Krevelen diagram for primary sludge and biocrudes, using different catalysts. The calculation of the atomic ratios H/C and O/C allow to represent the diagram [27]. The diagram allows an evaluation of the original used biomass and the state of maturity reached by the biocrude after the HTL process, being a possible indication of the severity of the treatment process.

The data obtained in the elemental analysis of the biocrudes allow the presentation of two main trends: i) the O/C atomic ratio of all the biocrudes is much lower than that of the original primary sludge; and ii) the H/C atomic ratio of the primary sludge is very similar to that of all biocrudes. The O/C atomic ratio of all biocrudes is between 0.11 and 0.37, when that of the primary sludge is 0.63. In fact, the reduction in the atomic ratio is between 42.2 % (case of Na_2CO_3) and 82.8 % (case of $CuSO_4$). In reality, the best results have been obtained by carrying out the process without a catalyst, with an obtained atomic ratio of 0.10 and 84.9 % of reduction in the O/C atomic ratio. These results can be explained by the fact that the transformation of primary sludge to biocrude has been done essentially through decarboxylation and dehydration reactions. The reduction of the O/C atomic ratio is very important since it leads to an improvement in the stability and viscosity of the biocrudes. On the other hand, a low O/C atomic ratio means that the expenditure of hydrogen to improve the qualities of the biocrude is much lower. All these facts show that HTL is a good technology when it comes to producing good quality biocrude [37].

However, it can be observed that the H/C atomic ratio of the biocrudes obtained with the different catalysts is very even with a value between 1.63 (cases of TiO_2 125 mg and Ni over SiO_2/Al_2O_3 10 %) and 1.77 (case of Pd/Al_2O_3, pellets 12 g). In fact, the experiment carried out without catalyst obtained a better value: 1.81. On the other hand, the value of the original primary sludge is 1.74. But, the atomic H/C ratio is still low when compared to that of oil with values of 1.90 or higher. In order to improve the H/C atomic ratio, the heteroatoms present in the biocrude must be eliminated. This is the only way to use biocrude as a real substitute for fuels of fossil origin. These encouraging results make it possible to lay the foundation for future refining processes of biocrude

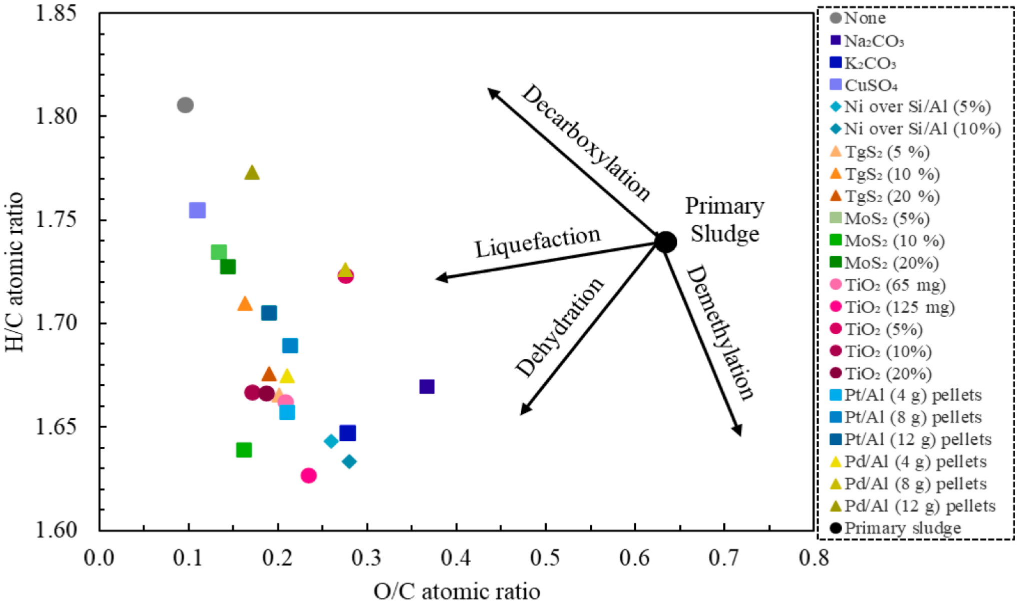

Fig. 4. Van Krevelen diagram of primary sludge and biocrude samples, effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

products that have been originated from wet biomass, as is the case of primary sludge from urban sewage treatment plants. On the other hand, there is still a large difference in the percentages of oxygen between biocrudes and oil. The high oxygen content in biocrudes makes them soluble in polar organic solvents, such as methanol or acetone, but they are difficult to mix with fuels of fossil origin [33].

Figs. 5a and 5b, respectively, present the relationship of the H/C and O/C atomic ratios and the biocrude yield. These two figures provide a very interesting supplement of information, since they allow to evaluate whether the improvement in yield is accompanied by an improvement in the quality of the biocrude.

In Fig. 5a it can be seen that generally, the improvement in biocrude yield is not accompanied by an improvement in the H/C ratio. The two cases that allow a considerable improvement are in the case of $CuSO_4$ where the biocrude yield achieved is 42.2 % and the H/C ratio is 1.75. The other case is the experiment carried out without a catalyst, where the biocrude yield achieved is 37.7 %, but the H/C ratio is the highest with 1.81. This behaviour was also noted in another study where 10 % of $CuSO_4$ was used in HTL municipal sewage and biocrude yield was improved from 38.78 % with a H/C ratio of 1.62 (without catalyst) to 47.45 % with a H/C ratio of 1.70 (with catalyst) [28,29].

It is surprising that Fig. 5b presents similar trends, that is, the improvement in biocrude yield is not accompanied by a substantial decrease in the O/C ratio. However, again, it should be noted that the two best experiments are those carried out with $CuSO_4$ and without catalyst. In addition to achieving very good yields, the decrease in the atomic O/C ratio is consistent until obtaining values of 0.11 and 0.10 respectively, in fact the two best values.

3.3.4. *FT-IR of biocrude samples*

FTIR spectroscopy gives more information about the functional groups present in the biocrude. FTIR spectra of biocrudes produced from HTL using homogeneous catalysts, heterogeneous powder catalysts and heterogeneous pellet catalysts are separated in Fig. 6. All the spectra were similar in shape, but different in intensity. So, all biocrudes are composed from the same functional groups. The presence of C and H detected by ultimate analysis is explained here by the important C–H stretching with CH_2 and CH_3 bending around 2961 cm^{-1} and 2852 cm^{-1}, double bond C stretching around 1655 cm^{-1}, triple bond C stretching around 2260 cm^{-1} and aromatics around 722 cm^{-1}. Esters and phenols are represented by C–O stretching peaks near 1030–1450 cm^{-1}. $C=O$ stretching peaks ranging between 1707 cm^{-1} and 1590 cm^{-1} belong to the functional groups of carboxylic acids, ketones and esters as detected by GC/MS analysis. Wide peaks around 3200 cm^{-1} and 3500 cm^{-1} correspond to N-compounds or OH compounds. The peaks around 500 cm^{-1} could be identified as compounds containing C–Cl or C–F bonds. Among all the homogeneous catalysts used, it can be observed that in HTL with acidic catalyst, the intensity of hydrocarbon peaks is higher; whereas, in HTL with basic catalyst, the intensity of acids and esters peaks is higher.

Regarding the spectra of HTL using heterogeneous catalysts, in the powder case, it can be observed that with TiO_2, TgS_2 and MoS_2, the intensity of peaks is very comparable. However, with Ni over SiO_2/Al_2O_3, its clear that the intensity of $C=O$ groups is much higher. In the case of heterogeneous pellet catalyst, the intensity of peaks when using Pt/Al_2O_3 was more visible than that of Pd/Al_2O_3.

3.3.5. *^1H NMR*

Similar to FTIR, NMR provides additional functional group information. Fig. 7 present the ^1H NMR spectres of samples of biocrude produced using different catalysts (homogeneous and heterogeneous).

H corresponding to the functional group of alkanes appears near 0.9 ppm and 1.8 ppm. Unsaturated hydrocarbons (alkenes) are observed around 2.1 ppm. However, the same spectra could belong to esters, carboxylic acids, amine, amide and ketones. The chemical shifts, located between 5 and 5.5 ppm are assigned to alcohol and phenols. Also, the same chemical shifts could belong to amide. The peak around 7.2 ppm correspond to the solvent used. Generally, all the biocrude contain the same functional groups, but with different intensity. The distribution of the groups and their intensity was dependent on the catalyst used. Regarding the results obtained from biocrudes HTL-homogeneous catalyst, it can be noted that Na_2CO_3 promoted the formation of hydrocarbons compounds whereas $CuSO_4$ promoted the formation of $C=O$ compounds. Considering the results obtained from biocrudes HTL-heterogeneous catalyst, by increasing the amounts of MoS_2 and Pt/Al_2O_3, less hydrocarbons were produced. With 5 % of Ni over Si/Al, more hydrocarbons were observed, while with 10 % of Ni over Si/Al, more $C=O$ compounds were noted. With TiO_2, Pd/Al_2O_3 and TgS_2, no significant changes were found. ^1H NMR spectra comply with FTIR and GC/MS analysis. As mentioned before, carboxylic acids and esters were derived from the lipids, phenols and alcohol could be originated from carbohydrates and nitrogenous compounds were produced from

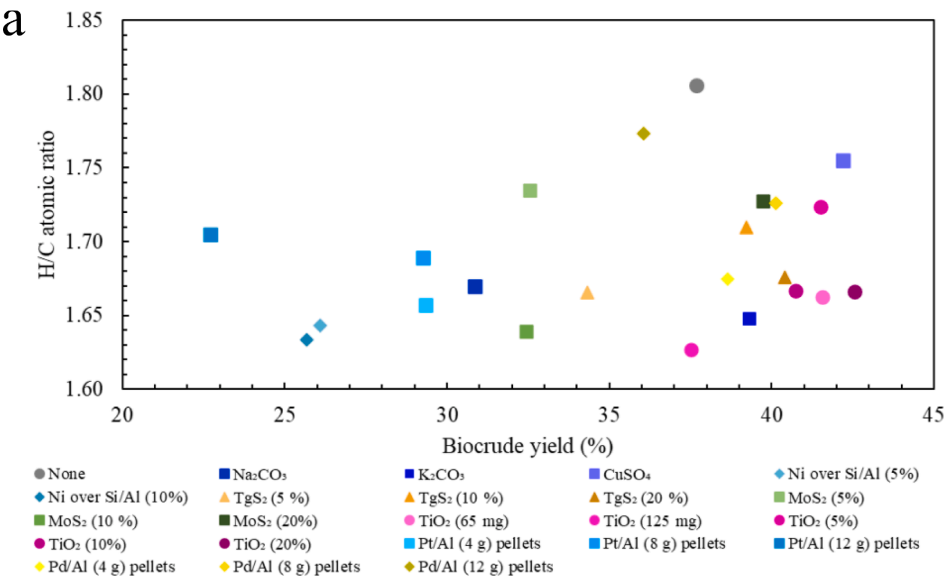

Fig. 5a. Relationship between biocrude yield and improvement of H/C atomic ratio, effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

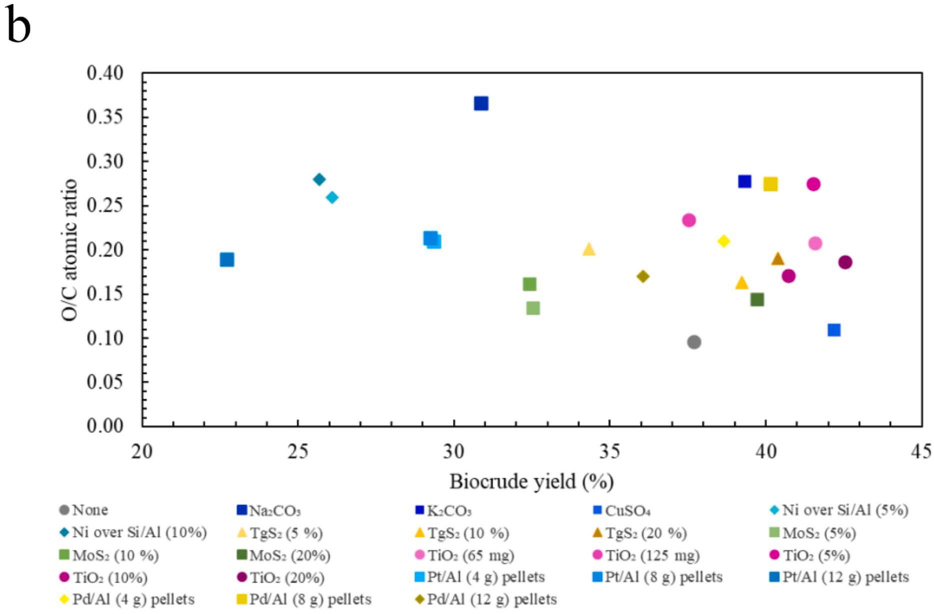

Fig. 5b. Relationship between biocrude yield and improvement of O/C atomic ratio, effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

proteins; all together constitute the main ingredients of primary sludge.

3.3.6. *Simulated distillation*

The fractional cuts of biocrude, produced from HTL using different catalysts (homogeneous or heterogeneous), are represented in Fig. 8. Íts clear that all the biocrudes present similar behaviour. The composition of biocrude is divided into fractions, from gasoline to vacuum residue. In other words, the fractions were detected in the form of boiling points in an ascending way from light to heavy with the mass fractions. As it can be observed, none of the biocrude contain a fraction in the range of gasoline. Only less than 5 % of the biocrude fraction is in the Jet Fuel range, except with 5 % of TiO_2 where no fractions in that range was detected. Proteins and lignin are probably the promoters for the production of substances in that fractional cut [1]. Likewise, less than 15 % of the biocrude fraction is in the Diesel range. Most of the substances in this fractional cut are mainly produced from proteins, and in small quantity from carbohydrates and lipids [1]. In fact, the most significant fractions of the biocrude belong to the vacuum gasoil range. Between 70 and 90 % were detected, demonstrating the presence of heavy and long chain molecules in the biocrude generated from lipids [1]. This confirms that biocrude should be subjected to further treatment in order to improve its quality. As the major substances produced from lipids are fatty acids, one solution could be the hydrodeoxygenation of fatty acids to produce alkanes. This linear – chain paraffin can be blended perfectly to biodiesel, helping in low temperature fluidity and better anti-oxidation stability [21]. Table SI2 (Supporting information) lists the values of composition of biocrudes by fractional cuts. The reference boiling cuts were obtained from Haider [12].

3.3.7. *SARA separation and quantification*

SARA fractions quantification was performed to all conditions and the results were also presented in Table 2. Biocrude was distributed between asphaltene and maltenes containing saturates, aromatics and resins. The composition of biocrude (asphaltenes and maltenes) as well as the composition of light phase (saturates, aromatics, resins) was dependent on the type and amount of catalyst. Biocrude produced from HTL without using any catalyst contained 68.35 % of saturates, 11.17 % of aromatics and 20.48 % or polars. Generally, maltene was predominant in biocrude, except with TiO_2 (65 and 125 mg), Pt/Al_2O_3 and Pd/Al_2O_3 (12 g). Among homogeneous catalysts, even though Na_2CO_3 presented the lowest oil percentage (13.5 %), it contained the highest percentage of saturates (54.2 %). While, with $CuSO_4$, polars were predominant in the oil phase (43.5 %). With Ni over SiO_2/Al_2O_3, the distribution of biocrude between maltenes and asphaltene was not affected greatly by the quantity added. However, by increasing the amount from 5 to 10 %, more saturates were detected (63.9 %). With TgS_2, it can be observed that by increasing the quantity added from 5 to 20 %, less polar compounds were noticed. In other words, with 5 %, polars were predominant (51.2 %), with 10 %, aromatics were predominant (80.5 %) and with 20 %, saturates were predominant (72.9 %). With TiO_2, the percentage of oils has increased along with the increase of the catalyst amount. This behaviour was also applied on the polar fraction. With Pd/Al_2O_3, with lower amount, more saturates were observed. While with higher amount, more polar compounds (aromatics and polars). Finally, with Pt/Al_2O_3, the oil fraction decreased along with the increase of the amount of pellets added. The same behaviour was noticed for aromatics and saturates. Consequently, polars were increasing with the increase of pellets amounts. By focusing on the quality of biocrude, using a heterogeneous catalyst was more favourable than using a homogeneous one, specifically with 20 % TgS_2 and 8 g of Pt/Al_2O_3 could have promoted the production of more saturates compounds to 72.94 % and 75.00 %. It seems that most of the remaining catalysts have helped in the production of heavy and long chain compounds, either aromatics or polars.

3.4. *Effect of catalysts on the biochar*

3.4.1. *Biochar yield*

Table 4 presents the results of biochar: yield, ash content, elemental analysis and HHV for each experimental condition.

The yield of biochar without addition of catalyst was 28.10 % containing 60.60 % of ashes. Regarding the results obtained in Table 4. The presence of catalyst has affected the biochar yield. In some cases. It has increased the percentage, while in others it has decreased the percentage. A further interpretation is provided.

In the case of homogeneous catalysis, results demonstrated that biochar, ash and volatile yields were not significantly affected by the presence of catalyst. With Na_2CO_3 and $CuSO_4$, biochar yield was increased to 30.60 % and 30.10 % with 56.38 % and 55.71 % of ash. In other studies, the acidic catalyst $CuSO_4$ improved both biocrude and

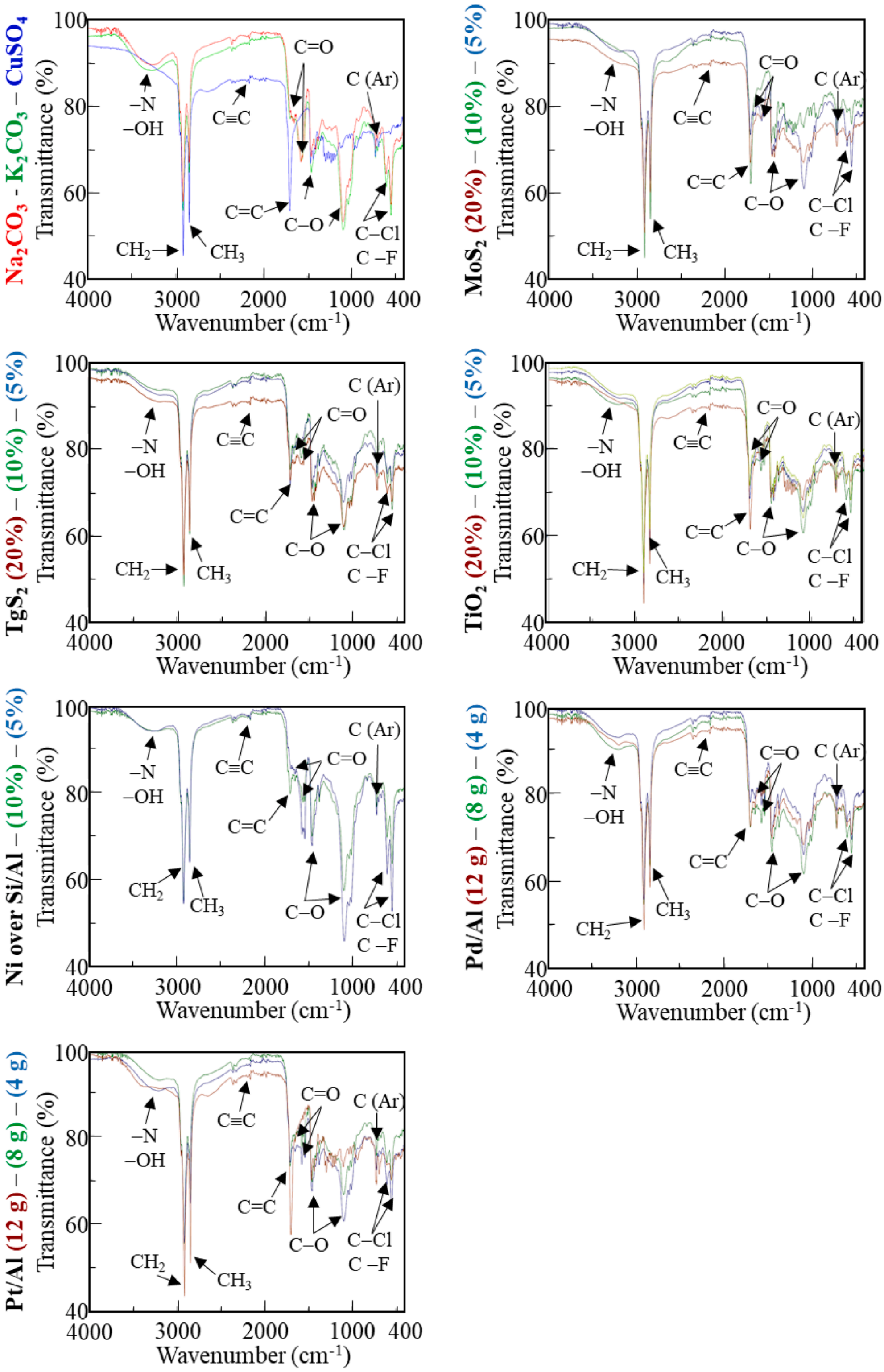

Fig. 6. FT-IR spectras of biocrude, effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

biochar yields, implying that $CuSO_4$ encourages the water-soluble intermediates conversion into biocrude and additional polymerized species into biochar [10]. Also, it was said that $NaCO_3$ promotes the hydrolysis of carbohydrate and diminish the conversion of protein and lipids [41]. In our case, even though primary sludge contained a significant amount of carbohydrate, neither biocrude yield was improved nor biochar yield was decreased. On the other hand, with K_2CO_3, 28.20 % of biochar were produced with 57.84 % of ash. The same behaviour was noted in another study when K_2CO_3 was added [4].

In the case of heterogeneous catalysis the catalyst affected the biochar yield considerably. According to the results presented in Table 4, a significant increase was observed when using a heterogeneous catalyst, either in powder form or in pellet form. With MoS_2, biochar yield was decreasing among with the increase of the amount added from 61.10 to 31.50 %. While with TgS_2, the yield of biochar was not affected by the percentage of catalyst. With Ni on SiO_2/Al_2O_3, biochar attained an

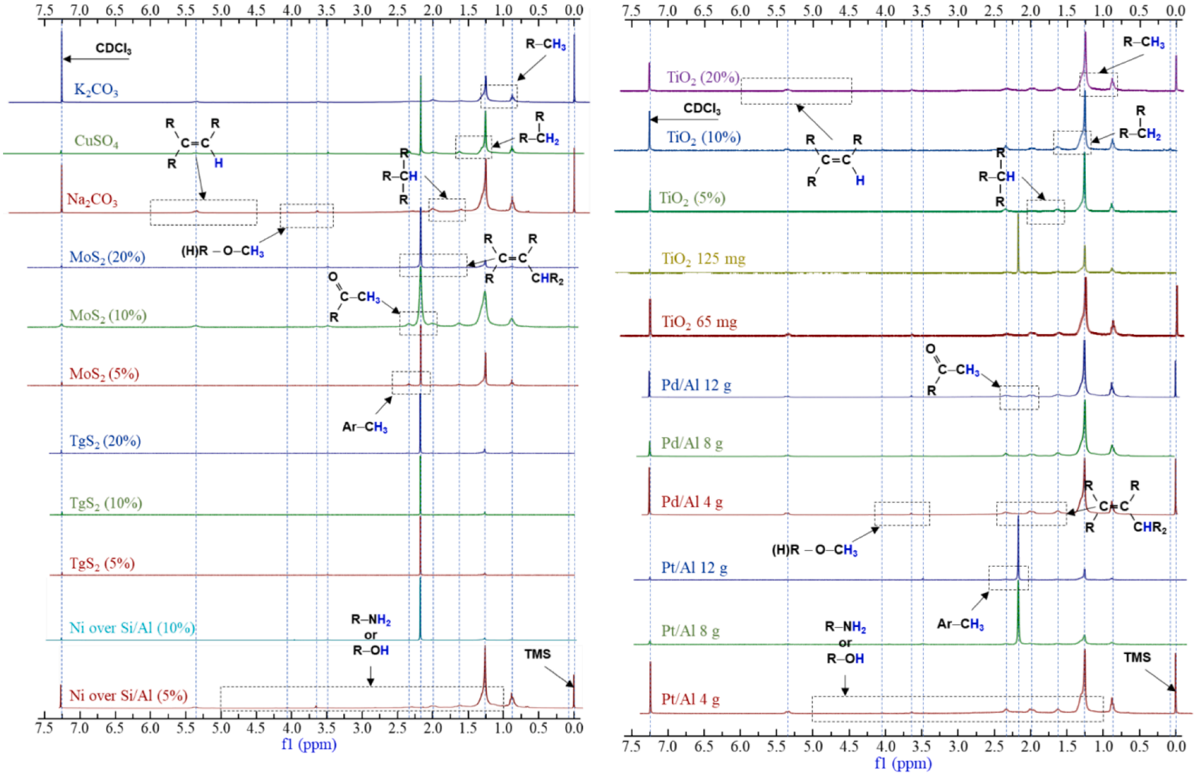

Fig. 7. ^{1}H NMR spectras of biocrude, effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

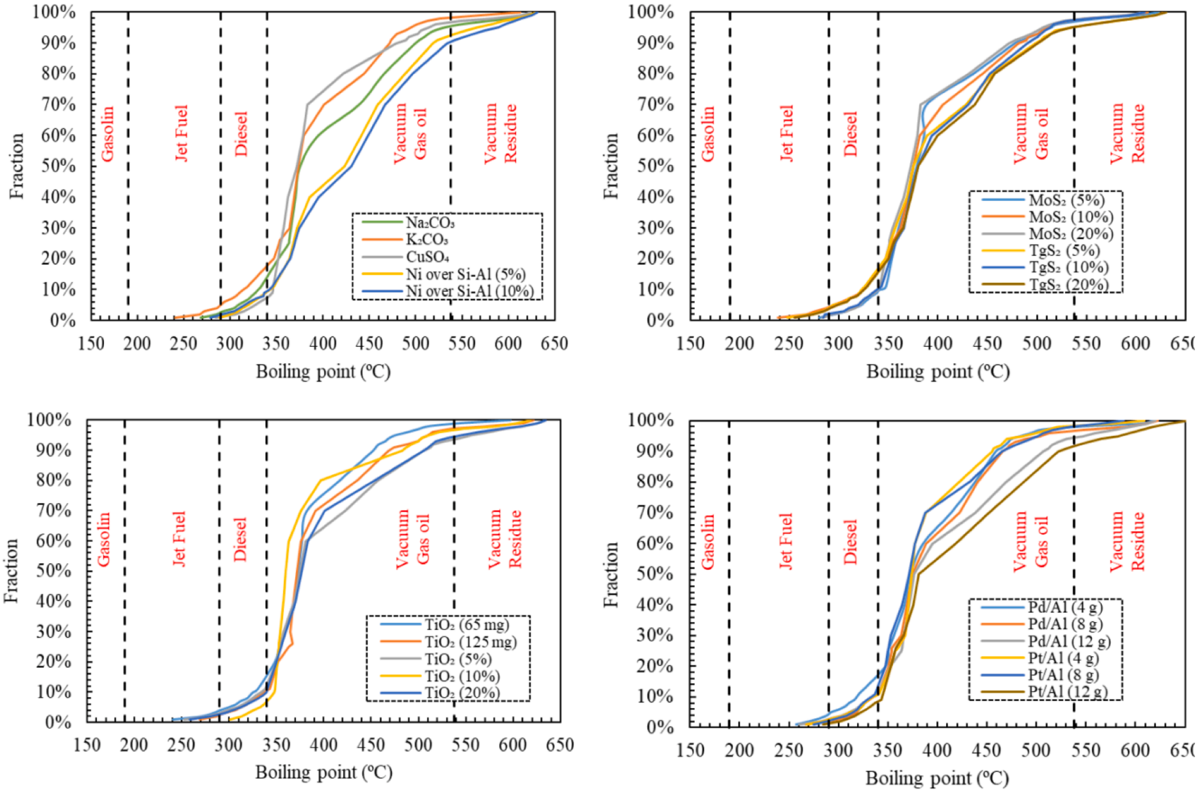

Fig. 8. Simulated distillation of biocrude samples, effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

optimum value (69.40 %) when 5 % of catalyst was loaded. With TiO_2, generally, biochar yield was decreasing with the increase of the amount of catalyst. However, with 165 mg TiO_2, a huge amount of biochar was noticed (64 %). This suggests an experimental error.

On the other hand, the number of pellets did not make any noticeable difference in the biochar yield, more improvement was noticed when

Table 4
Yield, ash content, ultimate composition and HHV of biochar, effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

Catalyst	Yield % (w/w_{TS})	Ash % (w/w_{TS})	Elemental composition (wt%)				HHV (MJ/kg)	ER
			C	H	N	O		
None	28.10 ± 0.94	60.60	71.50	9.80	3.00	15.80	35.48	53.00
Na_2CO_3 10 % (w/w_{TS})	30.60	56.38	71.07	10.68	2.68	15.57	36.65	59.60
K_2CO_3 10 % (w/w_{TS})	28.20	57.84	76.40	10.34	3.01	10.24	38.93	58.30
$CuSO_4$ 10 % (w/w_{TS})	30.10	55.71	35.42	3.34	2.84	58.39	6.27	10.00
Ni over SiO_2/Al_2O_3 5 % (w/w_{TS})	69.40	48.83	70.11	10.46	2.31	17.12	35.73	131.60
Ni over SiO_2/Al_2O_3 10 % (w/w_{TS})	56.00	47.41	56.63	8.22	1.96	33.19	25.04	74.40
TgS_2 5 % (w/w_{TS})	48.10	48.78	63.46	9.05	2.34	25.15	29.99	76.60
TgS_2 10 % (w/w_{TS})	50.0	51.27	64.67	9.24	2.47	23.62	30.95	82.10
TgS_2 20 % (w/w_{TS})	47.60	55.93	62.52	8.72	2.16	26.61	28.94	73.10
MoS_2 5 % (w/w_{TS})	61.10	45.68	57.04	0.59	2.08	40.29	12.88	41.80
MoS_2 10 % (w/w_{TS})	42.90	55.71	60.77	8.60	2.28	26.99	28.11	64.10
MoS_2 20 % (w/w_{TS})	31.50	59.07	62.30	8.54	2.18	26.99	28.53	47.70
TiO_2 65 mg	44.00	61.54	45.47	5.78	1.31	47.44	15.17	35.50
TiO_2 125 mg	64.00	25.52	46.68	6.86	1.88	44.58	17.65	60.00
TiO_2 5 % (w/w_{TS})	42.10	58.55	10.81	1.10	0.71	28.83	0.04	0.10
TiO_2 10 % (w/w_{TS})	35.10	69.09	11.67	1.12	0.76	17.36	2.43	4.50
TiO_2 20 % (w/w_{TS})	42.10	62.51	53.35	5.93	3.39	37.33	19.87	44.40
Pt/Al_2O_3 4 g pellets	35.30	51.51	52.98	0.77	2.76	36.55	12.44	23.30
Pt/Al_2O_3 8 g pellets	37.60	52.99	78.45	1.16	3.04	6.89	26.97	53.90
Pt/Al_2O_3 12 g pellets	32.80	52.87	79.32	1.12	3.35	6.08	27.36	47.70
Pd/Al_2O_3 4 g pellets	42.50	51.51	75.38	0.98	3.63	11.15	24.91	56.30
Pd/Al_2O_3 8 g pellets	43.90	52.99	83.96	1.08	4.07	1.16	29.76	69.40
Pd/Al_2O_3 12 g pellets	45.00	52.87	65.65	0.79	3.59	22.90	19.21	45.9

Ash content in biochar is catalyst-free.
* O is calculated by difference considering the percentage of ash.

Pd/Al_2O_3 was used than when Pt/Al_2O_3 was used. With Pt/Al_2O_3, biochar attained an averaged value of 35 % while with Pd/Al_2O_3, biochar reached an averaged value of 44 %.

3.4.2. *Ultimate analysis, ash content and HHV calculation*

The ultimate analysis, the ash content and the HHV of the biochar are also presented in Table 4. Solid phase from HTL without catalyst reached a HHV of 35.48 MJ/kg. In the presence of alkali salt catalyst (Na_2CO_3 and K_2CO_3), HHV has improved to 36.65 and 38.93 MJ/kg. While with acid catalyst ($CuSO_4$), HHV has significantly decreased to 6.27 MJ/kg. With TgS_2, HHV of biochar produced was similar, regardless the amount added. While with MoS_2 and Pt/Al_2O_3, by increasing the amount of catalyst, the HHV was improving. With Ni on SiO_2/Al_2O_3, better quality of biochar was obtained with lower amount of catalyst (5 %). While with Pd/Al_2O_3, HHV has increased along with the percentage of catalyst to 29.76 MJ/kg, then decreased to 19.21 MJ/kg at 12 g of catalyst. With TiO_2, unexpected results appeared from the elemental analysis. This suggests that the sample used for analysis contained mainly the recovered catalyst. Among all the catalysts used, the best quality of biochar in terms of its energetic value was obtained with K_2CO_3. As reported by Shah et al., biocrude yield and HHV were improved by 3 to 5 % at 350 °C and 400 °C with the presence of K_2CO_3 [27].

3.4.3. *Ash of solid phase characterisation*

SEM images and EDX spectra of ash in biochar are presented in Fig. SI2 (Supporting information). It was demonstrated that the variety and quantity of elements present mean that heavy metals are richly concentrated in the solid phase, biochar [35]. The same was noticed here. Most of the ashes were accumulated in the biochar, presenting diverse types of metals. In addition, the presence of catalysts affected the amount and the type of metals as some of them were recuperated with the solid phase. Based on the observations done, ashes were rich in oxides and salts containing Fe, Ti, Ca, Si, Al, W, P, Cl, Mg and S.

Table SI3 (Supporting information) shows the composition of species in the ashes of the biochar. As can be seen in this table, when a certain homogeneous or heterogeneous catalyst is used in the HTL, part of the metal is later found in the biochar ashes.

There are several very striking cases, such as when the sodium Na_2CO_3 catalyst has been used. At the end of the HTL process it can be observed that the percentage of sodium in the ashes was 42.1 % (w/w). The same happens with the K_2CO_3 catalyst, when at the end of the process it was 43.1 % (w/w). However, the same does not happen with $CuSO_4$, where copper was not detected in the biochar ashes. The same occurs with heterogeneous catalysts as aluminium or titanium (until 27.4 % w/w), or those containing sulphur. At the end of the process, the amount of these elements in the ashes is higher than in the other cases. This fact is normal with this type of catalysts, since it is assumed that they are not dissolved and, during the separation of products, they should remain in the solid phase. What is not normal, is that this high quantity of homogeneous catalysts appears in the solid phase and, is not in the aqueous phase.

3.5. *Effect of catalysts on the aqueous phase*

Analytical results of TOC, COD, proteins, carbohydrates and ash of the aqueous phase are presented in Table 5. Aqueous phase contained a small percentage of proteins. carbohydrates and ashes without any catalyst, when comparing to the initial properties of primary sludge. Also, the value of COD decreased and the value of TOC was comparable. In this study, the characteristics of aqueous phase change depending on the catalyst used whether it is homogeneous or heterogeneous, in the form of powder or pellets.

After each experiment, TOC, COD, proteins, carbohydrates and ash of soluble solids were determined in the aqueous phase. Also, a microanalysis through ESEM was performed for the ashes of the dissolved solids in the aqueous phase. Results are presented in Figure SI3 (Supporting information).

Based on the results obtained, the percentages of protein and carbohydrates in the aqueous phase produced from HTL with catalyst were significantly low. In all the scenarios, the value of protein was always less than 2.5 % and the value of carbohydrate was always less than 1 %. Even though the values of COD have decreased after HTL conversion, they are still considered high. A slight change (increase or decrease) was noted in TOC values, depending on the catalyst used. Concerning the ash content, all the dissolved solids contained a percentage lower than 2 %. The results obtained, specially from TOC and COD analysis, demonstrate

Table 5
Aqueous phase characterization. Effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

Catalyst	TOC (mg/L)	COD (mg/L)	Proteins % (w/w_{TS})	Carbohydrates % (w/w_{TS})	Ash % ($w/w_{TS\ of\ AP}$)
None	5696	11,649	1.01	0.03	0.39
Na_2CO_3 10 % (w/w_{TS})	6737	18,062	2.15	0.12	1.22
K_2CO_3 10 % (w/w_{TS})	7245	14,999	2.19	0.03	0.97
$CuSO_4$ 10 % (w/w_{TS})	6570	13,729	1.84	0.05	0.16
Ni over SiO_2/Al_2O_3 5 % (w/w_{TS})	3193	12,750	2.29	0.11	0.52
Ni over SiO_2/Al_2O_3 10 % (w/w_{TS})	4660	16,646	2.02	0.09	0.48
TgS_2 5 % (w/w_{TS})	4432	11,360	2.02	0.07	0.80
TgS_2 10 % (w/w_{TS})	4889	18,934	2.19	0.09	0.63
TgS_2 20 % (w/w_{TS})	4272	18,977	2.01	0.08	0.43
MoS_2 5 % (w/w_{TS})	6752	15,300	2.18	0.07	0.51
MoS_2 10 % (w/w_{TS})	5873	14,820	1.78	0.07	0.44
MoS_2 20 % (w/w_{TS})	6160	13,490	1.93	0.07	0.46
TiO_2 65 mg	6215	17,540	1.59	0.07	0.45
TiO_2 125 mg	6920	12,850	1.61	0.04	0.23
TiO_2 5 % (w/w_{TS})	9370	14,175	1.26	0.06	0.64
TiO_2 10 % (w/w_{TS})	6910	12,850	1.66	0.04	1.47
TiO_2 20 % (w/w_{TS})	7495	21,368	1.59	0.04	1.09
Pt/Al 4 g pellets	5805	19,620	1.86	0.04	0.68
Pt/Al 8 g pellets	6240	16,500	2.01	0.04	0.62
Pt/Al 12 g pellets	6895	18,900	1.58	0.04	0.77
Pd/Al 4 g pellets	2677	21,620	1.83	0.04	0.72
Pd/Al 8 g pellets	2910	12,800	1.49	0.05	0.49
Pd/Al 12 g pellets	2815	17,880	1.30	0.04	0.58

that aqueous phase contains a significant number of organic species, which devote its treatment before any discharge. Therefore, aqueous phase can be seen as a valued product, that can be used in further applications. One solution that can be proposed for aqueous phase is its use as a co-solvent in the HTL process to improve the biocrude yield [2]. Another one is to valorise the HTL-AP through catalytic hydrothermal gasification [34].

Table SI4 (Supporting information) shows the composition of species in the ashes of the dissolved solids in the aqueous phase. The results listed in the table demonstrate that, when a certain homogeneous or heterogeneous catalyst is used in the HTL. part of the metal is transferred to the ashes found in the dissolved solids of the aqueous phase. Following the HTL process, some solid parts went with the aqueous phase containing different metals. With Na_2CO_3, the same amount of sodium was found in the aqueous phase as in the solid phase, 42.1 % (w/w). This demonstrates that part of the catalyst was recuperated with the solid phase and other was filtered with the aqueous phase.

There are several very striking cases, such as when the sodium Na_2CO_3 catalyst has been used. The same behaviour was noted with K_2CO_3, where the same amount of potassium was retrieved in the aqueous phase, 43.1 % (w/w). However, with $CuSO_4$, copper was not detected, neither in biochar nor in aqueous phase. It can be suggested that the copper went to the biocrude phase. No titanium was detected in the ash of the aqueous phase, confirming that all of it was recuperated with the solid phase. The same was observed with aluminium. When comparing with the results obtained from HTL-catalyst with the one obtained from HTL-none and primary sludge, the percentage of metals were increased in some cases due to the contribution of catalysts. As it is neither reacted nor transformed, the catalyst is recuperated somehow in the products obtained, either in the solid phase, the aqueous phase or the biocrude during separation. Normally, catalyst should be retained on the filter paper with the solid phase. However, the results showed that some of them were present in the aqueous and suggested that some others could be in the biocrude. Therefore, the particle sizes of some catalysts were smaller than the size of filter, enabling it to be passed into other phases than solid phase. Finally, an ashes mass balance was realised and it is presented in Table 6.

All the ashes that have been introduced with the primary sludge plus the catalyst, must be found in all the products obtained after HTL, except in the case of gases. Based on the values obtained in Table 6, it can be demonstrated that most of the ashes present in the primary sludge were transferred to biochar and aqueous phase. In the case where the ash balance was not closed, the total ash is lower than the ash of the feedstock, it is clear that part of the ash went to the biocrude phase. However, it is shown some exceptions where the total ash calculated was higher than that of the feedstock. In this study, it was assumed that all the bottles of sludge contained the same solid content (4.3 % w/w). However, these exceptional cases suggest that some bottles contained different solid content, affecting consequently the ash content of feedstock.

3.6. *Effect of catalysts on the biogas*

The identification and relevant composition of biogas obtained from the catalytic HTL are listed in Table 7.

Mainly, the percentage of gas produced was small. The abundant compounds were CO and CO_2. The saturated hydrocarbons CH_4. C_2H_6

Table 6
Ash balance, effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

Catalyst	Ash $_{feedstock}$ (% $w/w_{total\ solids}$)	Total ash[*] (% $w/w_{total\ solids}$)
None	4.55	3.26
Na_2CO_3 10 % (w/w_{TS})	5.09	5.12
K_2CO_3 10 % (w/w_{TS})	5.04	4.47
$CuSO_4$ 10 % (w/w_{TS})	4.94	3.64
Ni over SiO_2/Al_2O_3 5 % (w/w_{TS})	1.64	1.98
Ni over SiO_2/Al_2O_3 10 % (w/w_{TS})	2.68	2.93
TgS_2 5 % (w/w_{TS})	3.36	3.46
TgS_2 10 % (w/w_{TS})	3.41	3.78
TgS_2 20 % (w/w_{TS})	3.62	3.06
MoS_2 5 % (w/w_{TS})	3.36	3.18
MoS_2 10 % (w/w_{TS})	3.54	3.69
MoS_2 20 % (w/w_{TS})	3.49	3.75
TiO_2 65 mg	5.16	4.79
TiO_2 125 mg	4.61	3.88
TiO_2 5 % (w/w_{TS})	5.15	5.52
TiO_2 10 % (w/w_{TS})	4.98	5.07
TiO_2 20 % (w/w_{TS})	3.39	3.89
Pt/Al 4 g pellets	5.09	3.28
Pt/Al 8 g pellets	5.10	3.51
Pt/Al 12 g pellets	4.83	2.92
Pd/Al 4 g pellets	4.94	4.58
Pd/Al 8 g pellets	5.07	5.04
Pd/Al 12 g pellets	5.22	5.27

[*] Total ash = ash (biochar) + ash (aqueous phase).

Table 7
Biogas composition. Effect of different catalysts. Temperature: 300 °C; Time of reaction: 30 min; Stirring rate: 100 rpm.

Catalyst	Biogas composition (mmol %)						
	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8
None	0.038	0.115	0.052	0.004	ND	ND	ND
Na_2CO_3 10 % (w/w_{TS})	ND	ND	0.054	0.004	ND	0.001	ND
K_2CO_3 10 % (w/w_{TS})	Not realised						
$CuSO_4$ 10 % (w/w_{TS})	0.081	ND	0.047	0.004	ND	0.001	ND
Ni over SiO_2/Al_2O_3 5 % (w/w_{TS})	Not realised						
Ni over SiO_2/Al_2O_3 10 % (w/w_{TS})	Not realised						
TgS_2 5 % (w/w_{TS})	0.131	0.14	0.404	0.011	0.01	0.122	0.011
TgS_2 10 % (w/w_{TS})	0.156	0.736	0.97	0.039	0.039	0.328	0.037
TgS_2 20 % (w/w_{TS})	0.14	0.418	0.327	0.044	0.037	0.322	0.037
MoS_2 5 % (w/w_{TS})	ND	ND	0.052	0.004	ND	ND	ND
MoS_2 10 % (w/w_{TS})	0.446	2.363	1.812	0.186	0.13	0.801	0.12
MoS_2 20 % (w/w_{TS})	0.051	0.059	ND	0.05	0.004	0.001	ND
TiO_2 65 mg	Not realised						
TiO_2 125 mg	Not realised						
TiO_2 5 % (w/w_{TS})	0.13	0.141	0.074	0.004	0.006	0.067	0.007
TiO_2 10 % (w/w_{TS})	ND	ND	0.05	0.004	ND	0.001	ND
TiO_2 20 % (w/w_{TS})	0.016	ND	0.05	0.043	0.004	ND	ND
Pt/Al 4 g pellet	0.127	0.713	0.148	0.032	0.035	0.331	0.034
Pt/Al 8 g pellet	0.132	0.767	0.148	0.042	0.052	0.469	0.051
Pt/Al 12 g pellet	0.017	ND	0.051	0.004	ND	ND	ND
Pd/Al 4 g pellet	0.095	ND	0.052	0.004	ND	ND	ND
Pd/Al 8 g pellet	0.417	0.8	0.143	0.059	0.057	0.489	0.056
Pd/Al 12 g pellet	0.166	0.493	0.16	0.028	0.032	0.286	0.034

ND: not detected.
Not realised: Amount of gas produced was not enough for analysis, occurred due to a leak in the system.

and C_3H_8 and the unsaturated ones C_2H_4 and C_3H_6. As shown in Table 7. It is obvious that the amount and diversity of gases were higher when heterogeneous catalysts were used. When employing homogeneous catalyst in the runs, few gases were released with percentages lower than 0.08 %. While adding heterogeneous catalyst liberated more gases. It can be noted that unsaturated gases were predominant. Also, significant amounts of CO and CO_2 were detected. Finally, the introduction of catalysts, specifically heterogeneous, promoted the production of biogas.

4. Conclusions

The improvement of biocrude yield from HTL of primary sludge was completed through the addition of a catalyst. Based on this study, HTL conversion without any catalyst reached a biocrude yield of 37.7 % (w/w_{VS}). The best improvements were attained with $CuSO_4$ (10 %) homogeneous catalyst, 42.20 % (w/w_{VS}), and TiO_2 (20 %) heterogeneous catalysts, 41.90 % (w/w_{VS}). Though, the use of heterogeneous catalyst was always a better option as it can be recovered easily and reused. The presence of catalyst affected as well the quality of biocrude, regardless the type and amount used. Biocrude was characterized by a higher heating value not lower than 30 MJ/kg with high carbon percentage (higher than 60 %). However, catalyst didńt help much in the production of lighter compounds. Analysis showed that the major fraction of biocrude belong to asphaltenes. Biochar was recuperated with high carbon content, which suggests its use in further applications. While the aqueous phase, with low protein and carbohydrate content, still presented high COD and TOC values. In same way, it could be advantageous to employ it in additional applications. Ash content present in the primary sludge was transferred mainly to biochar and aqueous phase. A small part went to the biocrude. This was verified by the ash balance performed as well as the analysis of metals. Definitely. the optimization of HTL process of primary sludge by the use of catalyst is a convenient pathway, when compared to other methods (alkali, water and acid pre-treatments) but with either a further post-refining step or with a change in the conditions for economic feasibility.

CRediT authorship contribution statement

Jacky Cheikhwafa: Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. **Esther Torrens:** Supervision, Resources, Project administration, Funding acquisition, Data curation, Conceptualization. **Christophe Bengoa:** Writing – review & editing, Validation, Supervision, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

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Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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