Hydrocarbon selectivity enhancement through catalytic fast co-pyrolysis of almond shell and plastic wastes blends

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INTRODUCTION
FAST PYROLYSIS

• ↑ Heating rates (°C/ms)
• Moderates temperaturas (400-600 °C)
• ↓ Residence time (0.5-15 s)

Hydrogen deficient nature

Undesirable BIO-OL properties

↓ HHV (MJ/kg)
↑ Viscosity
↑ Oxygen composition

Secondary cracking reaction
CO-FAST PYROLYSIS

Plastic waste

Pyrolysis vapors

Catalyst layer

HYDROCARBON COMPOUNDS

↑Decarboxylation

↑Decarbonylation

↑HHV

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Investigate the effect of CATALYTIC CO-FAST PYROLYSIS on hydrocarbon selectivity, looking for enhancing the production of value-added compounds, such as BTX.

The coupling effect of AAEMs from biomass and zeolite addition
METHODOLOGY

Feedstock samples

- Almond Shell (AS)
- Polyethylene (PE)
- Polystyrene (PS)

Catalyst preparation

- NH₄ZSM-5
  - Ion-Exchange
    - 5M NaNO₃
  - Calcination
    - 550°C 15h

- NaZSM-5 (NaZ)
  - Na⁺ = 2.04 wt.%

- HZSM-5 (HZ)
  - H⁺
1.5:1*
1:1.5*

Fast pyrolysis (650°C, 20°C/ms, 20s)

CO-FAST PYROLYSIS

1.5:1* 2 PE
1:1.5* 6 PS

CATALYTIC FAST PYROLYSIS

2:1 2 PE
1:1 6 PS
1:2

AS Plastic waste Zeolite

## RESULTS

### Sample characterisation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate analysis (wt.%)*daf</th>
<th>Ultimate analysis (wt.%)*daf</th>
<th>HHV (MJ/kg)</th>
<th>H/C_eff</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moisture</td>
<td>Ash</td>
<td>Volatile matter</td>
<td>Fixed carbon*diff</td>
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<tr>
<td>AS</td>
<td>3.11</td>
<td>4.24</td>
<td>78.48</td>
<td>14.16</td>
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<tr>
<td>PE</td>
<td>0.45</td>
<td>0.22</td>
<td>99.27</td>
<td>0.06</td>
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<tr>
<td>PS</td>
<td>0.26</td>
<td>2.39</td>
<td>97.30</td>
<td>0.04</td>
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</table>

<table>
<thead>
<tr>
<th>Mineral content (wt.%)</th>
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<tbody>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>0.29</td>
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</table>

<table>
<thead>
<tr>
<th>Chemical composition (wt.%)^db</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
</tr>
<tr>
<td>13.4</td>
</tr>
</tbody>
</table>
AS Fast pyrolysis

**PHENOLS**
- Syringol 7.4%
- Guaiacol 3.5%
- Coniferyl alcohol 8%

**CARBOXYLIC ACIDS**
- Acetic acid 20.1%

**ALDEHYDES**
- Furfural 7.9%

**ALKANES**

**ALCOHOLS**
- 3,5-Dimethoxyacetophenone 7.2%
Co-fast pyrolysis of AS/PE

1.5:1 AS/PE

- Oxygenates: 97.1%
- Hydrocarbons: 81.1%

Oxygenates
Hydrocarbons

91.1% HYDROCARBONS

Co-fast pyrolysis of AS/PE

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Catalytic fast pyrolysis of AS/PE

- Slightly enhancement of OXYGENATES
- Combined Catalytic effect

Inherent AAEMs + extra Na⁺ (NaZ)
Catalytic fast pyrolysis of AS/PE

- Slightly enhancement of OXYGENATES
- Combined Catalytic effect

Inherent AAEMs + extra Na⁺ (NaZ)

↑ HYDROCARBON production

70.7 to 90% yield as HZ ↑

Diversity of hydrocarbon compounds:

AROMATICs
AROMATICS (%) increase in detriment of ALIPHATIC fraction

↑ p-xylene
- 2.1% (2:1 AS/PE-HZ)
- 1.4% (1:2 AS/PE-HZ)

MAHs > PAHs
Co-fast pyrolysis of AS/PS

1:1.5 AS/PS

97.1% Oxygenates

83.7% Hydrocarbons

100% Hydrocarbons

Oxygenates

Hydrocarbons

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Catalytic fast pyrolysis of AS/PS

HYDROCARBON COMPOUNDS (%)

Inherent AAEMs + extra Na⁺ (NaZ)

↑ MAHs > ↓ PAHs

↑ HYDROCARBON production

100% for 1:2 AS/PS-HZ

↑ Aromatic compounds
1:1, 5 AS/PS
1:2 AS/PS-NaZ
1:1 AS/PS-NaZ
1:2 AS/PS-HZ
1:1 AS/PS-HZ
1:2 AS/PS-HZ
PS

Aromatic selectivity (%)

Benzenes
PAHs
Benzene
Toluene
Xylene

Deoxygenation
Isomeration
Oligomeration

MAHs < PAHs

↑Aromatics (%)

Catalytic effect

↑Toluene

AAEMs + extra Na⁺ (NaZ)

12% for 1:2 AS/PS-NaZ

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CONCLUSIONS

Catalytic co-fast pyrolysis of AS/PE and AS/PS blends enhanced hydrocarbon selectivity due to the catalytic action of zeolites.

In 1.5:1 AS/PE hydrocarbon fraction rose to 81 % yields: aliphatic compounds distributed 27.2 % in light olefins ($C_6-C_{11}$) and 54 % of long chains olefins ($C_{11}-C_{20}$).

AS/PE-HZ Zeolite action (HZSM-5): fomented the formation of AROMATICS up to 45 % yield.

In AS/PS hydrocarbon selectivity reached the 84 % yield.

AS/PS-HZ produced 100% hydrocarbon compounds, being toluene enhanced.
THANKS FOR YOUR ATTENTION!

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