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CORFU2022
9th International Conference on Sustainable Solid Waste Management
15-18 JUNE 2022

Catalytic Pyrolysis of Empty Fruit Bunch over Metal-modified Rice Husk Ash

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Outline

- Introduction
- Materials and Method
- Results and Discussion
- Conclusions
- References

Introduction

- In Southeast Asia, **palm oil industry** is one of the top agricultural industries in the region
  - Large amount of EFB generated has been leading to **disposal problems** and thus, EFB is often simply discarded via **burning**

(Fresh Fruit Bunch)

(Empty Fruit Bunch)

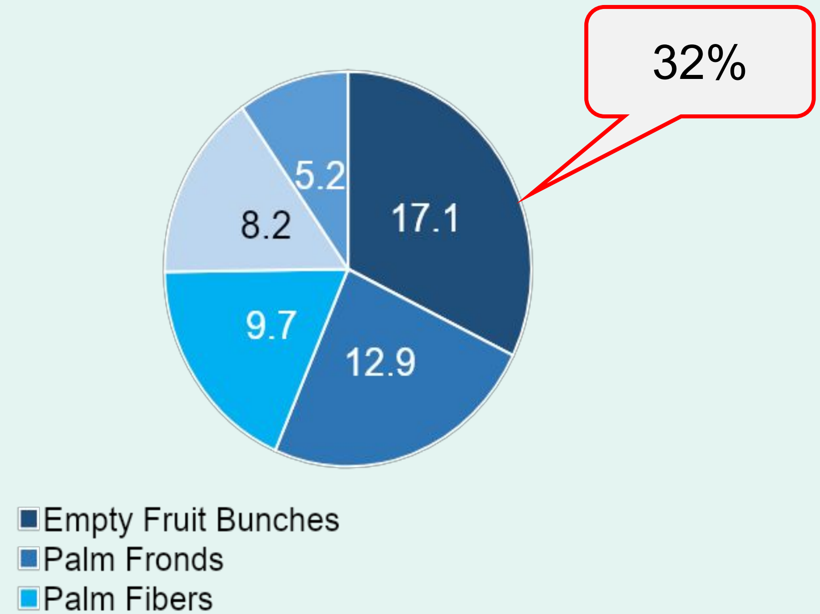


Figure 1. By-products from palm oil production in Malaysia (million tons per year) [1]

Introduction

- **Pyrolysis** – **thermal degradation** of material at high temperatures, usually between 300 °C and 700°C, in the **absence of oxygen** [2].
  - Products in the form of bio-oil, char and gas.

Transportation Fuel

Boiler Fuel

Gasoline Enhancers

- **Benefits** of using biomass
  - ✔ Low-cost
  - ✔ Renewable (does not take a long time to replenish like fossil fuels)
  - ✔ For agricultural residues – offers an alternative to conventional disposal method like burning
  - ✔ Bio-oil contains lower sulphur content [3]

- Still has its **limitations**
  - Low yield of bio-oil produced
  - Bio-oil contains high oxygen content – from compounds such as alcohols, acids and ketones [4]
  - Low heating value compared to fossil fuels [3]

Introduction

- To **improve** biomass pyrolysis – addition of **catalysts**
    - **Reducing** oxygen contents via decarboxylation, decarbonylation and aromatization
- Common catalyst used in pyrolysis – **Hydrogen-exchanged Zeolite Socony Mobil-5 (HZSM-5)**
    - **Unique structure** and **strong acidity** □ **promotes** the formation of hydrocarbons [5]
- Catalysts can also be **metal-modified** [4]
    - **Nickel** – to promote **aromatization**
    - **Iron** – **prevent polymerization** of monocyclic aromatic hydrocarbons (MAHs) that may lead to coking.
- Catalyst synthesis requires:

Silica source | **Alumina source** | **Organic template** | **Alkali compound**

- **Synthetic materials** are often used [6].

Introduction

- A step to make catalyst synthesis **greener** – use alternative materials
- **Rice husk ash (RHA)**
  - Rich in **silica** (94 wt%) after calcination [7]
  - Suitable as a silica source for catalyst synthesis

(Rice Husks) *(Calcined Rice Husk Ash)*

- **Lack of studies** on the **application** of RHA-sourced catalysts in pyrolysis [8-9].
- **Objective** of this study: to investigate the application of **RHA-sourced catalysts** on catalytic pyrolysis of EFB via fixed bed reactor
  - The synthesized catalyst will also be **metal-modified using metals Ni and Fe**

Materials and Method

1. Feedstock Preparation

(Empty Fruit Bunch)

Dried

Ground

Sieved

(EFB feedstock)

2. Catalyst Preparation

a). Silica from RHA

(Rice Husks)

(Pyrolyzed in N_2 at 900 °C, 1 hour)

(Rice Husk Ash)

(Calcined in air at 900 °C, 1 hour)

(Calcined Rice Husk Ash)

Materials and Method

2. Catalyst Preparation cont.

b). **RHA Catalyst** synthesis [9]

RHA

Sodium Aluminate

Sodium Carbonate Decahydrate

TPABr

Teflon-lined Autoclave Reactor: 150 °C, 72 hours

Washed with deionized water and filtered

Laboratory Oven:
Dried overnight at 110 °C

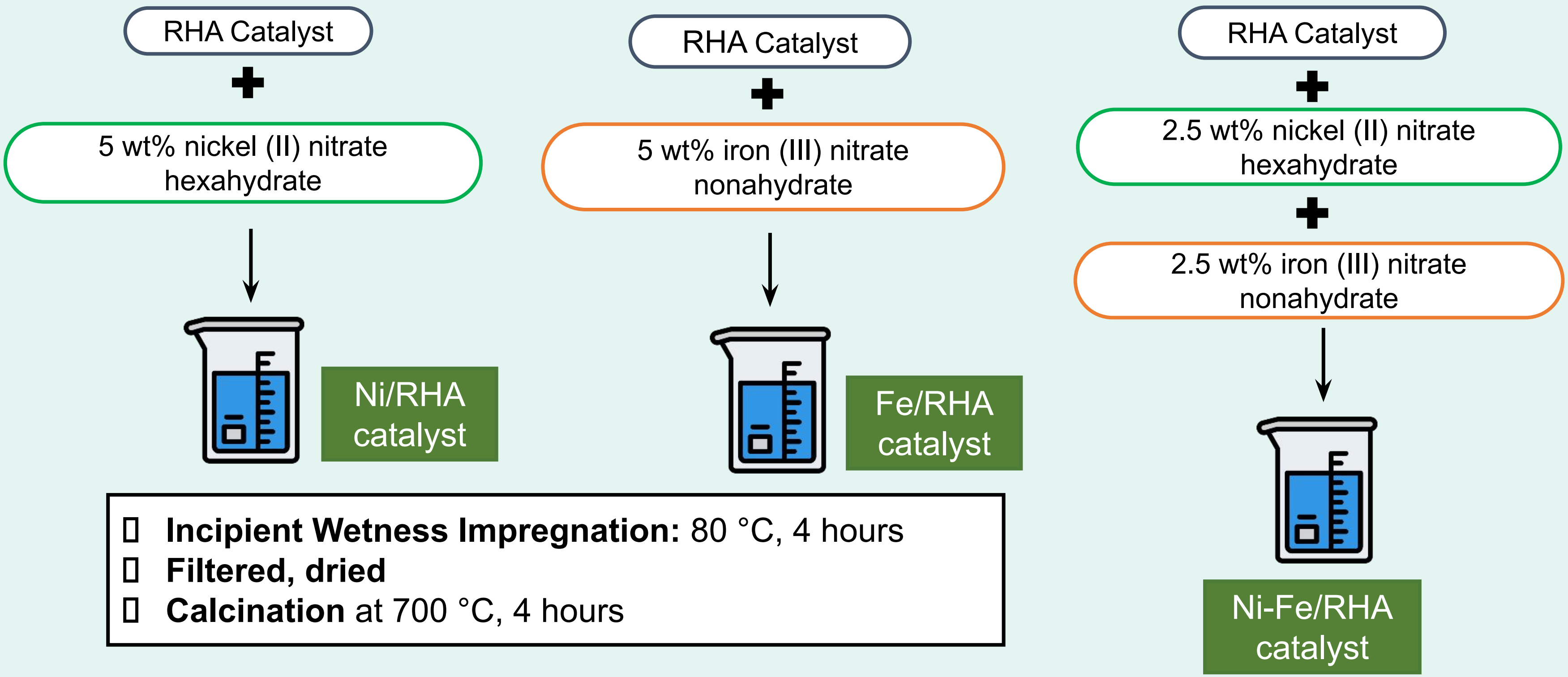
Muffle Furnace:
Calcined at 700 °C, 4 hours

Final RHA catalyst

Materials and Method

2. Catalyst Preparation cont.

c). **Ni/RHA**, **Fe/RHA** and **Ni-Fe/RHA** Catalyst synthesis

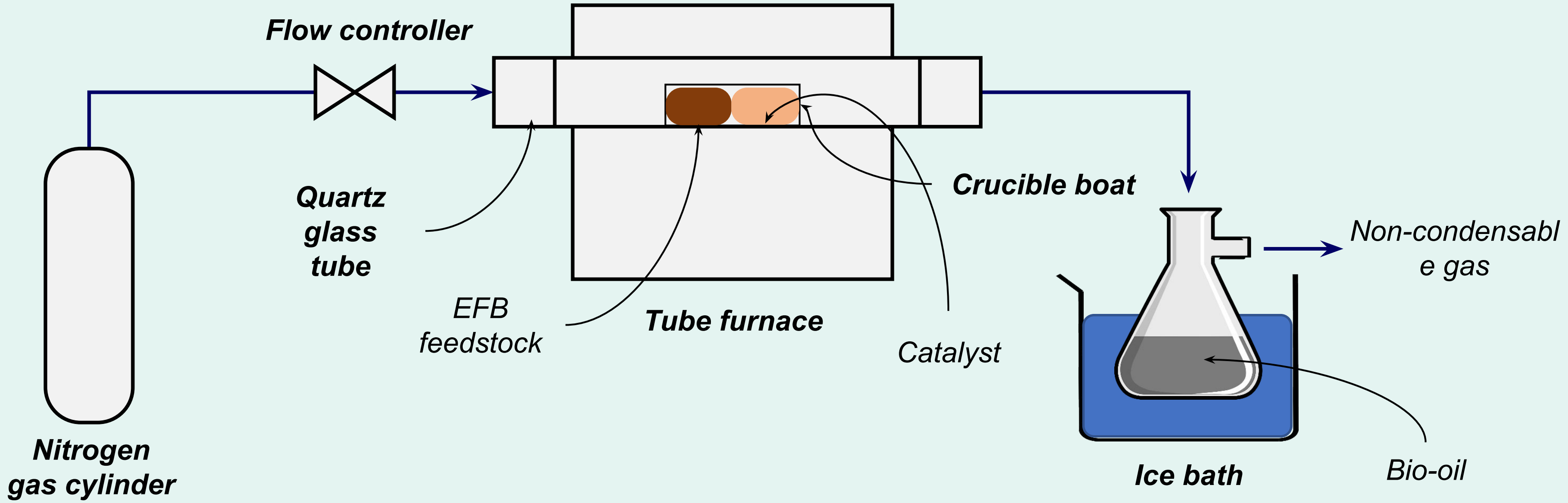


4. RHA Catalyst and Metal-modified RHA Catalysts Characterization

- X-Ray Diffraction (XRD)
- Field Emission Scanning Electron Microscopy (FESEM)
- Fourier Transform Infrared Spectroscopy (FTIR)

Materials and Method

5. Catalytic Co-Pyrolysis of EFB and HDPE via fixed-bed reactor



Operating conditions:
Nitrogen flow **50 mL/min**
Pyrolysis temperature **500°C**
Fixed **feedstock-to-catalyst** ratio of **1:1**

Pyrolysis runs:

- **Non-catalytic** pyrolysis
- Catalytic pyrolysis, over **RHA** catalyst
- Catalytic pyrolysis, over **Ni/RHA** catalyst
- Catalytic pyrolysis, over **Fe/RHA** catalyst
- Catalytic pyrolysis, over **Ni-Fe/RHA** catalyst

Results and Discussion

1. Phase Analysis via X-Ray Diffraction

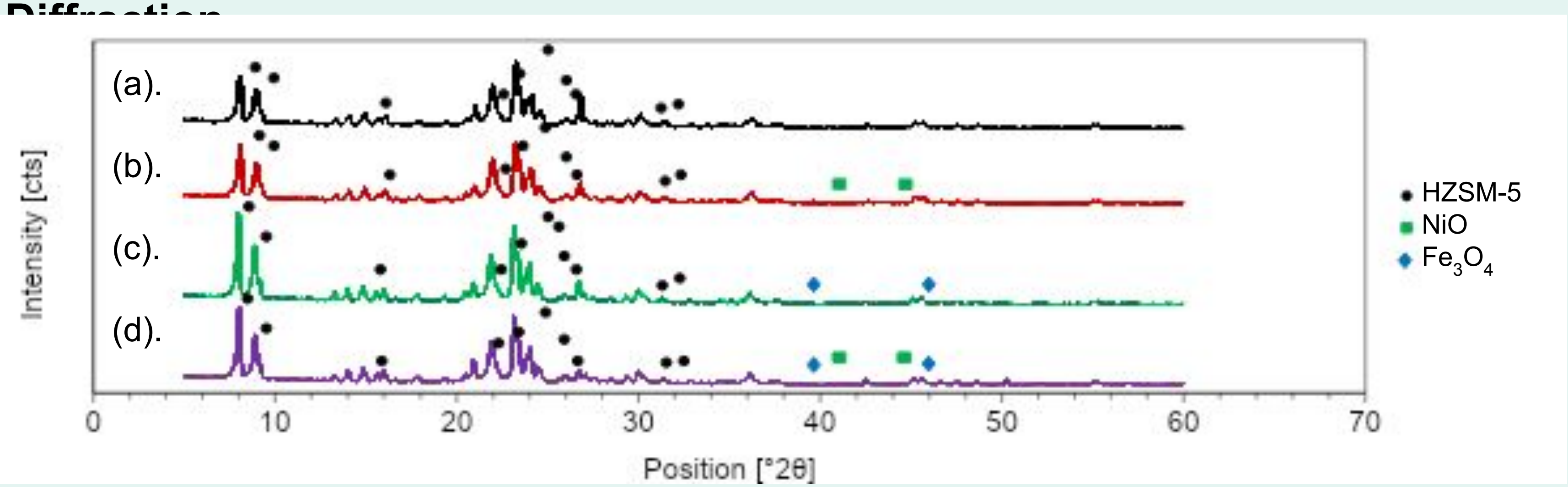


Figure 1. XRD pattern of (a). RHA catalyst, (b). Ni/RHA, (c). Fe/RHA and (d). Ni-Fe/RHA

RHA catalyst:

- Peaks observed at the 2θ position of **8.0° - 9.0°**, **13.0° - 17.0°**, and **21.0° - 23.0°**
  - **Characteristic peaks** of HZSM-5 [9].
- **Intense peaks indicating high** crystallinity.

Metal-modified RHA catalysts:

- No significant effects on XRD patterns with metal modification.
- Due to very low amounts of metal loaded [10].
- **No amorphous phase** observed from aggregation of particles – **metal oxide** species **highly dispersed**

Results and Discussion

2. Surface Morphology Analysis via Field Emission Scanning Electron Microscopy (FESEM)

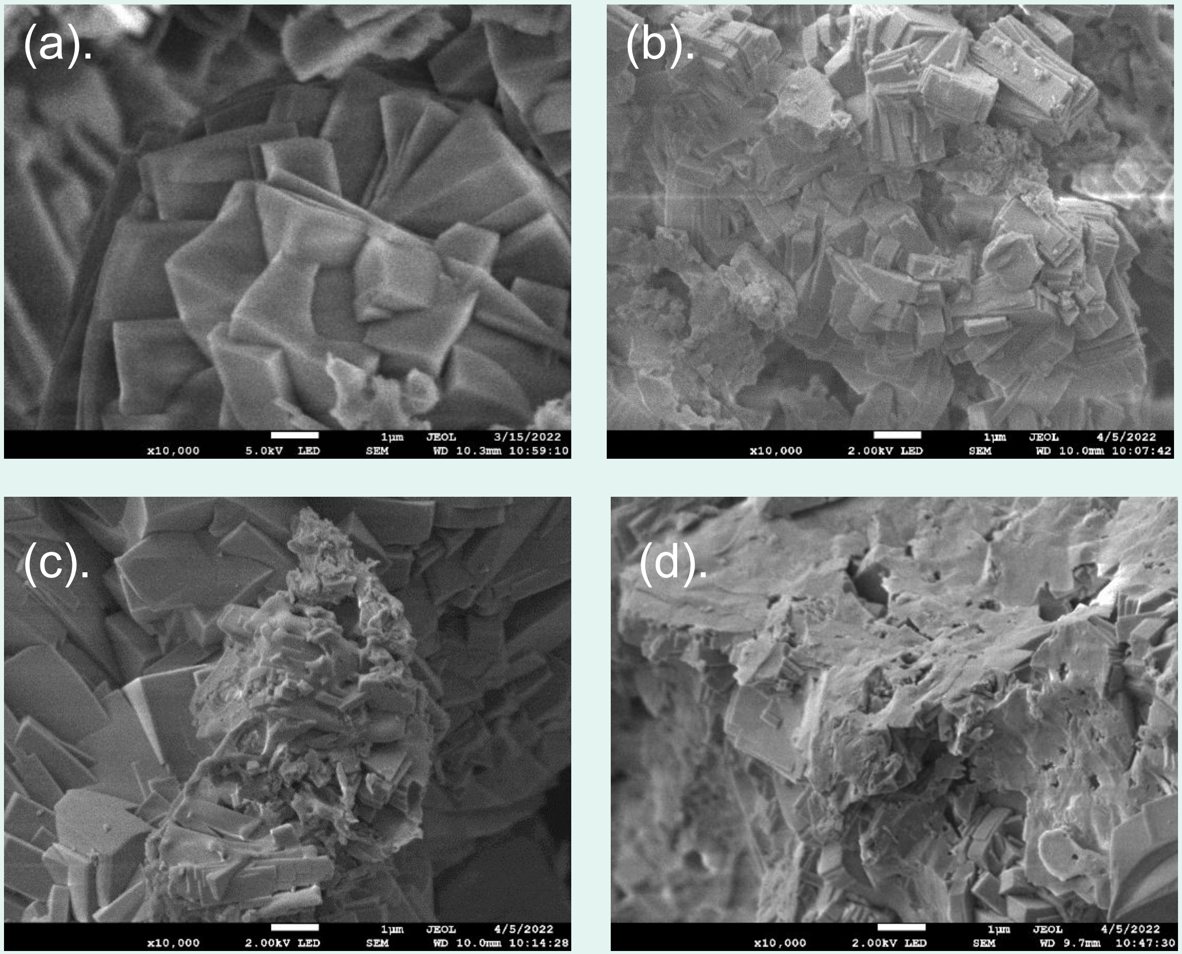


Figure 2. FESEM images of (a) RHA catalyst, (b) Ni/RHA, (c) Fe/RHA and (d) Ni-Fe/RHA

RHA catalyst:

- Rectangular.
- High crystalline structure.

Metal-modified RHA catalysts:

- Deposits seen on the surface – **metal oxide species**.
- Layering observed for Ni-Fe/RHA catalyst.

Results and Discussion

3. Framework Vibration Analysis via Fourier Transform Infrared Spectroscopy (FTIR)

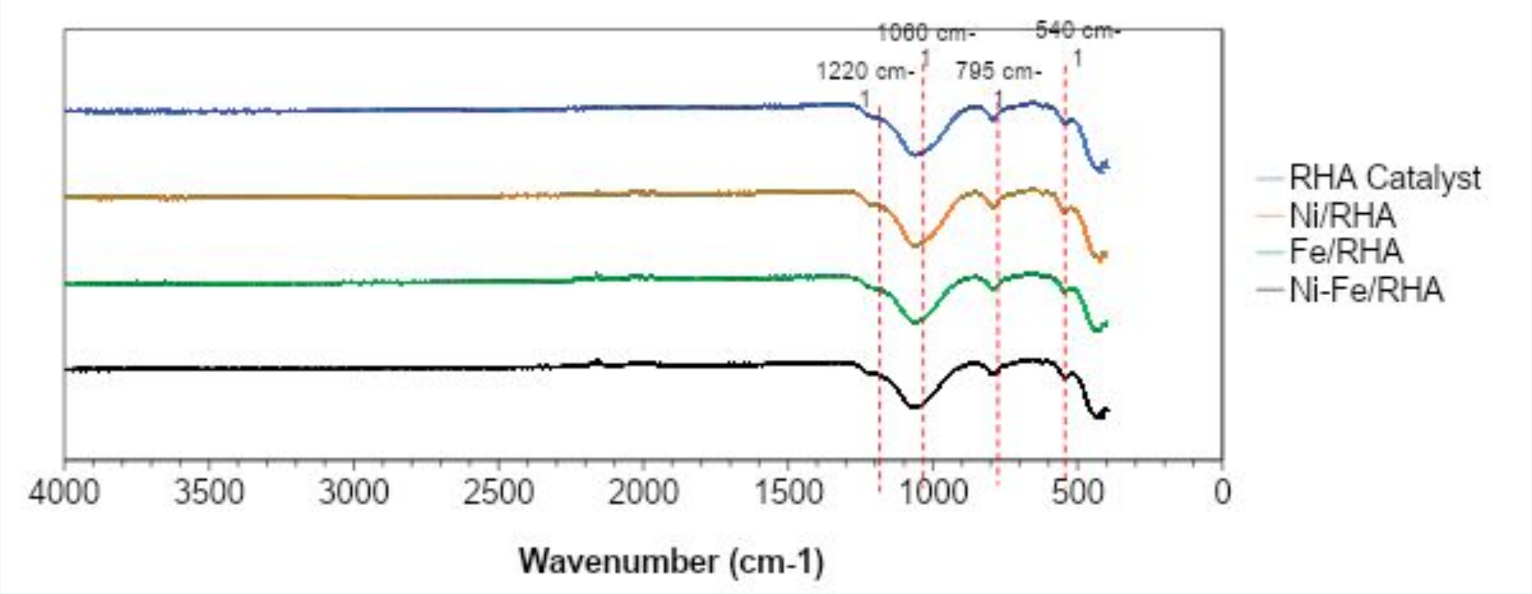


Figure 3. FTIR spectra of **synthesized** catalysts

RHA catalyst:

- Vibration bands around **540 cm^{-1}** and **1220 cm^{-1}** – presence of a **double 5-ring of HZSM-5** [9].
- Around **795 cm^{-1}** and **1060 cm^{-1}** – presence of **Si(Al)O_4 asymmetric stretching**.

Metal-modified RHA catalysts:

- **No shifts** in absorption bands – presence of metals **did not cause** any modification of original catalyst structure.

Results and Discussion

4. Non-catalytic and Catalytic Pyrolysis of EFB via fixed bed reactor

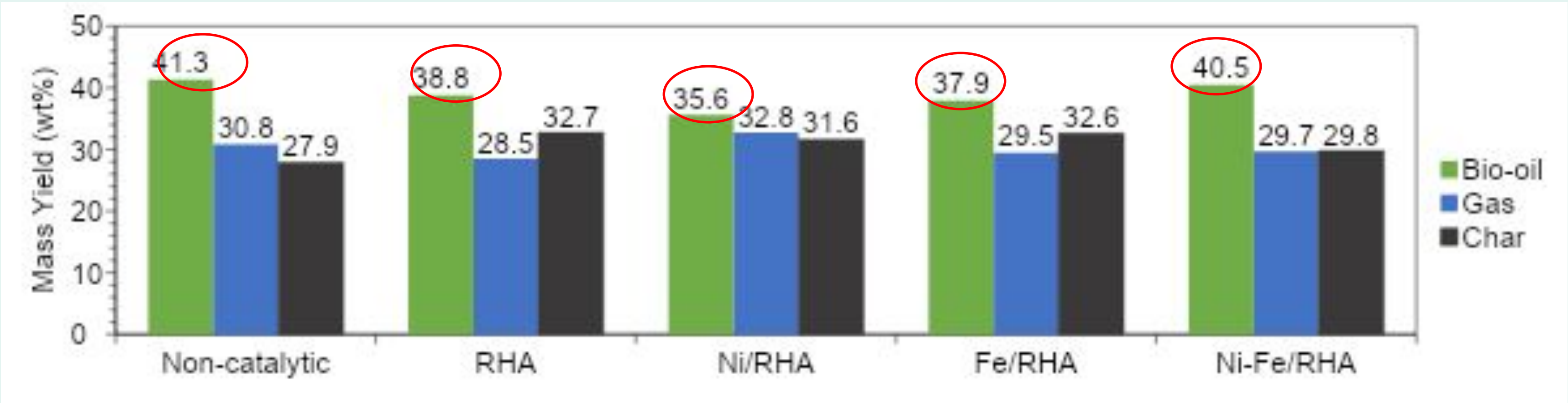


Figure 4. Product yield from non-catalytic and catalytic pyrolysis runs (catalyst-to-feedstock = 1:1, 500 °C)

- **Overall**, addition of catalyst led to a **decrease** in **bio-oil yield**.

- Comparing between **RHA catalyst** and **metal-modified RHA catalysts**:
  - **Ni/RHA:** decrease of bio-oil from 38.8 wt% to **35.6 wt%**.
  - **Fe/RHA:** decrease of bio-oil from 38.8 wt% to **37.9 wt%**.
  - **Ni** has **better** cracking performance that Fe [4] can be seen in the increase of gas yield when using **Ni/RHA**.

- Between the **catalytic runs** – **Ni-Fe/RHA** has **highest** amount of bio-oil yield **(40.5 wt%)**.
- **Chemical composition** of bio-oil not yet known – **further analysis** of bio-oil will be conducted in the future.

Conclusions

1

RHA is **suitable** to be used in catalyst synthesis with the added benefit of it being a **low-cost resource**.

2

Catalysts synthesized using RHA can be further be **metal-modified** to **fine tune** the catalytic functionality

- **Addition of metals did not disrupt original catalyst structure based on XRD and FTIR**

3

Catalytic pyrolysis of **empty fruit bunch** over **Ni/RHA**, **Fe/RHA**, **Ni-Fe/RHA**:

- **Highest** bio-oil yield – **Ni-Fe/RHA** (40.5 wt%)
- **Lowest** bio-oil yield – **Ni/RHA** (35.6 wt)

4

Further analysis of bio-oil, such as using GC/MS, should be conducted **to identify the chemical composition** of the bio-oil.

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