SEPARATION OF SHORT CARBON-CHAIN PRECURSOR MOLECULES FROM POST-CONSUMER PLASTIC PYROLYSIS OIL USING FRACTIONAL DISTILLATION

Waheed Zeb / June 17, 2022

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Introduction

Post consumer waste plastic

Recycling (feed stock quality)

Mechanical Recycling

Effective, proven at industrial scale

Challenges: Thermal degradation, loss of properties due to impurities, additives and residues

Chemical Recycling

Alternative to mechanical recycling: Wide range & mix polymers can be treated

Thermochemical process (Pyrolysis)

Thermochemical recycling

**Feed material**

**Pyrolysis**

- Gases
- Pyrolysis oil
- Char

**Direct Utilization**

- Problems: High density & viscosity
- Presence of oxygenated compounds: Blockages
- High Total Acid Number >0.5 mg KOH/g: corrosion

**Problems:**

- Corrosion & fouling
- Contamination of trace metals and halogens

**Upstream processing**

**Plastic feed stock**

- Pre-treatment (sorting, washing)

**Requires efficient downstream process**

**Wide carbon distribution (C5 to over C50)**

**Heteroatoms:** C, H, N, S, O
Pyrolysis oil

Downstream process

Distillation is considered as 1st logical downstream process for treatment of pyrolysis oil.

Routes of valorization of pyrolysis

Distillates

- Distilled fractions types & quality depends on target applications
- Fuel production: Gasoline & Diesel like fractions
- Steam cracking: Monomer production
- Isolation of molecules for chemicals preparation

Broad carbon distribution 5 & 10 carbon number

Requirements:
- Fuel production: Requires short carbon distribution & purity
- Steam cracking: Requires short carbon distribution & purity

FEED

Pyrolysis oil

Heavy
Isolation of molecules by fractional distillation

- Pyrolysis of polyolefins results in the formation of unsaturated Alkenes
- 44% olefins are present in the pyrolysis oil

3 Liner aldehydes are important for solvents, fine and specialty chemical industry.

However, commercial application of hydroformylation reaction is restricted to the lower carbon chain alkenes due to the solubility and mass transfer

How shorter carbon chain distribution can be obtained by fractional distillation?

Is distillation removes trace contaminations from pyrolysis oil?

Methodology

GC analysis of pyrolysis oil

Final distillation temperature for each C number

Preliminary Aspen simulation using bulk properties and GC analysis for process conditions & minimum carbon distribution

ASTM D2887

8 plates ASTM, Reflux ratio=2, ASTM D2892
- Pure fraction= 3 carbons
### Process conditions for distillation of each carbon cut

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Pressure (mbar)</th>
<th>Chiller temperature (°C)</th>
<th>Distillation temperature (°C)</th>
<th>Atmospheric equivalent temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅-C₇</td>
<td>Atmospheric</td>
<td>-20</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>C₈-C₁₀</td>
<td>Atmospheric</td>
<td>20</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>C₁₁-C₁₃</td>
<td>10±2</td>
<td>20</td>
<td>106</td>
<td>240</td>
</tr>
<tr>
<td>C₁₄-C₁₆</td>
<td>10±2</td>
<td>20</td>
<td>146.2</td>
<td>290</td>
</tr>
<tr>
<td>C₁₇-C₁₉</td>
<td>10±2</td>
<td>80</td>
<td>180</td>
<td>330</td>
</tr>
<tr>
<td>C₂₀-C₂₂</td>
<td>10±2</td>
<td>80</td>
<td>206</td>
<td>369</td>
</tr>
</tbody>
</table>

### Analysis

- **Qualitative**
  - GCMS
  - SVM 3001 Anton par

- **Bulk properties**
  - (Density & Viscosity)
  - ICP-OES

- **Trace contamination**
Step: 1
Atmospheric

Step: 2
Vacuum

Post-consumer plastic pyrolysis oil

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Batch Distillation Setup

1. Feed
2. Column
3. Reflux splitter
4. Vapor Prob
5. Chiller
6. Pressure sensor
7. Temperature sensor
8. Vacuum Pump
9. Dry ice traps
10. Pneumatic Stirrer

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Overview of distillation recovery & physical appearance

Distillation recovery PE (%)

- C5-C7
- C8-C10
- C11-C13
- C14-C16
- C17-C19
- C20-C22
- C22+
- Losses

Pyrolysis oil

Fractional Distillation

Distilled fractions

C5-C7  C8-C10  C11-C13  C14-C16  C17-C19  C20-C22  C22+
GCMS analysis of pyrolysis oil and fractions

Pure fractions of 3 carbon numbers were obtained using distillation 8 plates & 2 reflux ratio
### Overview of improvements in physical properties and contaminations

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pyrolysis oil</th>
<th>C_5^-C_7</th>
<th>C_8^-C_10</th>
<th>C_11^-C_13</th>
<th>C_14^-C_16</th>
<th>C_17^-C_19</th>
<th>C_20^-C_22</th>
<th>C_22+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.821</td>
<td>0.655</td>
<td>0.690</td>
<td>0.723</td>
<td>0.780</td>
<td>0.792</td>
<td>0.804</td>
<td>0.860</td>
</tr>
<tr>
<td>Viscosity (mm²/sec)</td>
<td>a</td>
<td>0.442</td>
<td>0.726</td>
<td>2.09</td>
<td>2.38</td>
<td>4.39</td>
<td>7.069</td>
<td>a</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trace contaminations</th>
<th>LOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (ppm)</td>
<td>280</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>130</td>
</tr>
<tr>
<td>Na (ppm)</td>
<td>146</td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>17.7</td>
</tr>
<tr>
<td>Pb (ppm)</td>
<td>3.8</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>7.6</td>
</tr>
</tbody>
</table>

* LOD: Limit of Detection

- Properties (i.e. density, viscosity) improved
- The level of contaminations decreased
Conclusion

- Fractional distillation improves bulk properties of fractions
- A pure fraction of minimum of three carbon number can be obtained by fractional distillation with reflux ratio of 2 and 8 theoretical plates
- Fractional distillation resulted in removal of trace metal contamination

Future work

- Quantitative analysis of distilled fractions
- Further improvements for removal of trace contaminations in lower detection limits
- Removal of acidic compounds
Thank you

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