



Full Length Article

Novel reductive extraction process to convert the bio-oil aqueous acid fraction into fuels with the recovery of iron from wastes



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HIGHLIGHTS

- Bio-oil aqueous acid fraction efficiently extracts iron of the red mud waste.
- Fe_{extracted}/aqueous fraction is converted into Fe/C composites valuable for the steel industry.
- The organics are decomposed to a potential fuel gas mixture consisting of H₂/hydrocarbon.

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ABSTRACT

In this work, bio-oil waste AAF (aqueous acid fraction) was used to recover iron from red mud (RM) waste by a reductive extraction process. In this process, extraction of iron from RM with AAF is followed by thermal treatment of AAF-Fe_{extracted} mixture, leading to the reduction of the Fe_{extracted} with the production of Fe/C composites, a valuable feedstock for the steel industry, and a gas fuel fraction. Analyses by IR, UV-vis, ESI-MS, CHN, potentiometric titration, TG, TG-MS, TOC and ¹H NMR showed AAF can efficiently extract Fe³⁺ present in RM waste. After extraction, the mixture AAF-Fe_{extracted} was treated at 400, 600 and 800 °C to decompose mainly into two fractions: solid (30–40 wt%) and gas (60–70 wt%). Mössbauer and XRD analyses of the solid fraction showed the presence of reduced iron phases, e.g. Fe²⁺, Fe⁰ and iron carbide, with 76% of carbon. TG-MS analyses of gas fraction showed the production of H₂ (58 mol%), C₁–C₄ (19 mol%) and CO_x (23 mol%), with potential application as a fuel.

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1. Introduction

Bio-oil is produced by flash pyrolysis of lignocellulosic biomass at relatively high temperatures, e.g. 500–650 °C, in the absence of oxygen. The three fractions produced in this process are bio-char, bio-oil and bio-gas, with typical yields of ca. 15–25, 60–75 and 5–15%, respectively. In this process, significant amounts of water are also formed, which is dragged with bio-oil producing two distinct immiscible liquid phases: bio-oil (approximately 80%) and the aqueous acid fraction (ca. 20%) [1–4].

Aqueous acid fraction (AAF) is a dark liquid comprising approximately 75–85% of water and 15–25% of organic compounds [5–7] as small carboxylic acids (C₁–C₃), and other oxygenated com-

pounds such as aldehydes and ketones [8–10]. This aqueous fraction is considered a waste and a drawback in pyrolytic process [6]. Different studies have investigated several pyrolysis conditions in order to minimize AAF's production [6,7,11] and few works in literature have studied its possible applications. Some of the applications investigated involve the mixture of AAF with bio-oils to be used as liquid fuel for gas turbines [8], AAF as raw material for the production of lipids by yeast [12] and steam reform of AAF to produce hydrogen [13–15].

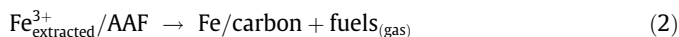
In this work, aqueous acid fraction (AAF) from bio-oil was tested in a process of iron reductive extraction from a Fe rich waste, i.e. red mud (RM). In this process, named “2W2P” (two wastes two products), AAF is used to solubilize iron from RM waste. In a posterior step of thermal treatment, the organic matter present in acid fraction carbonizes and reduces the extracted iron to form a Fe/C composite and a gas fraction with potential application as fuel (Eqs. (1) and (2); Fig. 1).

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Fig. 1. Schematic representation of the 2W2P (two wastes two products) process.



Red mud (RM) waste is produced in Bayer process of bauxite conversion to aluminum at 90 million ton/year worldwide [16]. Several applications have been studied for this waste, such as production of carbon nanotubes and nanofibers composites [17,18], indirect storage of natural gas [19], reduction of Cr(VI) [20], and also bio-oil upgrade [21,22]. As RM contains high concentrations of Fe, e.g. 40 wt%, the idea of iron recovery is very attractive. However, due to the strong interaction and dispersion of the iron oxide with impurities (Al_2O_3 and SiO_2 particles), physical separation is not possible. More complex processes have been used to recover iron and titanium from RM, such as smelting reduction of RM and direct reduction roasting followed by magnetic separation [23,24]. Attempts to convert the RM into a coagulant by Fe^{3+} dissolution in concentrated hydrochloric acid have also been suggested [25,26]. However, these processes are limited by the high costs.

Hereon, a reductive extraction process is described, where Fe^{3+} from RM is extracted and complexed with organic molecules and then thermally treated, leading to the formation of two products: reduced Fe dispersed in a carbon matrix (with potential use in steel industry) as well as hydrogen and small hydrocarbons with potential application as fuel.

2. Materials and methods

2.1. Characterizations

Potentiometric titrations of AAF were carried out with 0.5 mL of sample in 35 mL of KOH 0.091 mol L^{-1} . HCl 0.097 mol L^{-1} was used as titrant and the potential during titration was measured in a PHS-3C Bench pHmeter. Total organic carbon analysis was carried out in a Shimadzu TOC-V CPH. Thermogravimetric analyses (TG/DTA) were carried out in a Shimadzu TGA-60 ($10^\circ \text{C min}^{-1}$ under air or nitrogen flow). UV-vis spectra were obtained in a Shimadzu UV 2550 equipment. ^1H NMR spectra were recorded at room temperature in a Bruker DPX-200 Avance spectrometer, using d-chloroform as solvent. Infrared spectra (IR) were recorded in a Bruker ALPHA equipment, in the wavelengths between 4000 and 400 cm^{-1} , with 64 scans per sample. Elemental analyses were performed in a Perkin Elmer 2400 equipment. Mass spectrometry with electrospray ionization (ESI-MS) was performed in a Thermo Electron spectrometer, model LCQ Fleet, in the positive mode. Powder X-ray diffraction (XRD) data were obtained in a Rigaku equipment model Geigerflex using $\text{Cu K}\alpha$ radiation, scanning from 10 to 80° (2θ) at a scan rate of 4° min^{-1} . Atomic absorption analyses were performed in a Hitachi-Z8200 equipment. Transmission Mössbauer spectroscopic experiments were carried out in a CMTE spectrometer model MA250 with a $^{57}\text{Co/Rh}$ source at room temperature using $\alpha\text{-Fe}$ as reference. Raman spectra were recorded in a Bruker Senterra equipment, using 532 nm laser with 5 mW. Thermogravimetric-mass spectrometry (TG-MS) analyses were

performed in a NETZSCH equipment model STA 449 F3, coupled to a mass spectrometer NETZSCH Aëolos model QMS 403C, using argon as carrier gas.

2.2. Acid extraction experiments

Acid extraction experiments were carried out in sealed flasks, with a mixture comprised of 5 mL of aqueous acid fraction and 500 mg of red mud. The flasks were kept at 100°C in an oil bath for 8, 24, 48 and 72 h. Other reactions were carried out with 5 mL of aqueous acid fraction with different amounts of red mud (50–500 mg) at 100°C for 48 h. After reactions, the mixtures of aqueous acid fraction and red mud were centrifuged for an hour to separate the silica/alumina byproduct, and the supernatant was removed. In order to determine the content of iron extracted from red mud, the supernatant was mineralized with concentrated nitric acid at 80°C and analyzed by atomic absorption, as previously described.

2.3. Thermal treatment of $\text{Fe}_{\text{extracted}}^{3+}$ /aqueous acid fraction (AAF)

The product obtained after 48 h of reaction of aqueous acid fraction and red mud (AAF/Fe) was thermally treated at different temperatures, e.g. 400, 600 and 800°C . The treatments were carried out with 1 g of AAF/Fe under N_2 atmosphere (50 mL min^{-1}), in a quartz tube into a horizontal furnace (BLUE M. Lindberg) at a heating rate of $10^\circ \text{C min}^{-1}$, keeping the final temperature for 1 h. These treatments lead to the formation of a black magnetic solid, a liquid and a gas fraction.

3. Results and discussion

The aqueous acid fraction (AAF) used in this work is a slightly viscous liquid containing high concentration of acidic organic molecules. Characterization of AAF by potentiometric titrations showed negative pH with acid concentration of ca. 3 mol L^{-1} . Total Organic Carbon analysis indicated carbon concentration of $154 \text{ g}_{\text{Carbon}} \text{ L}^{-1}$ (ca. 15 wt%). TG/DTA analysis of aqueous acid fraction presented an endothermic event related to water loss (approximately 70 wt%), followed by an exothermic weight loss of 30% related to degradation/oxidation of organics in AAF (Fig. S1). UV-vis analysis (Fig. S2) indicated the presence of bands centered at 218 and 264 nm related mainly to small concentrations of benzene and naphthalene derivatives [27]. ^1H NMR spectrum of AAF (Fig. 2), which is soluble in d-chloroform, exhibited peaks in the range of 1.0–2.5 ppm related to H bonded to aliphatic carbon atoms ($\gamma\text{-CH}_3$, $\beta\text{-CH}_3$, CH_2 and $\gamma\text{-CH}$ or further from an aromatic ring) [28]. The peaks between 3.5 and 5.0 ppm are related to H bonded to C–O, and the small peaks between 6.5 and 7.0 ppm indicate the presence of H bonded to aromatic species [29,30].

IR spectra obtained for the dried AAF_{powder} (powder obtained after evaporation of water, Fig. S3) showed the presence of bands related to oxygenated groups, e.g. O–H stretching around 3500 cm^{-1} combined with the bands in 1780 cm^{-1} (C=O) and 1290 cm^{-1} (C–O), likely related to phenolic and carboxylic groups. The bands around 1650 and 1450 cm^{-1} can be attributed to C=C stretching of aromatic structures.

Elemental analysis of the dried AAF_{powder} showed ca. 49% C, 6% H and likely 45% oxygen, suggesting the presence of highly oxygenated molecules. ESI-MS analysis indicates the presence of three main groups of molecules containing up to C_{10} , $\text{C}_{10}\text{--}\text{C}_{30}$ and some signals related to molecules higher than C_{30} (Fig. S4).

Fe rich waste used in this work, red mud (RM), showed by XRD the presence of hematite ($\alpha\text{-Fe}_2\text{O}_3$, PDF 1-1053), silica (SiO_2 , PDF 1-424), alumina (Al_2O_3 , PDF 10-414), calcium oxide (CaO, PDF

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