

# Hydrothermal Liquefaction of Biomass using Waste Material as Catalyst: Effect on the Bio-crude Yield and Quality

Benedetta de Caprariis, Martina Damizia, Lingyu Tai, Paolo De Filippis

Department of Chemical Engineering, Sapienza University of Rome

[benedetta.decaprariis@uniroma1.it](mailto:benedetta.decaprariis@uniroma1.it)

Hydrothermal liquefaction (HTL) is one of the most promising technologies to produce valuable compounds from biomass and waste. The use of water as solvent makes this process extremely convenient for high moisture feedstock and also environmentally sustainable. However, the obtained product, the bio-crude, is not ready to the end use, its oxygen content is quite high making the oil physically and chemically instable and thus difficult to handle and store. The use of heterogeneous catalysts and hydrogen producers can improve the product quality during the hydrothermal process being also easy to be separated and recirculated. In this work the use of reduced red mud acting as hydrogen producer is tested in the hydrothermal process of oak wood. Red mud is composed mainly by  $\text{Fe}_2\text{O}_3$  that was reduced with the char produced by HTL and by a simulated syngas which is obtained from char gasification. The reduced red mud was mixed with the biomass and fed into the HTL batch reactor with variable red mud biomass ratio. The reduction temperature was optimized in order to obtain zero valent Fe able to produce hydrogen reacting with water in HTL conditions. The tests were conducted at 330 °C with a reaction time of 10 min. The obtained bio-crude was characterized with elemental analysis. The results in terms of oil yield and quality were compared with those obtained with pure iron powder showing that red mud can be used successfully as hydrogen producer in HTL process and recycled after its reduction with char or syngas. The use of red mud leads to an increase of the oil yield of 20% with respect to the blank test and looking at the oil composition the hydrogenation effect is evident, the amount of hydrogen increases while the amount of oxygen decreases.

## 1. Introduction

The increasing interest towards biofuels and green chemical compounds has driven the development of renewable processes in this decade. Many renewable processes are now ready to be industrialized however the development of processes to produce liquid biofuels to be used in the transportation sector is not straightforward. Only ethanol and hydrocarbons from vegetable oils are produced in industrial scale plants and used as fuels. Liquid biofuels will be fundamental to respect the European Commission strategy which foresees zero  $\text{CO}_2$  emissions by 2050. While the road transportation sector can rely on the development of the batteries and of the hydrogen to be fed to fuel cells to lower the  $\text{CO}_2$  emissions, the aviation sector cannot abandon liquid fuels and thus alternatives to fossil ones have to be found. In this context hydrothermal liquefaction able to convert biomass and waste into bio-crude can be a viable solution. Continuous pilot scale plants are under development in the last years (Rizzo et al, 2020; Castello et al., 2018) . Subcritical HTL process works at medium temperature (250-350 °C) and high pressure (7-20 MPa) using water in subcritical liquid state as solvent. The advantages are linked to the presence of water which allows the use of high moisture feedstocks such as sludges, organic fraction of waste and others and which acts as solvent but also reagent into the process. Water, in fact, in the HTL conditions changes its properties, the dielectric constant and the viscosity decrease making it a perfect solvent for organic compounds and a good medium for mass transfer processes, furthermore its ionic product increases giving to water a catalyst function in acid/base catalysed organic reactions (Gallakota et al., 2018). However, the quality of the produced bio-crude is not acceptable, mainly due to its high oxygen content which leads to low heating value and also to high instability and high viscosity. The bio-crude up-grading to make the product suitable for its final use is usually made with high hydrogen pressure in a

hydrodeoxygenation reactor. To lower the amount of hydrogen needed in the up-grading and produce directly in the HTL a stable bio-crude which can be eventually stored and transported, the use of hydrogen producers and catalyst is mandatory. Many homogeneous hydrogen donors and catalysts such as formic acid, ethanol, NaOH,  $K_2CO_3$  and KOH have been used in HTL to increase oil yield and quality however it is impossible to recover them making the water a difficult waste to treat (Nagappan et al., 2021). The presence of hydrogen during the HTL is fundamental to increase the oil yield avoiding the repolymerization of the formed fragments into char and to make the oil more stable by the hydrodeoxygenation reactions. Heterogeneous hydrogen producers such as zero valent metals (ZVM) are good candidate to produce hydrogen into the HTL reactor, ZVM reacts with water to be oxidized producing active hydrogen. In authors previous work, it was demonstrated that Fe and Zn act as hydrogen donors increasing the oil yield and quality consistently (Tai et al, 2021). The use of pure metals can affect considerably the price of the process so it can be interesting to use as source of ZVM a waste stream. Red mud is a waste generated from the bauxite production rich in  $Fe_2O_3$  (more than 60 % depending on the type of red mud) and thus suitable to be used as substitute of Fe in HTL. Red mud was already employed in HTL as catalyst to enhance bio-crude yield and quality by few authors however its action as hydrogen producer was never explored (Rahman et al., 2021). Saral and Ranganathan (2022) utilized red mud as catalyst for the HTL of microalgae obtaining a considerable increase of oil yield of 30 %.

Goal of this article is to investigate the activity of red mud in oak wood HTL on the oil yield and quality, comparing the obtained results with those obtained with pure Fe. The tests are made in batch micro-reactor keeping constant the biomass to water ratio and the running temperature. The amount of red mud was varied in order to study the effected of their addition on the obtained products. A preliminary study to optimize the reduction conditions of the red mud with char and syngas was conducted. A possible scheme of the HTL process assisted by red mud including its recycling is proposed in the article. Two possibilities were studied for the red mud recovery, the first one implies the reduction with the char produced during the HTL, the other envisages a first step of gasification of the char residue to produce a syngas used to reduce the red mud. This last option will allow to lower the reduction temperature and recover energy.

## 2. Materials and methods

### 2.1 Red mud reduction

The red muds were analyzed with X-ray diffraction analysis in order to know their composition and the amount of  $Fe_2O_3$ . The reduction tests were conducted using HTL char and syngas as reductant agents at different temperatures and reaction times. The reduction with char was performed in a temperature range of 800-1000 °C for 4 hours while the reduction with a simulated syngas ( $N_2$  70 %, 15 % CO and 15 %  $H_2$ ) was performed at 650 °C for 1 hour. After all the reduction tests the samples were analyzed with X-ray diffraction.

### 2.2 HTL tests

The tests were conducted in batch microreactors (12 ml) using a biomass to water ratio of 5 and a temperature of 330 °C. The red mud particles were added into the reactor with variable amount 0.1 and 0.5 g. The reactor was heated in a sand bath till the reaction temperature and then 10 min of reaction time was considered. After the reaction the reactor was immediately quenched in cold water, the reactor was opened, and the gas were vented off. The water was separated by filtration and the oily phase extracted with acetone. The yields of the different phase were measured gravimetrically. The composition of the bio-crude was analyzed with an elemental analyzer. The red mud was recovered together with the char and was reduced to be reused. Tests with the recycled red mud were also performed. The results obtained with red mud were compared with results obtained from blank test and test using pure Fe as hydrogen producer.

## 3. Results and discussion

### 3.1 Red Mud reduction tests

From X-ray diffraction analysis the samples result to be composed by  $Fe_2O_3$  for 58 %, the other oxides present are  $Al_2O_3$  and  $SiO_2$ , small amounts of  $TiO_2$  and CaO were also detected (Table 1).

*Table 1: Red mud composition.*

Compound	% wt.
$Fe_2O_3$	58 %
$Al_2O_3$	13 %
$SiO_2$	15 %
$TiO_2$	6 %
CaO	8 %

In Figure 1 the XRD of the red mud samples reduced with char are reported. It is clear that at least a temperature of 900 °C is needed for the reduction of almost all the  $\text{Fe}_2\text{O}_3$  to Fe. The sample reduced at 800 °C is composed exclusively by magnetite while at 900 °C the peak related to Fe appears. At 1000 °C the  $\text{Fe}_2\text{O}_3$  is almost all converted in Fe. It is important to observe that after the HTL reaction the Fe is oxidized to  $\text{Fe}_3\text{O}_4$  thus less energy is required for its reduction with respect to the fresh red mud. The reduction tests performed using the simulated syngas as reducing agent reported that at 650 °C all the  $\text{Fe}_2\text{O}_3$  is converted to Fe.

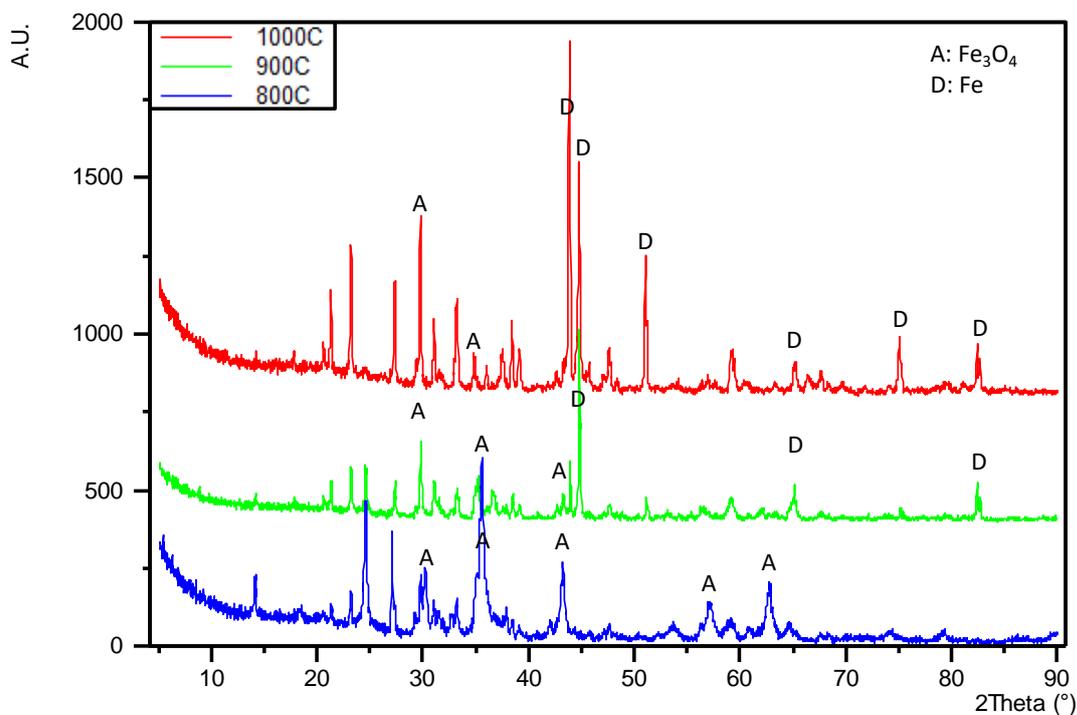


Figure 1: XRD of the char reduced red mud at the three different temperatures tested.

### 3.2 HTL tests

The results in terms of oil yield of the performed tests are reported in Figure 1. The amount of oil produced during the blank test is 32 % with respect to the initial biomass weight, using pure Fe the amount increases of 25 % while the red mud leads to an increase of 15 % and 20 % when amounts of 0.2 g and 0.5 g of the material is used, respectively. The results are very interesting if the goal is the substitution of the pure Fe with the red mud. The differences in the performances of these two materials are due mainly to the non-complete reduction of the Fe in the red mud which implies a lower production of hydrogen and to a non-homogeneity of the red mud powder. In fact, from the XRD results it appears clear that the amount of  $\text{Fe}_2\text{O}_3$  is not constant in the red mud waste, it can vary of 10 % and so the amount of Fe can be less than the expected one. The behaviour of red mud is expected to be similar to that of pure Fe: Fe is oxidized by water with the reaction  $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ , hydrogen is produced in atomic form and thus, before it is converted into molecular  $\text{H}_2$ , it results to be very active towards biomass fragment stabilization and hydrodeoxygenation reactions (Miyata et al., 2018).

HTL tests on the regenerated red mud were also performed and the results are reported in Table 2. Using the syngas as reducing agent the obtained results are almost the same than those obtained using fresh red mud while a little decrease in the oil yield is registered when the material is reduced with char. This behavior is due to the non-complete reduction of red mud with char at 900 °C, to have a complete reduction 1000 °C are needed, while with the simulated syngas the reduction is complete.

Table 2: Oil yield obtained with the recycled red mud.

Reductant	Oil yield (%)
Char	36.3 %
Syngas	37.2 %
Fresh	37.5 %

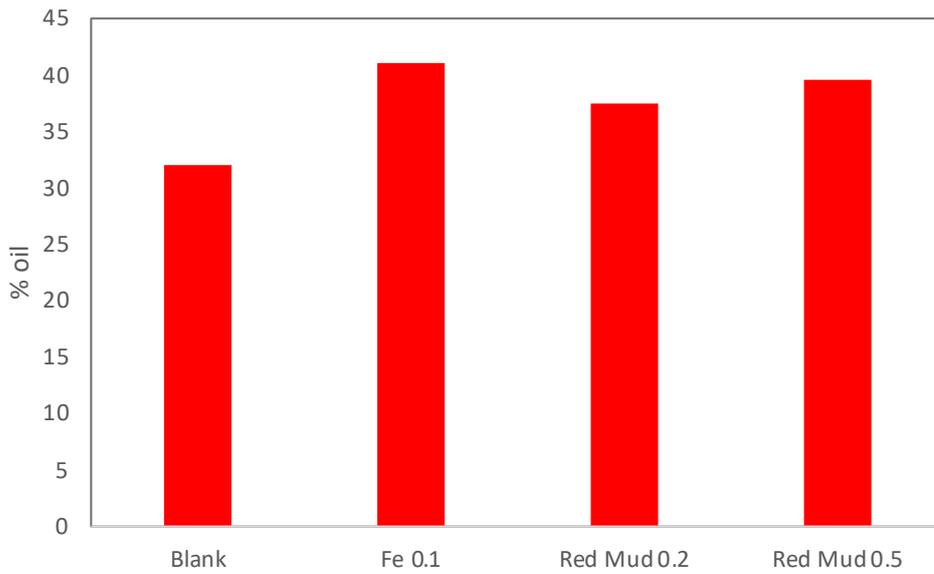


Figure 2: Bio-crude yields obtained by the performed tests.

Two different regeneration methods are envisaged. The process schemes are reported in Figure 3. In the first the solid residue, containing exhausted red mud and char is sent to a reduction reactor having a temperature of 900 °C (Figure 3a). The second method consists in sending the HTL residue to a gasification reactor, fed with water vapor where the char is converted into a syngas which is then sent to a second reactor where the red mud is reduced at 650 °C (Figure 3b). The red mud to be integrated in every cycle is about 10 % of the total.

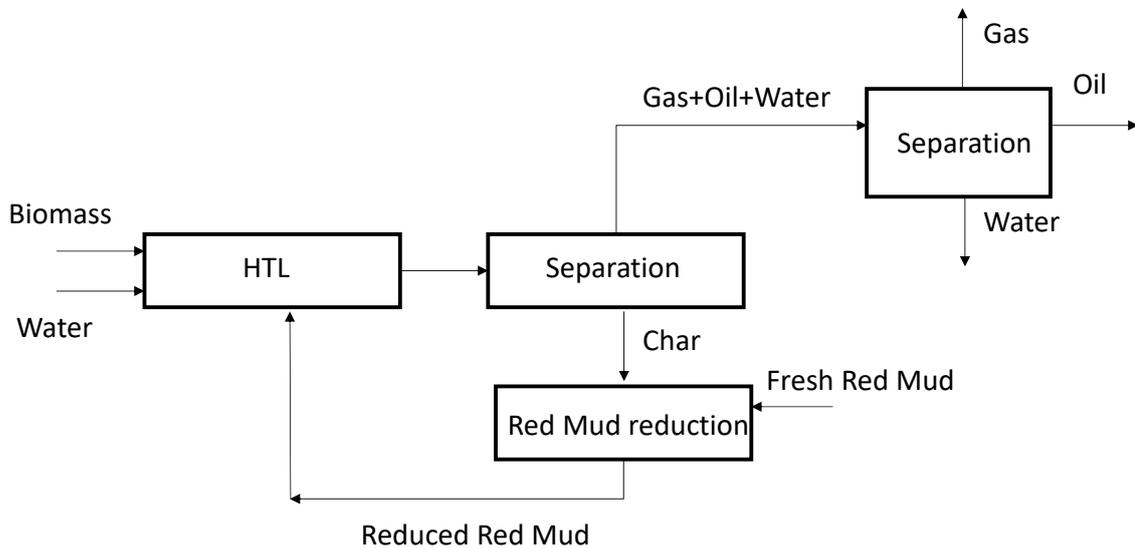


Figure 3a: Two possible processes for the HTL of biomass using red mud as hydrogen producer.

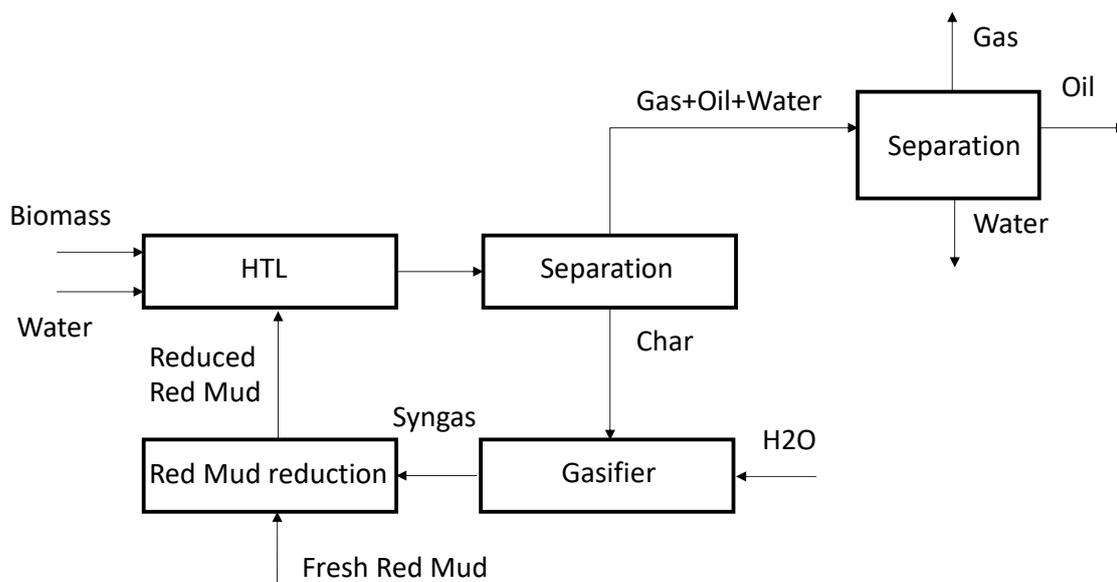


Figure 3b: Two possible processes for the HTL of biomass using red mud as hydrogen producer.

Elemental analysis of the bio-crudes was performed in order to understand the effect of the addition of red mud on the oil quality. The results are reported in Table 3. The HHV was calculated with the Dulong formula while the ER value represents the energy recovery index calculated by Eq. 1.

$$ER (\%) = \% \text{ bio - crude} * HHV (\text{bio - crude}) / HHV (\text{biomass}) \quad (1)$$

Table 3: Elemental analysis of the bio-crudes.

	H/C	O/C	HHV (MJ/kg)	ER (%)
Blank	0.92	0.25	27.84	44.12
Iron	1.05	0.23	28.88	55.29
Red Mud (0.2 g)	1.04	0.24	28.12	51.24
Red Mud (0.5g)	1.04	0.23	28.57	54.93
Red Mud (Char)	1.02	0.24	27.96	48.12
Red Mud (Syngas)	1.04	0.24	28.35	52.15

As expected with respect to the blank test the addition of Fe leads to an improvement of the produced bio-crudes. The H/C value increases quite significantly, from 0.92 to 1.05 for the bio-crude produced with the addition of pure Fe. The addition of Red Mud also enhances the oil quality leading to a lower oxygen content which means a more stable oil with higher HHV. The Energy Recovery index for the tests with red mud is higher than 50 % meaning that more than 50 % of the biomass energy is recovered in the oil fraction. From the results it is clear that the reduction with syngas is more efficient as already determined by the XRD analyses.

#### 4. Conclusions

This work aims to demonstrate the feasibility of using a waste stream as hydrogen producer in oak wood HTL in order to obtain bio-crude with higher yield and better quality. The production of liquid fuels from HTL is still not ready for industrial application due to the low quality of the produced oil and to the high production cost. The use of a waste stream such as red mud as hydrogen producer/catalyst brings several advantages, the HTL becomes a waste consuming process, the cost of the catalyst is zero and the quality of the oil is improved. The tests demonstrate that the addition of red mud, used as active hydrogen producer, leads to an increase of the bio-crude yield of 20 %. The bio-crude produced owns better quality, with lower oxygen content and higher HHV. The red mud particles were also recovered with the char and reduced with syngas and char and then reused again in a HTL process. The activity of the reused material is still acceptable, the reduction with syngas in the chosen conditions is preferable since it allows the complete reduction of Fe and thus a better activity towards hydrogen production.

**References**

- Castello D., Pedersen T.H., Rosendahl L.A., 2018, Continuous Hydrothermal Liquefaction of Biomass: A Critical Review, *Energies*, 11, 3165.
- Gallakota A.R.K., Kishore N., Gu, S., 2018, A review on hydrothermal liquefaction of biomass, *Renewable and Sustainable Energy Reviews*, 81, 1378–1392.
- Miyata Y., Sagata K., Yamazaki Y., Teramura H., Hirano Y., Ogino C., Kita Y., 2018, Mechanism of the Fe-Assisted Hydrothermal Liquefaction of Lignocellulosic Biomass, *Industrial & Engineering Chemistry Research*, 57, 14870-14877.
- Nagappan S., Bhosale R.R., Nguyen D.D., Chi N.T.L., Ponnusamy V.K., Woong C.S., Kumar G., 2021, Catalytic hydrothermal liquefaction of biomass into bio-oils and other value-added products – A review, *Fuel*, 285, 119053.
- Rahman T., Jahromi H., Poulami R., Adhikari S., Hassani E., Oh T., 2021, Hydrothermal liquefaction of municipal sewage sludge: Effect of red mud catalyst in ethylene and inert ambiances, *Energy Conversion and Management*, 245, 114615.
- Rizzo A.M., Dell’Orco S., Miliotti E., Chiamonti D., 2020, Design, Commissioning And Start-Up of a New Hydrothermal Liquefaction Continuous Pilot Unit, *Chemical Engineering Transaction*, 80, 367-373.
- Saral J.K., Ranganathan, P., 2022, Catalytic hydrothermal liquefaction of *Spirulina platensis* for biocrude production using Red mud, *Biomass Conversion and Biorefinery*, 12, 195-208.
- Tai L, de Caprariis B., Scarsella M., De Filippis P., Marra F., 2021, Improved Quality Bio-Crude from Hydrothermal Liquefaction of Oak Wood Assisted by Zero-Valent Metals, *Energy and Fuels*, 35, 10023-10034.