# Catalysts from Waste: Red Mud as a Heterogeneous Catalyst for Bio-oil Upgrading

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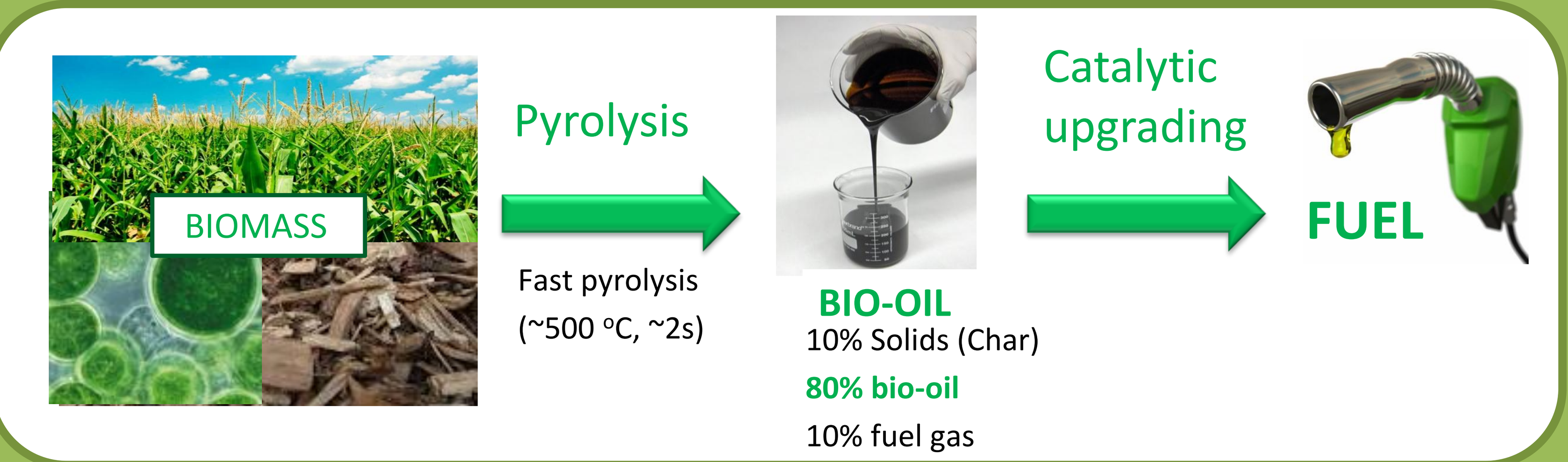
## Introduction:

- Fast pyrolysis (~500 °C, ~2s) of advanced generation biomass produces high yields (~75%) of bio-oil, a potential replacement for gasoline and diesel transportation fuels.
- High oxygen content, acidity and chemical instability
- Chemical upgrading required to produce commercial grade fuel.[1]

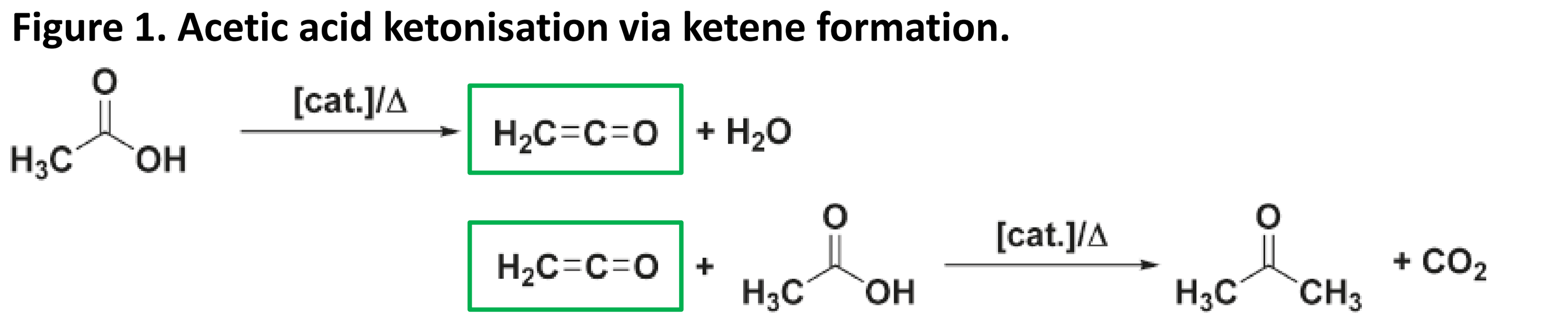



### Ketonisation of carboxylic acids present within pyrolysis oils:

$$RCOOH + RCOOH \rightarrow RCOR + CO_2 + H_2O$$

- An efficient route to increasing the energy density and pH of bio-oil with water and carbon dioxide as benign by-products.[2]

Figure 1. Acetic acid ketonisation via ketene formation.




## Experimental Goal:

- Red mud[3] is an industrial waste by-product of alumina production.
- Potential low cost, non-toxic catalyst for bio-oil upgrading.
  - For every ton of alumina, ~2 tons of red mud are produced.
    - 30-40% $Fe_2O_3$
    - 15-25% $Al_2O_3$
    - 10-20% $SiO_2$
    - 3-8% $TiO_2$
    - 1-6% CaO
    - 5-10% $Na_2O$

A cheap multifunctional acid/base, hydrogenation, water-gas shift reaction (WGSR), and Fischer-Tropsch catalyst ($Fe_xO_y$, $TiO_2$, and $SiO_2$)

- Aims:
- Understand the catalytic activity of each red mud component.
- Do synergistic effects exist? Can these may be exploited to improve the catalysts properties.
- Achieved by preparation and catalytic testing of a range of synthetic red mud analogues of increasing complexity.

**The reactor:** packed bed, continuous flow reactor for vapour phase ketonisation of acetic acid, a common acidic component of bio-oil.

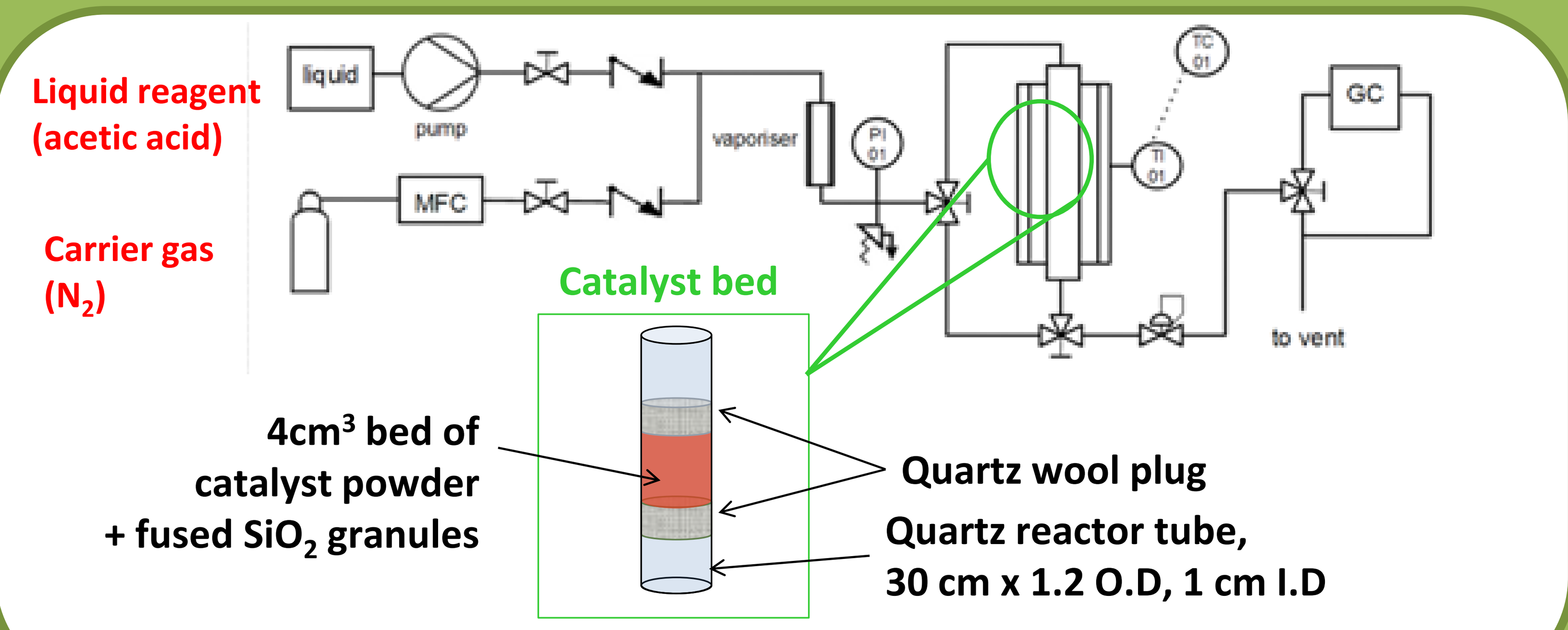
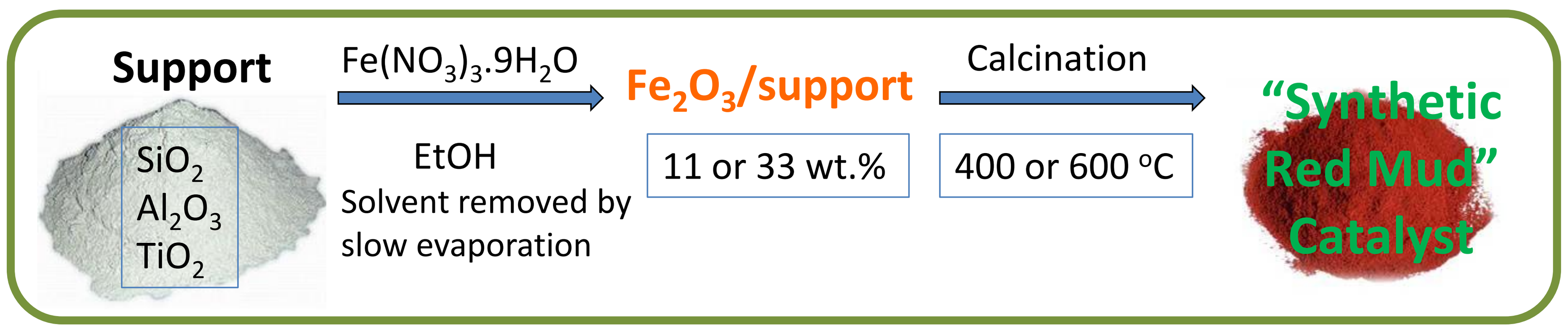



Figure 2. Schematic of the continuous flow reactor for ketonisation.

**Catalyst Preparation:** A series of materials based on the major components of red mud were prepared by wet impregnation of an iron salt followed by slow evaporation and calcination.




Characterisation was performed by XRD (phase determination, particle size), porosimetry (BET surface area, pore size) and XPS and XRF (elemental composition).

## Results and Discussion:

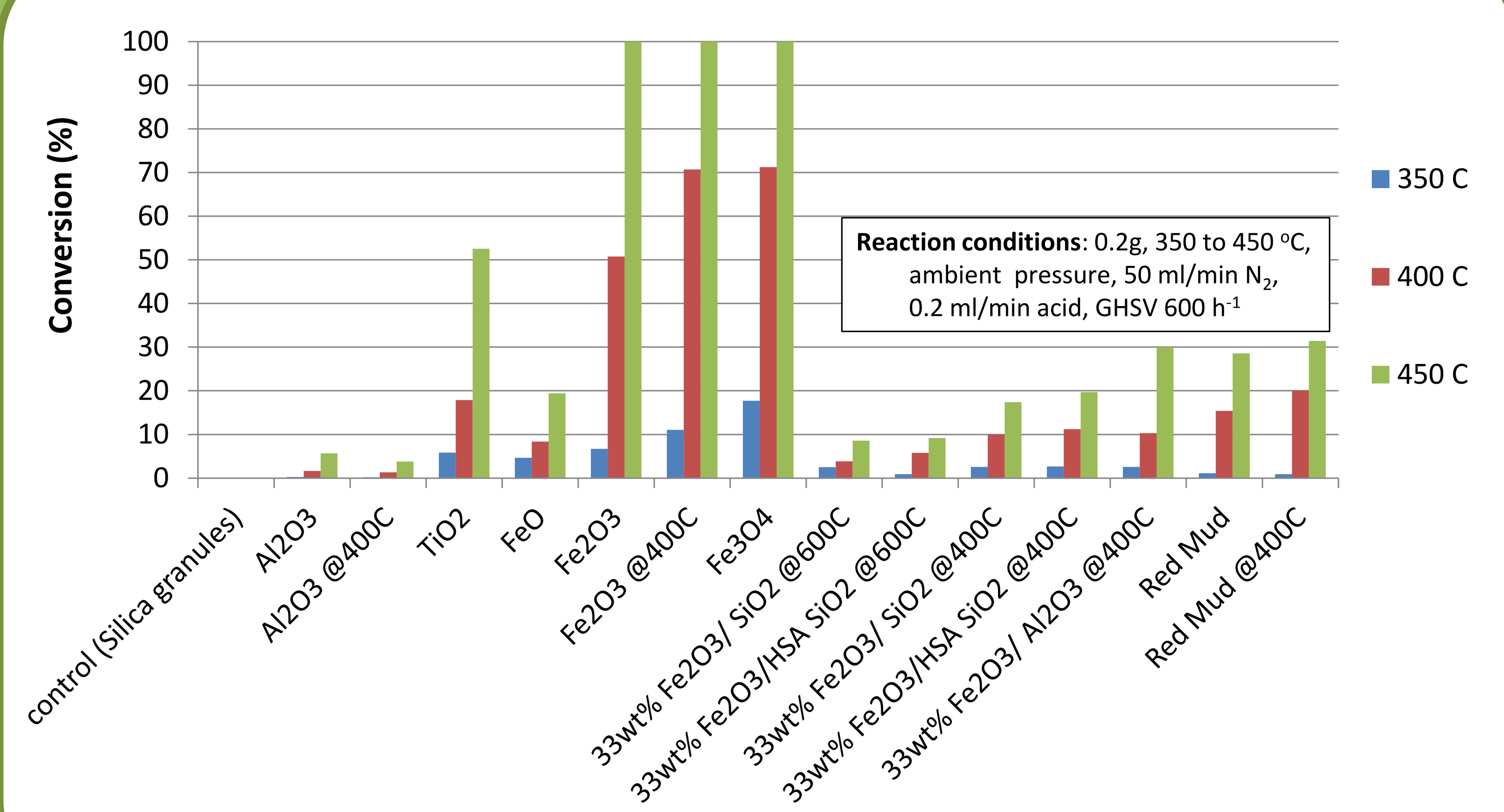



Figure 3. Steady state conversions of acetic acid using a range of catalysts at 3 reaction temperatures.

- During ketonisation, $Fe_2O_3$ is reduced to $Fe_3O_4$ (XRD analysis).
- Tests comparing FeO, $Fe_3O_4$ and $Fe_2O_3$ (Fig. 4) suggest $Fe^{2+}$ sites, in FeO and $Fe_3O_4$, are more active for ketonisation than $Fe^{3+}$ sites, in $Fe_2O_3$ and $Fe_3O_4$.
- FeO gives lowest conversion due to low surface area (1.5 $m^2$)
- FeO gives a higher rate per $m^2$ of iron oxide.

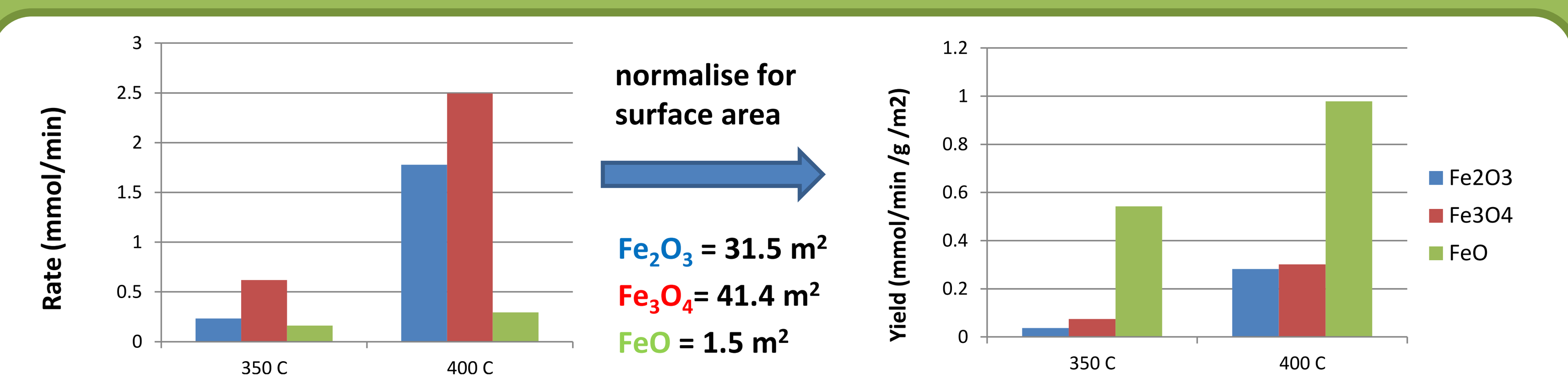



Figure 4. Rates of acetic acid conversion and space time yields for iron oxide of different Fe oxidation state.

- Iron oxide one of the most active phases within red mud (Fig. 3) but red mud is a more active $g^{-1}$ $m^{-2}$ than pure $Fe_2O_3$ (Fig. 5).
- Indicates the mixture may benefit from synergistic effects.
- These effects will be the subject of further study along with development of iron oxide-based catalysts using dopants not associated with red mud.

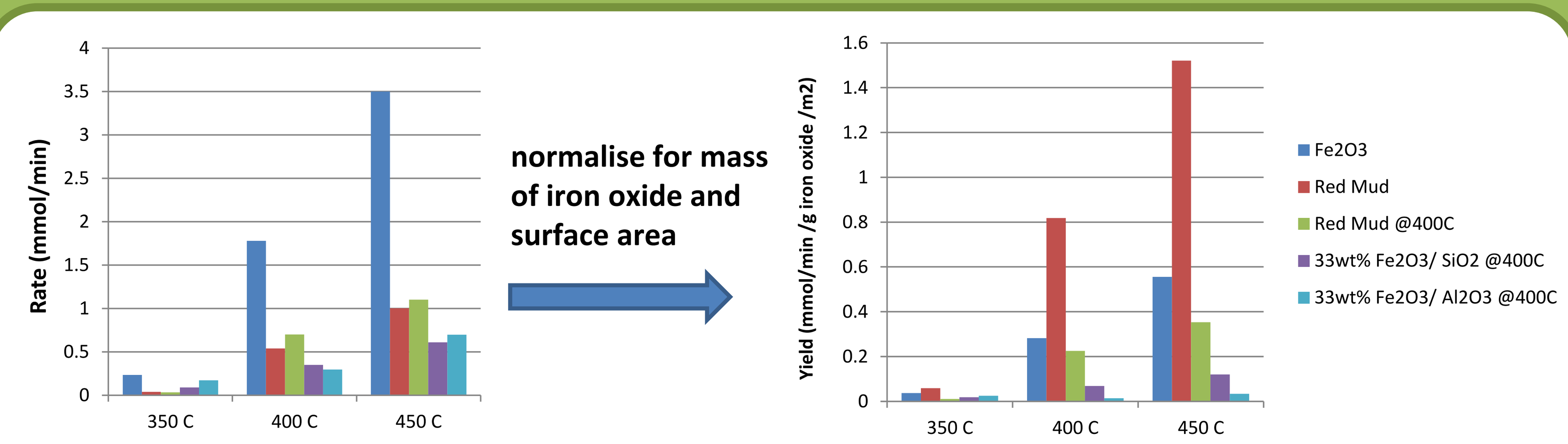



Figure 5. Rates of acetic acid conversion and space time yields for $Fe_2O_3$, red mud waste and synthetic red mud.

**References: 1.** Bridgwater, A. V. *Biomass and Bioenergy* **2012**, *38*, 68. **2.** Pham, T. N.; Sooknoi, T.; Crossley, S. P.; Resasco D. E. *ACS Catal*. **2013** *3*, 2456. **3.** Karimi, E.; Freitas Teixeira, I.; Passos Ribeiro, L.; Gomez, A.; Lago, R. M.; Penner, G.; Kycia, S. W.; Schlaf, M. *Catalysis Today* **2012**, *190*, 73.