

# Exploratory Study of Selective Aromatic Ring Opening Using Oxidative Pre-treatment

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## Introduction

Recent environmental legislations on diesel fuel have placed significantly more stringent restrictions on the levels of sulphur and polynuclear aromatics, and cetane number [1]. Therefore, there are increased interest and need for developing processes that can improve the cetane number of middle distillates from bitumen-derived crude and heavy oils to meet the expected new specifications for low polynuclear aromatics and a high cetane number [1, 2]. It has been proposed that the quality of both light and heavy gas oils could be improved by catalytic hydrogenation of aromatics followed by opening of the resulting cycloparaffinic rings [2]. However, the current commercial selective ring opening bifunctional catalysts, including metal sulfides and noble metals supported on acidic supports, do not provide satisfactory performance due to the extensive cracking of side chains and high propensity to poisoning by sulphur compounds present in the feedstocks [2].

We explored the viability of using an oxidative pre-treatment and subsequent ring opening by hydrotreating or oxidation upgrading process, in order to improve the cetane number of middle distillate from bitumen-derived crude and heavy oils that are rich in polyaromatics. In theory, this proposed concept is analogous to adipic acid synthesis via benzene ring opening, and could result in reduced polynuclear aromatics and thus an increased cetane number of middle distillates without losing carbon atoms.

## Materials and Methods

Two ring aromatics including naphthalene, tetralin and decalin were used as starting materials. Air oxidation, oxidative cracking and hydrodeoxygenation were explored. Products were identified by gas chromatography mass spectrometry.

## Results and Discussion

Analogous to benzene ring opening process for adipic acid synthesis [3], four possible reaction schemes are proposed and described in Fig. 1. The first possible scheme is through the direct oxidation of naphthalene. Xylenes could then be formed by the hydrodeoxygenation of phthalic anhydride. For the case of 1,4-naphthoquinone, the final product could be 1-methyl-2-propylcyclohexane or butylcyclohexane or diester of resulted carboxylic acid. The second reaction route is through the oxidation of tetralin derived from the selective hydrogenation of naphthalene. Similarly, 1-methyl-2-propylcyclohexane would be formed as the final product. The third route is through the oxidation of decalin derived from full hydrogenation of naphthalene. Decane as the final product with straight chain would be formed via hydrodeoxygenation to remove oxygen. Alternatively, esters could be formed through the esterification of the resulted acid. The fourth route is through the oxidation of octalin obtained from selective hydrogenation of naphthalene. The oxidation of octalin might

open two rings simultaneously by breaking the double bond by forming cyclodecane-1,6-dione. Subsequently, cyclodecane-1,6-dione might be selectively opened to 5-oxodecanedioic acid. The final product would be decane or methyl ester of 5-oxodecanedioic acid.

We have been focusing on the route to selective ring opening via hydrogenation followed by oxidative cleavage. Octalin was successfully synthesized via birth reaction. The oxidative cleavage and further hydrodeoxygenation were performed using the octalin/tetralin mixture from the birth reaction. Our exploratory tests indicated that the selective opening of aromatic rings using oxidative pretreatment to activate rings followed by ring cleavage using either hydrotreating or oxidation without losing carbon atoms is challenging and needs further testing.

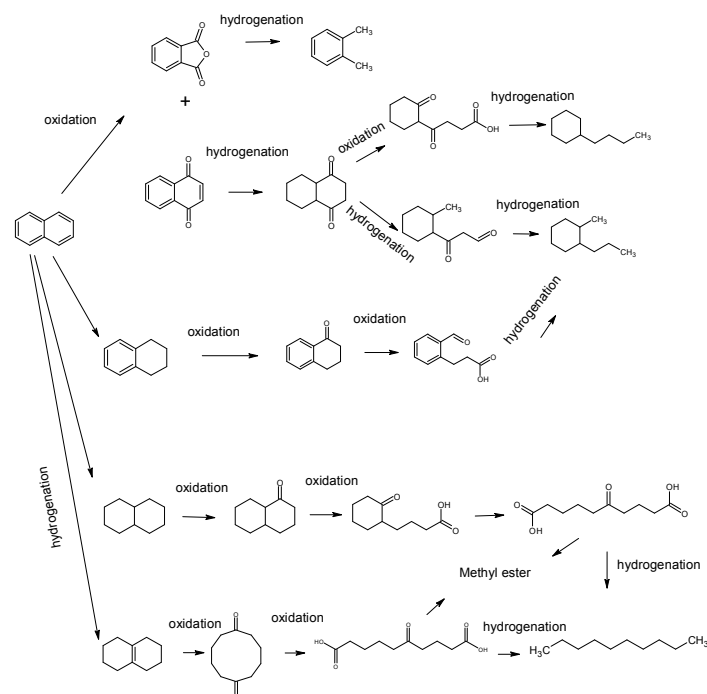


Figure 1. Proposed possible reaction schemes for the oxidative pre-treatment and subsequent ring opening by hydrotreating or oxidation.

## References

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