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

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Outline

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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](image1)

![Empty Fruit Bunch](image2)

**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.

- **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

• 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

1. Feedstock Preparation

2. Catalyst Preparation

2. Catalyst Preparation

a). Silica from RHA
Materials and Method

2. Catalyst Preparation cont.
   b). **RHA Catalyst** synthesis [9]

- **Laboratory Oven**: Dried overnight at 110 °C
- **Muffle Furnace**: Calcined at 700 °C, 4 hours
- **Teflon-lined Autoclave Reactor**: 150 °C, 72 hours
- **Washed with deionized water and filtered**

**Materials**:
- RHA
- Sodium Carbonate Decahydrate
- TPABr
- Sodium Aluminate

**Synthesis Process**
1. **RHA**
2. **Sodium Carbonate Decahydrate**
3. **TPABr**
4. **Sodium Aluminate**
2. Catalyst Preparation cont.
   c). **Ni/RHA, Fe/RHA and Ni-Fe/RHA** Catalyst synthesis

   - **Ni/RHA** catalyst
   - **Fe/RHA** catalyst
   - **Ni-Fe/RHA** catalyst

   **Incipient Wetness Impregnation**: 80 °C, 4 hours
   - **Filtered, dried**
   - **Calcination** at 700 °C, 4 hours

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

**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**

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

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

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.

Figure 2. FESEM images of (a) RHA catalyst, (b) Ni/RHA, (c) Fe/RHA and (d) Ni-Fe/RHA
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 $540 \text{ cm}^{-1}$ and $1220 \text{ cm}^{-1}$ – presence of a double 5-ring of HZSM-5 [9].
- Around $795 \text{ cm}^{-1}$ and $1060 \text{ cm}^{-1}$ – 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.
References


Thank you