A catalyst for conversion of lignin to carboxylic

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Introduction

Converting lignin, a low-value product of the pulp and paper industry and bioethanol production, to value-added products are challenges for the emerging bio-refinery industry. Lignin is a complex aromatic polymer with a three-dimensional amorphous structure that consists of hydroxylated, methoxylated, and phenylpropane units [1-3]. When cracked and oxidized, it could become a primary source of monomers and carboxylic acids such as maleic acid and acrylic acid [4].

Group V and IV metal oxides like vanadium, molybdenum, and tungsten when mixed with phosphoric, arsenic, or boric acids are relatively low in activity and have a controllable oxidation rate [5]. In this study, the performance of three kinds of catalysts on the oxidation of lignin to carboxylic acid was studied. In addition, other reaction variables such as temperature, oxygen concentration, and lignin concentration on carboxylic acid yield were explored.

The reactions were run in a micro-fluidized bed reactor suitable for screening. Mass transfer between gas and catalyst is high due to the small bubbles and the solids backmixing that minimize radial thermal and concentration gradients for the gas phase [6].

Materials and Methods

Lignin solutions were successfully injected into a micro-fluidized bed operating at high temperature (Figure 1). The solution was fed from the top of the reactor and atomized through a nozzle. Argon fluidized the catalyst from the bottom.

The non-condensible effluent was monitored on-line by MS and the condensables were analyzed by a Varian HPLC. Surface area of catalyst was measured by BET. Catalyst was screened and then analyzed by a Horiba to ensure the particle size distribution (PSD) was over 100 μm (Table 1). SEM images of the catalyst are given in Figure 2.

Results and Discussion

Lignin was successfully cracked and oxidized to carboxylic acid at 370 °C. In blank tests (absence of catalyst) traces of maleic anhydride (MA), fumaric acid, and lactic acid were detected in the quench. Acids such as acetic acid, acrylic acid, and phthalic acid were produced in the presence of catalysts. With vanadyl pyrophosphate (VPP) the concentration of MA was approximately 5X that detected with the blank tests. Also, acrylic acid production was 100 times more in comparison to other catalysts. Yield of phthalic anhydride was highest with the Al-V-Mo.

Table 1. PSD and BET result for catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Al-V-Mo</th>
<th>Silica-V-Mo</th>
<th>VPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSD(μm)</td>
<td>141</td>
<td>110</td>
<td>120</td>
</tr>
<tr>
<td>BET(m²/g)</td>
<td>147</td>
<td>113</td>
<td>37</td>
</tr>
</tbody>
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Figure 1. Schematic of high temperature fluidized bed setup

Figure 2. SEM images: A) Al-V-Mo, B) Silica-V-Mo, C) VPP.

Acknowledgments

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References