SYNERGISTIC CO-PROCESSING OF RED MUD WITH PYROLYSIS BIO-OIL: FROM NEUTRALISATION TO CATALYSIS

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Abstract

Pyrolysis bio-oil is obtained by the rapid heating of ligno-cellulosic biomass to ~ 770 K for a few seconds with the exclusion of oxygen. It is composed of carboxylic acids and a blend of ketones, aldehydes and alcohols. By co-processing bio-oil and Red Mud at low mass ratios, bio-oil can be viewed as a renewable biomass sourced "reagent" for the conversion of Red Mud to a neutralised and reduced carbon containing magnetic gray-black material that may allow full re-vegetation with sodium tolerant plants, be acceptable as a soil additive or could serve as an iron ore binder. At high bio-oil/Red Mud ratios the complex blend of iron, aluminium, silicon, titanium, and sodium oxides typically present in Red Mud can – contingent on the type and quality of the bio-oil used – act as a multi-functional "sacrificial catalyst" to upgrade the bio-oil to a usable fuel while again being transformed into a non-hazardous carbon-rich solid.

Introduction

Arguably the most problematic quality of Red Mud bauxite processing residue is its high alkalinity.[1] While a neutralisation with anthropogenic mineral acids (e.g., H_2SO_4) is in principle chemically possible, the scale of production required and the associated economic and ecologic cost and impact would likely completely negate the benefits of such an approach. An alternative source of sustainably sourced acid is pyrolysis bio-oil derived from agricultural (wheat and rice straw, corn stover, seed husks, etc.) or forestry and orchard (wood chips, bark, brush cuts, etc.) residues that globally are available in quantities in excess of 200×10^9 t/a.[2] Depending on the mass ratio of bio-oil to Red Mud and the type, actual composition and quality of bio-oil employed this approach can potentially also yield an upgraded bio-oil of lower oxygen and higher energy content usable as a low-grade fuel with the metal-oxides in the Red Mud acting as the upgrading catalysts. Here we give an overview on the synergistic co-processing of acidic bio-oil and other biomass derived feedstocks such

as levulinic acid with Red Mud and discuss the underlying chemical principles and the perspectives for and challenges to a large-scale implementation.

Pyrolysis Bio-Oil

Production of pyrolysis bio-oil

Pyrolysis bio-oil is produced by rapidly heating (> 1000 °C/s) pelletised air-/pre-dried lignocellulosic biomass to ~500 °C for 1-2 seconds followed by condensation of the resulting gaseous products into a brown-black liquid (*"liquefied wood"*) with simultaneous formation of a carbon-rich bio-char (directly usable as a fertiliser and soil additive) and non-condensable gases (CO, H_2, CH_4, etc.) that can be burned to power the process making it potentially self-sustaining.[3]

Composition and chemical properties

Pyrolysis bio-oil is characterised by a high water (up to 40 wt%), carboxylic acid (up to 15 wt% of HCOOH/HOAc) and phenolics content as well as a complex and self-reactive blend of ketones, aldehydes and alcohols. The oil is highly acidic with a typical *p*H ≈ 2. Chart 1 gives an overview of the chemical compound classes present.[4]

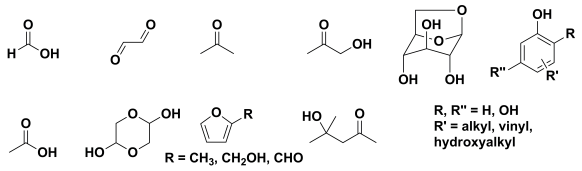
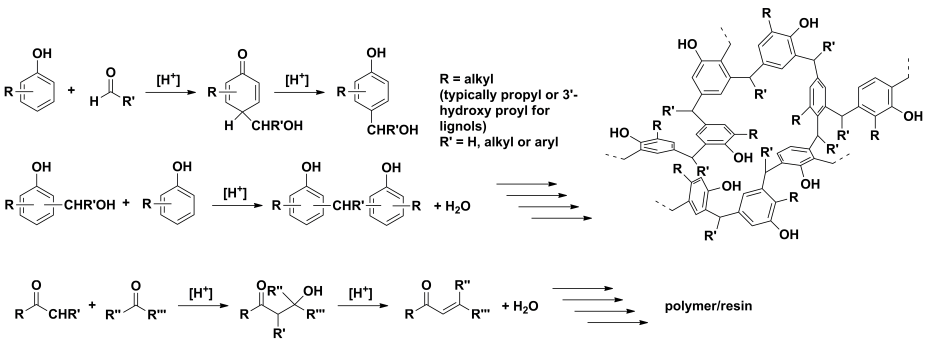


Chart 1: Components typically present in pyrolysis bio-oil

The oil is corrosive, and through acid-catalysed aldol and phenol condensations unstable against uncontrolled polymerisation to a resin and aqueous phase separation (Scheme 1).[5]



Scheme 1: Reactions leading to the re-polymerisation and resin formation of bio-oil

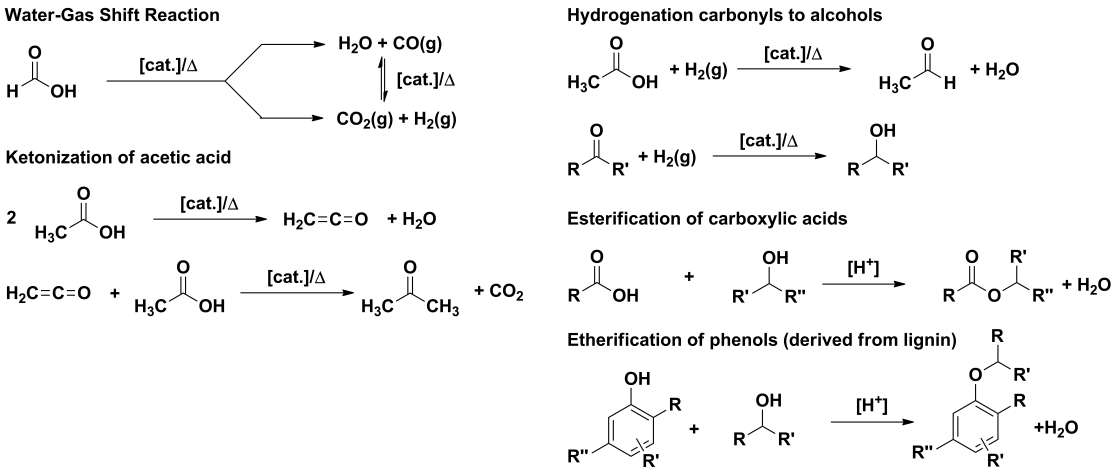
In combination with its low energy density this makes the oil unsuitable as fuel "as is", requiring a catalytic upgrading process. This constitutes a major and unresolved challenge, as the aggressive chemical nature of the oil rapidly destroys typical hydro-deoxygenation and reforming catalysts by coking, fouling and leaching of the active metal (e.g., Ni, Pd, Pt, Ru), which to date has prevented the large-scale use of pyrolysis bio-oil as a source of fuel.[6] Recognising that the complex blend of iron, aluminium, silicon, titanium, and sodium oxides typically present in Red Mud can in fact be viewed as a multi-functional hydrogenation, ketonisation and Brønstedt/Lewis acid/base catalyst and that the material has an effectively negative value, we began a study on the use of Red Mud as a "once-through" *sacrificial catalyst* (a deliberate contradiction in terms) for this purpose. At the same time the high acidity of the bio-oil also immediately suggested its use as a sustainably sourced stoichiometric reagent for the neutralisation of alkaline Red Mud. With both uses, that are only distinguished by the relative mass ratio of bio-oil to Red Mud and process parameters (time, temperature, externally supplied hydrogen), the Red Mud is transformed into to a neutralised non-hazardous, partially reduced magnetic material of high carbon content with concomitant and chemically necessary generation of a phase separated aqueous by-product phase.

Co-Processing of Pyrolysis Bio-Oil with Red Mud

High bio-oil/red mud ratios: catalytic upgrading reactions

Under aqueous acidic and reducing conditions (autogenic or externally supplied hydrogen gas) at elevated temperatures (T > 325 °C, 0-20 MPa H_2) the Fe_2O_3 present in Red Mud is reduced by CO or H_2 gas to iron sub-oxides and/or carbides that along with traces of Cr or other trace metals can act as hydrogenation, water-gas-shift reaction (WGSR) and Fischer-Tropsch (FT) catalysts. Simultaneously, TiO_2 can act as an acid ketonisation catalyst, while the other main components SiO_2, Al_2O_3, CaO, Na_2O are Brønstedt/Lewis acid/base catalysts or serve as promoters with possible additional synergistic effects between the individual metal oxide components. Scheme 2 summarises the reactions catalysed by Red Mud along with the subsequent ester- and etherification of the alcohols generated, which together can effect a complete removal of free carboxylic acids, a rejection of oxygen as water or CO_2 and the hydrogenation of reactive C=C and C=O double bonds. This results in an increase of the energy density of the oil and its stabilisation against polymerisation and resin formation. The principle viability of this approach was initially demonstrated by the quantitative conversion of blends of acetic and formic acid (2-3 mol % of Fe_2O_3 w.r.t. acid substrate, 325 °C, 4 h),[7] with the latter acting as an internal source of hydrogen. This was successfully extended to levulinic acid as a biomass derived substrate,[8] that by ketonisation and hydrodeoxygenation is converted into

C9 products in up to 75 % yield (2,5,8-nonatrione and derivatives) that could directly serve as a feedstock for refineries producing conventional fuels.[9] In this case the catalytic activity of the Red Mud increases with reuse. Using a light bio-oil fraction obtained by pyrolysis of hardwood sawdust, it was also possible to obtain an upgraded oil with a *p*H > 5 and higher heating value of 34 kJ/g (compared to *p*H = 2.8 and hhv = 12 kJ/g for the untreated oil) in 15-25 % yield.[10]



Scheme 2: Upgrading reactions in the bio-oil catalysed by Red Mud

The success of the bio-oil upgrading reactions is however highly dependent on the age, type and quality of the oil used and also very sensitive to the process parameters employed. Notably slow heating rates lead to polymerisation of the oil before the Red Mud is reduced and becomes active as a catalyst (T > 300 °C) yielding no liquid organic products, but only a carbonaceous solid mixed with catalyst along with the always produced aqueous by-product phase. A study to solve this problem is presently under way in our laboratories by developing a process in which bio-oil is rapidly injected into a reactor at temperature and pressure (T > 350 °C, 5.5 MPa H_2) containing pre-activated Red Mud catalyst prepared in situ, resulting in very high heating rates and an anticipated higher relative kinetic competence of the iron suboxide catalysed hydrogenation and TiO_2 catalysed ketonisation upgrading reactions vs the undesired acid/base catalysed polymerisation reactions.

Low bio-oil/red mud ratios: neutralisation

In all reactions with acidic biomass-derived liquids, Red Mud is converted into a neutral gray magnetic material, which prompted us to also explore the use of bio-oil as the limiting reagent for Red Mud neutralisation at inverted bio-oil/Red Mud mass ratios. Here the quality of the bio-oil is not of concern, in fact a higher, normally undesirable, acid content is in fact advantageous. An overall vision for such a process is given in Figure 1. Using a Design of Experiment approach we systematically

optimised an example process using a low quality bio-oil (~ 40 wt% water , *p*H = 2.8).[11] Co-processing Red Mud with this bio-oil in a stainless steel reactor at 349 °C and a bio-oil/Red Mud mass ratio of 1.53 for 30 minutes generates 3-8 MPa of autogenic pressure of CO_2 and steam (by micro-GC; vented to atmosphere), < 0.1 mass equivalents (relative to Red Mud used) of an aqueous phase with *p*H = 6 ± 0.5 and a sodicity of 17 ± 1 mg/mL and ~ 1.25 mass equivalents of a magnetic gray solid that reacts close to neutral (*p*H < 7.8) when extracted with water.

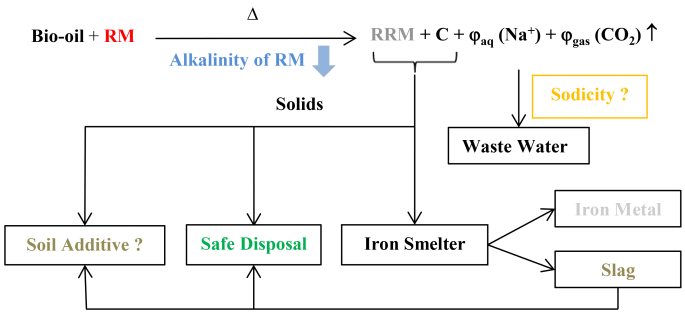


Figure 1: Proposed overall process for the neutralisation of Red Mud by pyrolysis bio-oil (RRM = carbon-rich Reduced red Mud)

The source of neutralising acidity in this solid is believed to be a combination of carbonic acid from CO_2 forming carbonates and carboxylic acid functions from oxidation of the surface of the biomass derived carbon deposited into the matrix. Table 1 compares key properties of this material (RRM) to those of virgin Red Mud.[12]

Table 1: Key properties of Red Mud before and after co-processing with pyrolysis bio-oil

Material	*p*H[a]	% C [wt%]	χ_{lf} [10^{-5} m^3 kg^{-1}][b]	Sodicity [Na mg/g]	Visual Appearance
Red Mud	> 12	< 0.5	0.0149	51.4	
Reduced Red Mud	7.74 ± 0.13	25.81 ± 0.62	5.52 ± 0.29	28.9	

[a]Filtered solution from 0.5 g RM or RRM sonicated in 5 mL of water. [b]Magnetic susceptibility at 0.46 kHz.

By powder XRD and/or Mössbauer spectroscopy the material contains – in addition to unreduced hematite (Fe_2O_3) and goethite (FeO(OH)) – varying proportions of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3, by in situ re-oxidation of magnetite) as well as smaller amounts of wuestite (FeO) and iron carbides (Fe_xC_y) along with mixed Fe(Al/Si) oxides. It has an overall carbon content of 25 ± 1 wt% (by TGA) and a magnetic susceptibility (measured at 0.46 kHz) of 5-6 χ_{lf} (10^{-5} m^3 kg^{-1}). Unfortunately all attempts to effect an enrichment of the iron oxides by magnetic separation failed, as the magnetic components are homogeneously dispersed through the oxide matrix

of the reduced material (RRM). However, a magnetic separation rather than filtration of the RRM from the aqueous phase is possible. Notable is the lower specific sodicity of the RRM, which is caused by both leaching of some of the soluble Na^+ into the aqueous by-product phase and by the relative weight increase of the solid by the biomass derived carbon deposited into the material. Within the limits of our laboratory's capabilities, the process appears to be scalable. It is thus conceivable that the substantially lower *p*H and lowered sodicity may allow the use of RRM as a soil additive or even re-vegetation with sodium tolerant plants, which will however require systematic field trials, which are beyond the expertise and capabilities of the authors. The carbon content of the material is anticipated to also play a positive supportive role in this respect. Another conceivable application of the RRM is its use as an iron ore binder or iron ore additive, which however again would require larger scale metallurgical trials beyond the authors' capabilities. A further issue is the fate of the aqueous by-product that due to its slightly acidic *p*H caused by the presence of traces of residual carboxylic acids and phenols will likely require treatment and stewardship before its ultimate release into the environment.

Cost and economic considerations

Beyond the process development and scale-up issues and field/metallurgical tests required as discussed above, the actual viability of the co-processing approach will depend on taking into account a series of cost factors the detailed analysis of which is beyond the scope of this paper:

a) CapEx for construction of a co-processing facility.
b) The availability of biomass in geographic proximity to Red Mud deposit sites and the cost of its transportation to the sites (ideally by barge/ship or rail).
c) The cost of pyrolysis bio-oil production, which including the cost of point a) is currently estimated to be 50-100 US $/tonne,[13,14] but could be substantially lower depending on location, particular in (sub-) tropical environments, and economies of scale. In this context the thermal energy required for the production of the oil (T ≈ 500 °C) could in principle be furnished by concentration of solar radiation.
d) The amount of upgraded bio-oil obtained usable as a fuel, which could be sold or used directly on-site to operate the process making it potentially self-sustaining w.r.t to fuel and energy requirements and thus act as a cost off-set.
e) The price of iron ore (mining and shipment) and coal, if RRM is to be used in metallurgic applications.
f) The unknown, but potentially very high costs of the long-term stewardship of Red Mud deposit sites and resulting liabilities to aluminium producers or ultimately tax payers,[15] if the original operators cease to exist as legal entities or default through bankruptcy.

Outlook and Challenges

The use of acidic pyrolysis bio-oil as a co-processing material for Red Mud is a previously untried and unexplored approach to the Red Mud legacy problem that proposes to use a renewable biomass derived resource as a means of remediation. While demonstrated in principle at the laboratory scale, further progress and an actual possible implementation will be contingent on the engagement of all stakeholders involved in the generation, management and regulation of Red Mud.

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