

## **SUPPORTING INFORMATION**

### **Ozonation of oilsands bitumen**

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#### **A.1 Introduction**

The purpose of the Supporting Information document is to provide additional detail about the identification and classification of oxidation products found during the study.

Gas chromatography coupled with mass spectrometry was employed as primary analytical technique to identify the products. The investigation into oxidation with ozonated air, followed on previous investigations into oxidation with air.<sup>(1)(2)</sup> Low oxidation conversion was maintained to elucidate the reaction pathways and hence little degradation of the carbon structure of the feed was observed in the products.

Due to the complexity of the reaction product, the oxidation products were divided into three classes to assist with interpretation of the results:

(a) Primary oxidation products. These are products derived from the feed materials through the introduction of a single oxygen-containing functional group. In air oxidation these would be hydroperoxides, alcohols and ketones, with the carbon structure of the feed otherwise unaltered. As will be explained in Section A.2, this became more complicated when using ozonated air.

(b) Secondary oxidation products. These are products derived from the feed materials through secondary oxidation. These products included oxidation reactions at the same position as the primary oxidation product to produce esters or carboxylic acid functional

groups, or more commonly found, oxidation on a different position to introduce another hydroxyl or carbonyl group.

(c) Addition products. The addition product included all compounds with more carbon atoms in the product than the feed material, irrespective of whether the resulting product has an oxygen-containing functional group or not.

It was found that when the oxidation products were separated on a non-polar column (see experimental section in manuscript), the primary oxidation products eluted first, followed by the secondary oxidation products and lastly by the addition products, which had the longest retention times. In this way it was possible to group the compounds based on retention time range. This was beneficial, because it enabled discussion of oxidation selectivity in broad terms that could be applied to multiple feed materials. It also reduced the analytical effort, because only the major products were checked to confirm identity and classification and not the minor products that were classified based on retention time without elucidating their identity. This was a pragmatic decision.

## **A.2 Modification of classification for ozonation**

It would have been preferable to employ the same classification system for the present study using ozonated air as was used for air. This is illustrated by the classification as applied to the oxidation of indene with ozonated air (Figure A.1).

This classification worked well for products that were typically also found during air oxidation, such as the primary oxidation product indenone (Figure A.2) and the secondary oxidation product indandiol (Figure A.3). However, ozonation can lead to degradation of the carbon structure of the feed even at low oxidation conversion. Products of ring-opening with loss of carbon also appeared in the oxidation product, such as 2-methyl benzoic acid (Figure A.4). Similarly, it was found that some addition products were formed that had a loss of carbon, so that the carbon number of the addition product was not an integer multiple of the feed (Figure 8 in the manuscript).

The mass spectra in the chromatographic retention time range for primary and secondary oxidation products therefore consisted of three groups: (i) isomers of mono-alcohols or mono-ketones, (ii) isomers with two alcohol groups, two ketone groups or one alcohol and one ketone groups, and (iii) products of ring-opening. It was realized that the strategy to divide primary and secondary oxidation products based on chromatographic retention was no longer reliable measure to differentiate between primary and secondary oxidation products, because these two classes overlapped when ozonated air was employed as oxidant.

Furthermore, the complexity of the chromatogram increased when ozonated air was employed as oxidant. This was particularly evident in the case of naphthalene oxidation with ozonated air. Identifying each of the main products became very time consuming (Figures A5 and A6). The specific identity of ozonation products was determined by interpretation of the electron ionization mass spectra with the help of the electron ionization mass spectra library of National Institute of Standards and Technology (NIST). However, the suggested identification by the software was in some cases unrealistic based on the chemistry of the process.

Unlike the previous studies,<sup>(1)(2)</sup> the aim of the investigation was more applied in nature. It was decided to differentiate only between the addition products and the rest of the oxidation products (primary and secondary combined) that could be done reliably. Even though it was not always clear that the molecular ion was present, if the fragmentation pattern indicated more carbon atoms in a molecule than was present in the feed, it could be labeled as an addition product. It was a pragmatic decision.

### **A.3 Infrared spectrometry**

Infrared spectrometry was performed on all of the products after oxidation with ozonated air to check for the presence of C=O, C–O, and O–H functional groups. The wavenumber ranges that were observed that could correspond to these functional groups are listed in Table A.1. The infrared spectrum of indene before and after oxidation is also show as an example (Figure A.7).

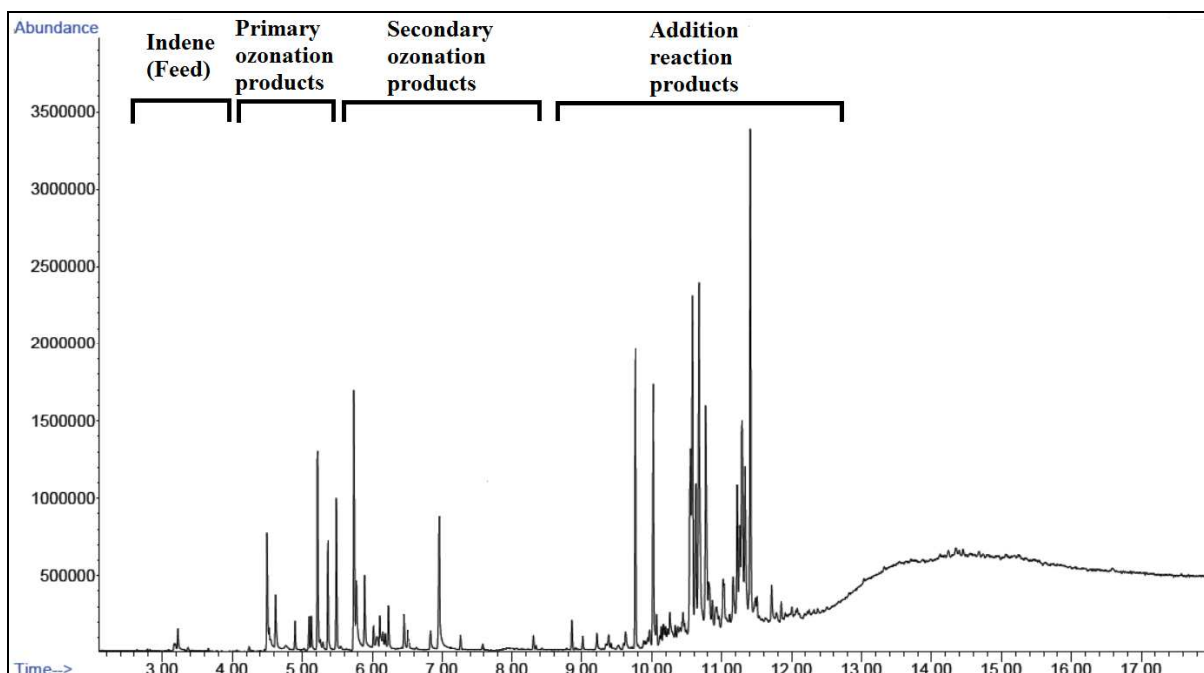
## Literature cited

- (1) Siddiquee, M. N.; De Klerk, A. Hydrocarbon addition reactions during low-temperature autoxidation of oilsands bitumen. *Energy Fuels* **2014**, 28, 6848-6859.
- (2) Siddiquee, M. N.; De Klerk, A. Heterocyclic addition reactions during low temperature autoxidation. *Energy Fuels* **2015**, 29, 4236-4244.

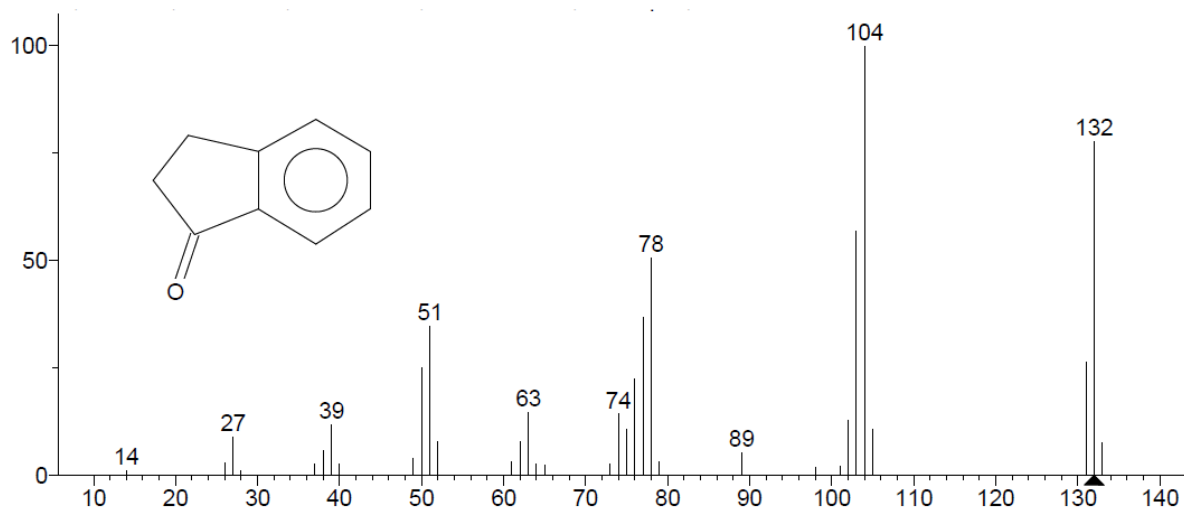
**Table A.1** Wavenumber ranges in the infrared spectra of the products after oxidation with ozonated air that correspond to C=O, C–O and O–H vibrations.

Compound oxidized	Infrared wavenumber range (cm <sup>-1</sup> )		
	C=O	C–O	O–H
naphthalene	1796-1647	1201-1181	- <sup>a</sup>
tetralin	1746-1649	1165-1142; 1087-1051; 1031-1020; 1015-993	- <sup>a</sup>
indane	1753-1662	1285-1270; 1213-1195; 1050-1027	- <sup>a</sup>
indene	1795-1649	1305-1234; 1223-1186; 1172-961	3608-3236
decalin	1749-1683	- <sup>a</sup>	- <sup>a</sup>
<i>p</i> -cymene	1787-1640	1296-1250; 1223-1135; 1126-1106	- <sup>a</sup>
<i>n</i> -decane	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>
2,3-dihydrobenzofuran	1782-1699	- <sup>a</sup>	- <sup>a</sup>
benzofuran	1782-1568	1312-1220; 1186-1046	
thianaphthene	1766-1667	- <sup>a</sup>	- <sup>a</sup>
indoline	1801-1692	1236-1141	- <sup>a</sup>
indole	1726-1561	- <sup>a</sup>	- <sup>a</sup>
quinoline	- <sup>a</sup>	1239-1222	- <sup>a</sup>

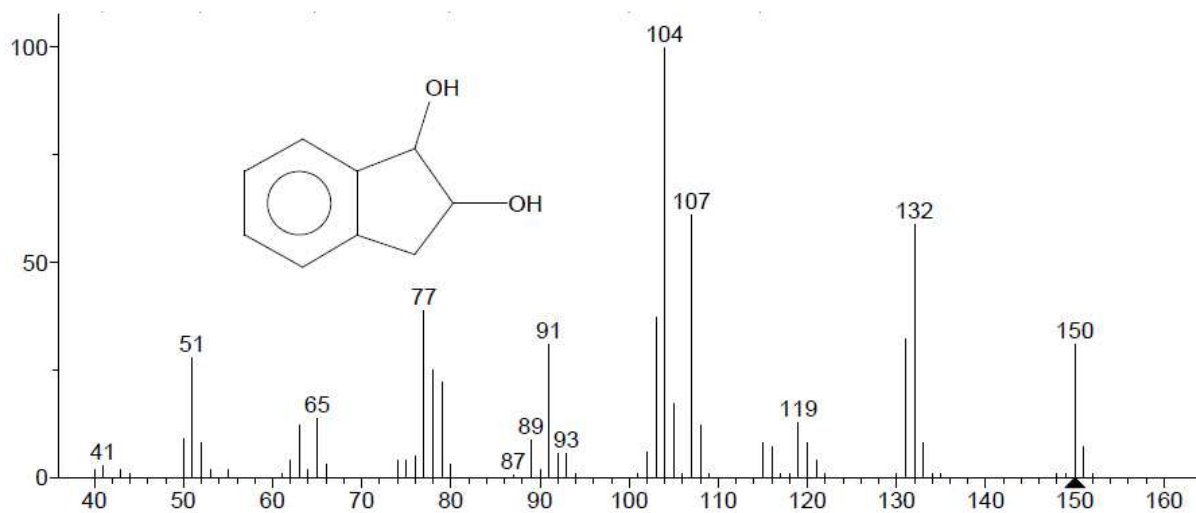
<sup>a</sup> Small absorption, or not observed.



**Figure A.1** Total ion chromatogram by GC-MS of the product after oxidation of indene with ozonated air after 6 h reaction time at 130 °C showing the grouping of products into classes.

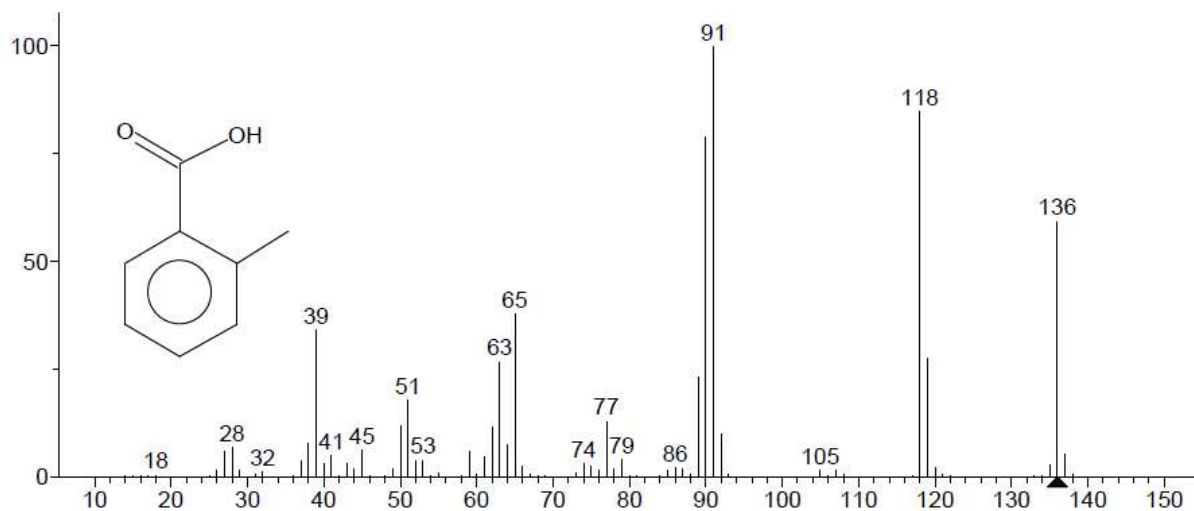


**Figure A.2** Electron impact mass spectrum of indenone, the compound with retention time of 4.897 min in Figure A.1, which is a primary oxidation product of indene with ozonated air.

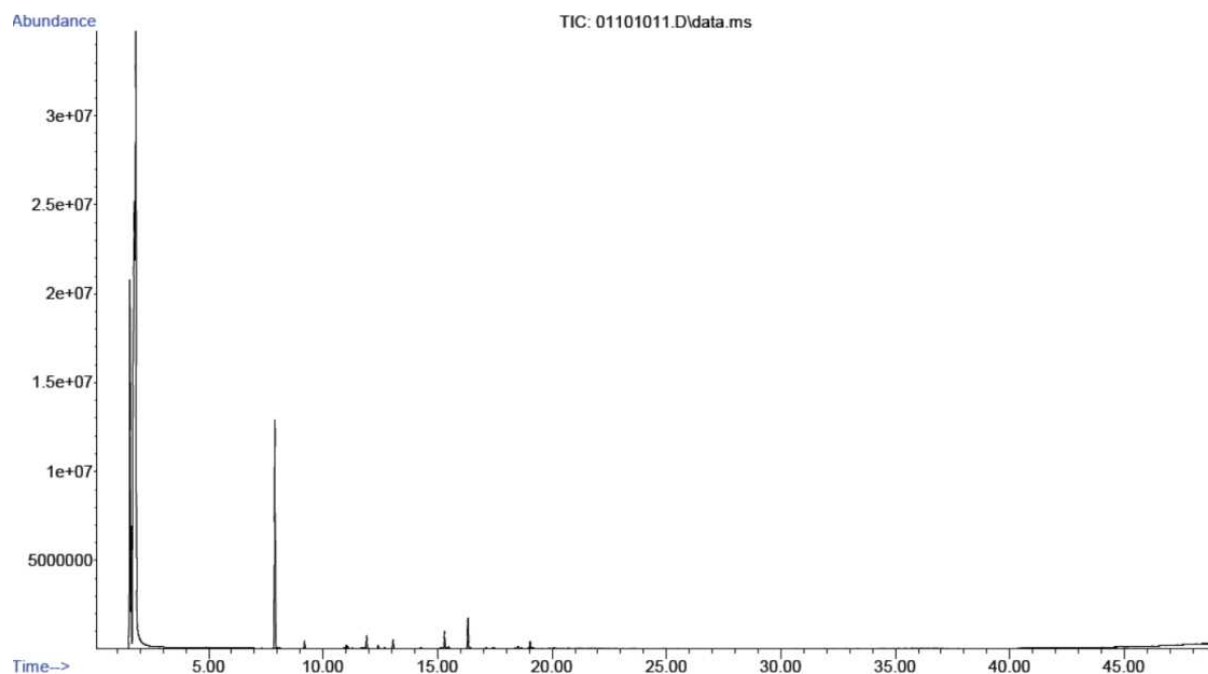


**Figure A.3** Electron impact mass spectrum of indandiol, the compound with retention time of 5.899 min in Figure A.1, which is a primary oxidation product of indene with ozonated air.

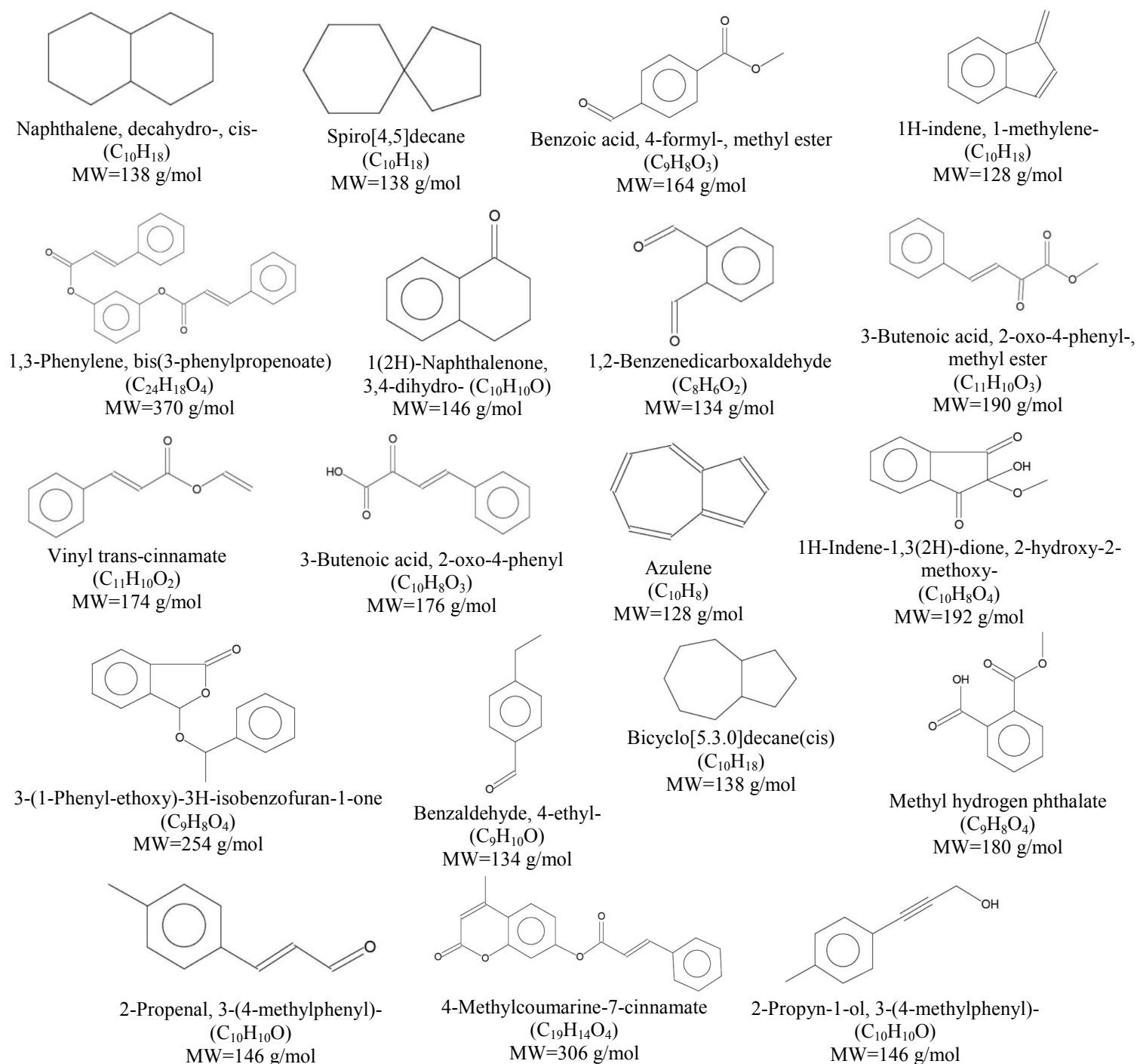




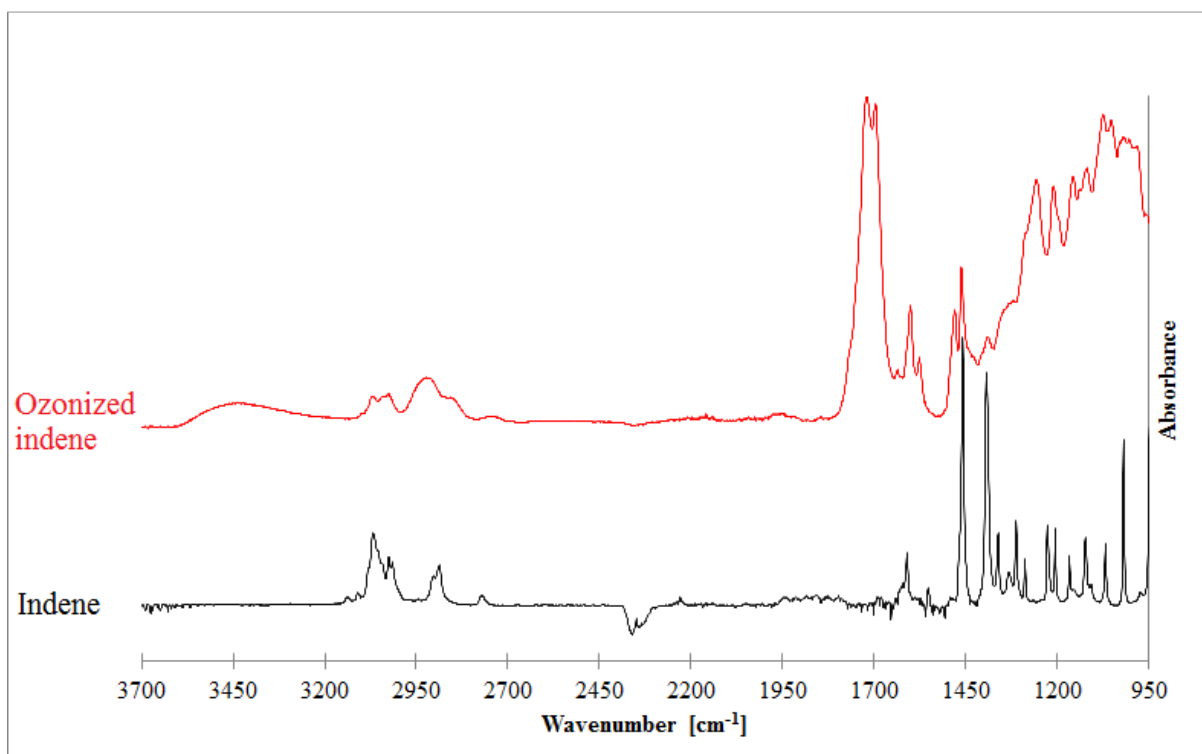
**Figure A.4** Electron impact mass spectrum of 2-methyl benzoic acid, the compound with retention time of 6.963 min in Figure A.1, which is a secondary oxidation product of indene with ozonated air.



**Figure A.5** Chromatogram of the oxidation product of naphthalene with ozonated air after 60 min at 130 °C. The peak at 7.9 min is not an oxidation product but an internal standard (hexachlorobenzene) that was added to assist with quantification.



**Figure A.6** Product identification based on mass spectra of compounds in Figure A.5.



**Figure A.7** Infrared spectra of indene and indene after oxidation with ozonated air.