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Ethanol to Para-xylene via Methyl Benzaldehyde

May 2022

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Prepared for
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Abstract

Para-xylene is an intermediate compound to several valuable commodity chemicals including polyethylene terephthalate (PET) and currently produced from fossil feedstock through a complex sequence of steps utilizing energy intensive process. Recent work from PNNL has demonstrated the conversion of ethanol produced from waste feedstocks such as municipal solid waste to para-xylene via simple three step process.

Summary

Introduction and Project Description: From ethanol, para-xylene is produced in three chemical steps: ethanol → acetaldehyde → methyl benzaldehyde(s) → para-xylene. Research was focused on achieving higher selectivity to methyl benzaldehyde(s), reaction mechanism development to understand the selectivity between para and ortho methyl benzaldehyde and developing catalysts for methyl benzaldehyde(s) hydrodeoxygenation to respective xylene(s) and demonstrating the viability of modular distributed units.

Results and Accomplishments: Over a heterogeneous catalyst acetaldehyde conversion to methyl benzaldehyde(s), was demonstrated via a sequence of three cascade steps in a single catalytic bed. Based on the experimental results a patent application titled “Method and system embodiments for converting ethanol to para-xylene and ortho-xylene” was submitted and already approved (Patent # US 11,325,783).

Acknowledgments

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Contents

Abstract.....	ii
Summary.....	iii
Acknowledgments.....	iv
Acronyms and Abbreviations	Error! Bookmark not defined.
1.0 Introduction	1
2.0 Results and Discussion.....	2
3.0 References.....	Error! Bookmark not defined.

Figures

Figure 1.	Conversion and selectivity (%) results obtained for a hydrogenation <i>ortho/para</i> methyl benzaldehyde was reacted over a Pd based catalyst.	2
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Tables

No table of figures entries found.

1.0 Introduction

The worldwide consumption of PET in the year 2016 is 100 MT with an estimated annual growth of 4 percent. For PET synthesis, para-xylene is obtained from naphtha reforming with extensive purification. Purification costs are sensitive to even small changes in the complex feed mixture. Industry efforts to date to produce bio renewable PET have met with success in generating the ethylene glycol part of this polymer from ethanol, but advances are still needed to renewably produce the para-xylene component. One of the alternative pathways is to convert ethanol to produce para-xylene via methyl benzaldehyde intermediate and enable renewable production of PET. From ethanol, para-xylene is produced in three chemical steps: ethanol \rightarrow acetaldehyde \rightarrow methyl benzaldehyde(s) \rightarrow para-xylene. Research was focused on achieving higher selectivity to methyl benzaldehyde(s), reaction mechanism development to understand the selectivity between para and ortho methyl benzaldehyde and developing catalysts for methyl benzaldehyde(s) hydrodeoxygenation to respective xylene(s) and demonstrating the viability of modular distributed units. Conventional para-xylene process includes expensive separation units due to the complex mixtures in the feed stream. In our approach, the feed stream for the separation unit includes only para-xylene and ortho-xylene. This makes the separation simple, economical, and viable at smaller scales that are relevant to the size of a renewable ethanol plant.

2.0 Results and Discussion

Over a heterogeneous catalyst acetaldehyde conversion to methyl benzaldehyde(s), occurs via a sequence of three cascade steps in a single catalytic bed. First step is the base catalyzed aldolization to form 3-hydroxybutanol followed by the acid catalyzed dehydration to form crotonaldehyde followed by the dimerization and cyclization. To accomplish this chemistry in a single catalytic step it requires bi-functional acid-base mixed oxide catalyst. Both the 3-hydroxybutanol and crotonaldehyde are very reactive so maintaining the optimum balance between the active sites and identifying the operating conditions (e.g., temperature, pressure, weight hourly space velocity) are imperative in achieving the high methyl benzaldehyde(s) yield. In this work several mixed catalysts containing both acidic and basic properties (MgO-Al₂O₃, MgO-ZrO₂, MgO-SiO₂, MnO-ZrO₂-ZnO, and ZnO-ZrO₂) were tested in a plug flow experimental system and demonstrated the single pass acetaldehyde conversion over 75% while maintaining the ortho to para methyl benzaldehyde ratio of one the product distribution. Conversion and selectivity (%) results obtained for a hydrogenation ortho/para methyl benzaldehyde was reacted over a Pd based catalyst. Methyl benzaldehyde(s) hydrogenation to respective xylene(s) was tested over various catalyst containing platinum group metals with a goal to achieve complete conversion to methyl benzaldehyde and high selectivity to xylene(s) while avoiding the undesired side reactions such as isomerization and cracking. After the thorough study palladium supported on carbon catalyst was identified for this reaction. As shown in the figure above, the palladium-based catalyst developed in this work was very stable, and it was demonstrated beyond 500 hours of time on stream (TOS) in a plug flow reactor arrangement without any deactivation signs for both the methyl benzaldehyde(s) conversion and the selectivity to xylene(s).

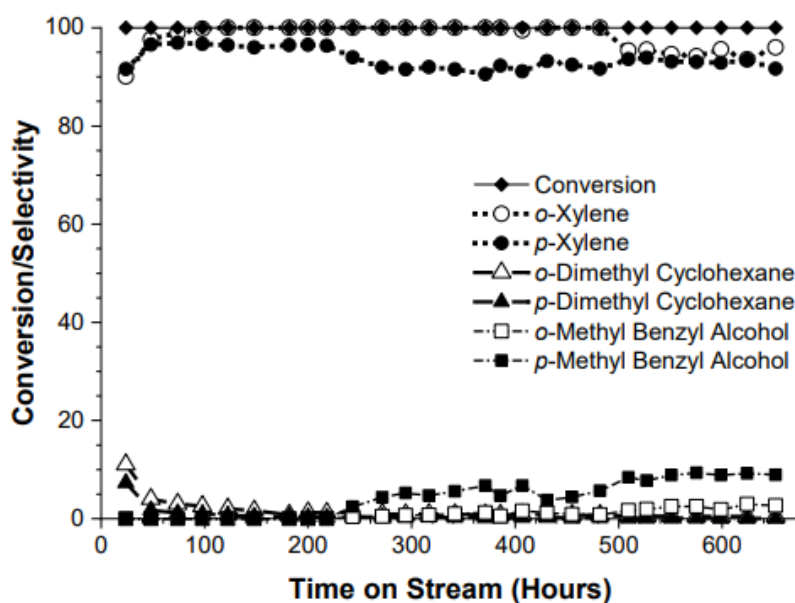


Figure 1. Conversion and selectivity (%) results obtained for a hydrogenation *ortho/para* methyl benzaldehyde was reacted over a Pd based catalyst.

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