

## TREATED RED MUD AS CATALYST AND IRON-BASED HYDROGEN SOURCE FOR THE HYDROTHERMAL LIQUEFACTION OF PINEWOOD

Martina Damizia, Department of Chemical Engineering, Sapienza University of Rome  
Martina.damizia@uniroma1.it

Martina Damizia, Department of Chemical Engineering, Sapienza University of Rome  
Maria Paola Bracciale, Department of Chemical Engineering, Sapienza University of Rome  
Serena Monaco, Department of Chemical Engineering, Sapienza University of Rome  
Paolo De Filippis, Department of Chemical Engineering, Sapienza University of Rome  
Benedetta de Caprariis, Department of Chemical Engineering, Sapienza University of Rome

Key Words: Red Mud, Lignocellulosic biomass, hydrothermal liquefaction, bio-crude

Red mud (RM), the primary solid waste generated by the aluminum industry, is rich in iron oxides ( $\text{Fe}_2\text{O}_3$ , 20–30%) and also contains significant amounts of other metals, including aluminum, titanium, sodium, calcium, and silicon. Many of these elements are known to act as heterogeneous catalysts in hydrothermal liquefaction (HTL) processes. In this study, red mud (RM) is investigated as a sustainable heterogeneous catalyst and a low-cost iron source for the hydrothermal liquefaction (HTL) of pinewood, with the objective of enhancing both bio-crude yield and quality. In its role as an iron source, RM is utilized to promote in situ hydrogen generation through oxidation reactions between metallic iron and water under HTL conditions. This  $\text{H}_2$  can enhance the hydrogenation and deoxygenation of biomass-derived intermediates, improving the quality of the bio-crude. At the same time, the catalytic contribution of the other metal oxides present in RM is evaluated to understand their role in promoting key HTL reactions. The study ultimately aims to clarify whether the beneficial effects of RM derive primarily from hydrogen generation or from the catalytic synergy of its mixed metal oxides, while also proposing a sustainable route for the valorization of this industrial waste. The HTL tests were carried out in 12 mL batch reactors, heated in a sand bath at 330 °C for a reaction time of 10 minutes. The amount of red mud used in each experiment was adjusted to ensure a constant Fe content of 0.05 g per gram of biomass. RM activity was investigated after different pretreatments: reduced red mud (RRM), thermally treated red mud (CRM), acid-washed red mud (ARM), acid-washed followed by a thermal treatment (ACRM), and acid-washed RM followed by a reduction treatment (ARRM). The reduction step was carried out at 900 °C using the hydrochar produced from HTL as reductant aiming to minimize the HTL byproducts. A schematic of the red mud treatment pathways is shown in Figure 1. All materials were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, and inductively coupled plasma optical emission spectrometry (ICP-OES). The characterization results revealed that thermal treatments mainly enhance the CaO formation while the acid washing significantly enhances the RM surface area. These chemical and morphological changes of RM influence both the availability of iron for in-situ  $\text{H}_2$  production and the overall catalytic activity of the material in HTL processes.

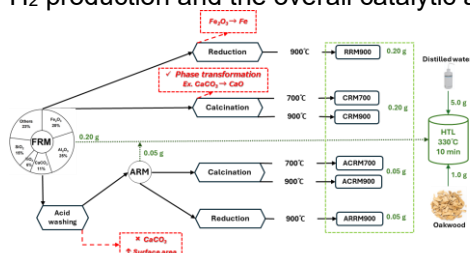


Figure 1: Red Mud pretreatment pathways and Red Mud composition.

The metal leaching from RM into both the aqueous and oily phases was assessed to evaluate the stability of the catalyst under reaction conditions and to quantify the potential presence of contaminants in the bio-crude. The results show that both the reduction treatment and the acid washing have a significant impact on the bio-crude yield and quality. Maximum bio-crude yields of 48wt% were obtained using RRM and ARRM. The increase in specific surface area resulting from the acid washing treatment positively affected the quality of the bio-crude, confirming the higher accessibility of iron sites and the enhanced rate of hydrogen production. In particular, the highest higher heating value (HHV) of 30 MJ/kg was achieved in the bio-crude produced using ARRM. However, the analysis on the metal leaching demonstrated that when iron is in form of metal, significant amounts of this metal are found in the oil (about 500 ppm). In conclusion, RM, especially in its reduced form, proved to be an effective and low-cost hydrogen producer and catalyst for the HTL process, enabling a 30% increase in bio-crude yield and a 20% improvement in HHV. This approach allows for the simultaneous valorization of two waste streams, significantly contributing to climate change mitigation through improved resource efficiency and waste-to-energy conversion.