

# CO-OXIDATION OF REFRACTORY BAYER ORGANICS USING SODIUM MALONATE DERIVATIVES AND WET AIR OXIDATION

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## Abstract

Organic impurities in the liquor have a negative impact on both productivity and product quality in Bayer process refineries. Of the many organics removal processes that have been investigated, Wet Air Oxidation (WAO) is one of the few that has been successfully applied in practice. One of the limitations to wider application of WAO is that high temperatures (>275 °C) are required to achieve a high level of removal of Bayer organics. Previous investigations have shown that oxidation reactions can be accelerated by the presence of free radicals produced by reaction of malonate with oxygen. This effect, in which the oxidation of a reactive compound facilitates the oxidation of less reactive compounds, has been termed "co-oxidation".

This work extends the study of co-oxidizers to include a series of malonate derivatives, and examines some of the reaction products. It was found that reactivity of the co-oxidizer compounds themselves decreases with increasing molecular weight, in the order: malonate  $\approx$  methyl malonate > ethyl malonate > phenyl malonate for WAO at 200 °C in a synthetic Bayer liquor. The effectiveness of these compounds as co-oxidizers for succinate followed a similar order, suggesting a common mechanism. Sodium oxalate is a product of reaction in all cases, and some acetate is produced in the oxidation of methyl, ethyl and phenyl malonate.

## 1. Introduction

The need for the removal of organic impurities from Bayer liquor is well documented [Yamada *et al.* 1973, Guthrie *et al.* 1984, Grocott 1988, The *et al.* 1985] and has led to a number of studies on organics removal processes [Armstrong *et al.* 2007, Beach *et al.* 2007, Deabridges 1977, Sato *et al.* 1982, Matyasi 1986, Marciano *et al.* 2006, Shaw 2005, Soucy *et al.* 2004]. Of the many processes that have been investigated, Wet Air Oxidation (WAO) is one of the few that has been successfully applied in practice. This process basically involves aqueous phase oxidation of organic (or inorganic) compounds using air or pure oxygen as an oxidant.

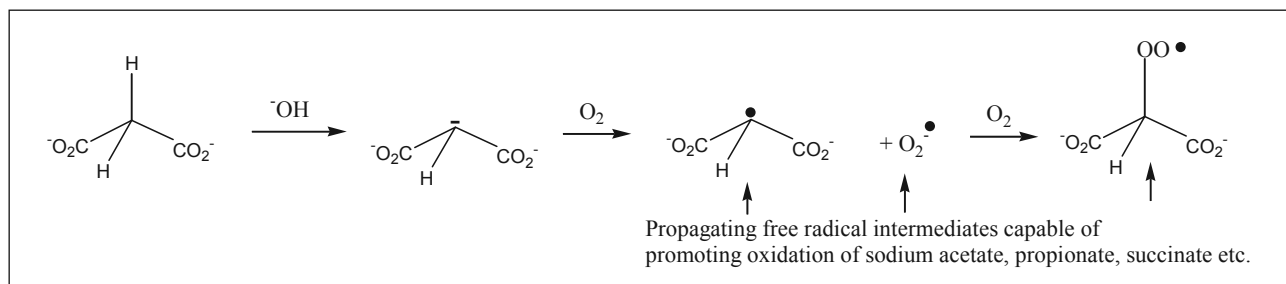
Some of the key issues to be considered in treating Bayer liquor by WAO are (i) high temperatures (>270 °C) are required to achieve a high extent (>80%) of total organic carbon (TOC) removal using reasonable residence times, (ii) scale formation, and (iii) the consequently high capital and operating costs potentially involved. Methods to reduce the temperatures required are therefore of interest. The most widely used method to reduce the reaction temperature is via a catalyst [Bhargava *et al.* 2006, Eyer *et al.* 2002, Tardio *et al.* 2004, Brown 1989, Yamada *et al.* 1981]. Another method that has proved successful has been to increase the alkalinity of Bayer liquor beyond usual levels prior to (and during) treatment by CWAO (Catalytic Wet Air Oxidation) [Baker *et al.* 2006]. Although these methods have been successful in reducing reaction temperature, relatively high temperatures (~220 °C) are still required to achieve a high extent of TOC removal. In addition, the use of a catalyst leads to additional costs and potential product contamination issues.

Another possible way to reduce the temperature needed for efficient WAO is to use an additional oxidant. The most widely studied oxidant that has been used in conjunction with WAO is hydrogen peroxide [Prasad *et al.* 2007, Lei *et al.* 1998, Kim *et al.* 2003, Melerio *et al.* 2007, Rubalcaba *et al.* 2007]. The use of hydrogen peroxide is usually most effective under acidic conditions and therefore most likely not suitable for treating

Bayer liquors. The use of other common oxidants such as ozone and potassium permanganate is also either not efficient or is unsuitable for other reasons; for example, ozone has poor solubility at temperatures greater than 50 °C. The discovery of an additive (oxidant) that can complement WAO but does not release foreign species or require a removal step is therefore of interest.

Studies by Tardio [Tardio 2002] using model compounds in synthetic Bayer liquor have identified that a common Bayer organic, sodium malonate, which is not known as an oxidant, has the ability to co-oxidise "hard to oxidise" Bayer organics such as sodium acetate and sodium succinate under relatively mild WAO conditions (165 °C, 4.4 M NaOH, 500 kPa O<sub>2</sub>). The ability of sodium malonate to act as a co-oxidant (sodium malonate also undergoes oxidation during the co-oxidation process) under these conditions is most likely due to the action of active free radical intermediates which are produced during malonate WAO. A schematic of the proposed reaction mechanism for malonate WAO under highly alkaline conditions is given below. Briefly, it is assumed that WAO of malonate is initiated by abstraction of a relatively acidic alpha hydrogen by hydroxide, leading to the formation of a carbanion intermediate which reacts rapidly with oxygen to form a range of radical intermediates.

The aim of this research was to explore the oxidation of compounds very similar to malonate to determine if the structural feature of malonate that has been hypothesised to be responsible for the ease of oxidation of this compound (O<sub>2</sub>C-CH-CO<sub>2</sub>) also leads to significant oxidation of similar compounds (methyl malonate, ethyl malonate and phenyl malonate) under relatively mild WAO conditions. The ability of these compounds to produce free radical intermediates that can co-oxidise succinate, a hard to oxidise Bayer organic, was also investigated.



Reaction Scheme 1. Proposed free radical intermediates produced during low temperature WAO of sodium malonate.

## 2.0 Experimental

All experiments were conducted in synthetic Bayer liquor (Table 1) which was prepared using the following chemicals: Al(OH)<sub>3</sub> (Alcoa C31 Hydrate), NaOH, NaCl, Na<sub>2</sub>SO<sub>4</sub>, and Na<sub>3</sub>PO<sub>4</sub>. The method used to prepare synthetic Bayer liquor is given elsewhere [Tardio *et al.* 2004].

Table 1. Composition of synthetic Bayer liquor.

Component	Concentration (M)
Al	1.96 (100g/L as Al <sub>2</sub> O <sub>3</sub> )
NaOH	4.40 (176g/L)
Na <sub>2</sub> CO <sub>3</sub>	0.40 (42g/L)
NaCl	0.34 (20g/L)
Na <sub>2</sub> SO <sub>4</sub>	0.18 (25g/L)
Na <sub>3</sub> PO <sub>4</sub>	0.002 (0.37g/L)

The following organic compounds were used as received in WAO tests: malonic acid, methyl malonic acid, ethyl malonic acid, phenyl malonic acid and succinic acid.

All WAO tests were conducted in a 1.2 L inonel autoclave (Parr Instruments Co. USA). The autoclave was equipped with a magnetically driven stirrer (consisting of two six blade impellers), and fittings for gas addition and sample removal. The autoclave set-up also included a Parr 4843 controller to allow temperature and stirrer speed to be maintained at predetermined values. Pressure readings were obtained from a pressure transducer directly attached to the autoclave assembly.

All autoclave reactions were conducted as follows: 600 mL of synthetic Bayer liquor was added to the reaction vessel, followed by the organic compound(s) to be studied. All organic compounds used were added in their acid form though it can be readily assumed these were quickly converted to their sodium salt form in synthetic Bayer liquor based on the pKa values of the organics studied and the pH of synthetic Bayer liquor (pH>=14). The reaction vessel was then sealed and evacuated to -65 kPa to remove oxygen in the headspace area, to minimise the possibility of oxygen induced oxidation before reaching the set point temperature. The reaction solution was then stirred and heated until reaching the desired set point temperature. The time at reaching the set point temperature was designated time zero. Once the desired temperature was reached oxygen (Linde, minimum purity of 99.5%) was added at the partial pressure required (500 kPa). The partial pressure of the added gas was maintained constant throughout the course of the reaction. Samples were removed at pre-determined times throughout the course of the reaction.

Total organic carbon was measured using an OI-Analytical Total Organic Carbon (TOC) Analyser. The concentration of organic compounds was determined using HPLC and IC.

## 3.0 Results and Discussion

### 3.1 WAO of malonate, methyl malonate, ethyl malonate, phenyl malonate and succinate.

The WAO reactions of malonate, methyl malonate, ethyl malonate and phenyl malonate were investigated individually. The WAO of succinate, an organic compound which is common in Bayer liquors, was also investigated. Succinate does not contain the O<sub>2</sub>C-CH-CO<sub>2</sub><sup>-</sup> referred to above which we believe to be responsible for the ease of oxidation of malonate. The molecular structures of the compounds that were investigated are given in Table 2. The results from the tests are presented in Figure 1 in terms of the percentage removal of each compound studied as a function of reaction time.

Table 2. Molecular formulae and structure of organic compounds studied.

Compound	Molecular formulae	Molecular structure
Malonate	C <sub>3</sub> H <sub>2</sub> O <sub>2</sub> <sup>2-</sup>	
Methyl malonate	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub> <sup>2-</sup>	
Ethyl malonate	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub> <sup>2-</sup>	
Phenyl malonate	C <sub>9</sub> H <sub>6</sub> O <sub>4</sub> <sup>2-</sup>	
Succinate	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub> <sup>2-</sup>	

The rates of oxidation of malonate and methyl malonate were found to be very similar, and both were oxidised considerably faster than ethyl malonate. Succinate was not oxidised

appreciably under the conditions used. The rate of oxidation of phenyl malonate could not be determined directly by HPLC, so was inferred from the analysis of products of reaction. On that basis, approximately 41% of phenyl malonate was oxidised after 90 minutes, however this may be an under-estimate as discussed in Section 3.2 below. The order of extent of oxidation observed for malonate and the malonate derivatives was found to be related to the size of the group substituted at the alpha carbon position. This is consistent with the order: no substitution  $\approx$  methyl > ethyl > phenyl. Other factors that would be expected to influence the rate of oxidation of the compounds studied include:

- influence of group substituted at alpha position on acidity of alpha hydrogen
- "leaving" properties of group substituted at alpha position
- Types (reactivity) of intermediates formed (i.e. the quantity of propagating intermediates formed)

The lack of oxidation of sodium succinate compared to the rapid oxidation observed for methyl malonate is an interesting observation because these compounds are chemically identical but are structural isomers. This observation is contrary to the hypothesis proposed by Imamura [Imamura 1999] that the WAO of organic compounds is related to their C:O ratio, and demonstrates that structural factors can also be important.

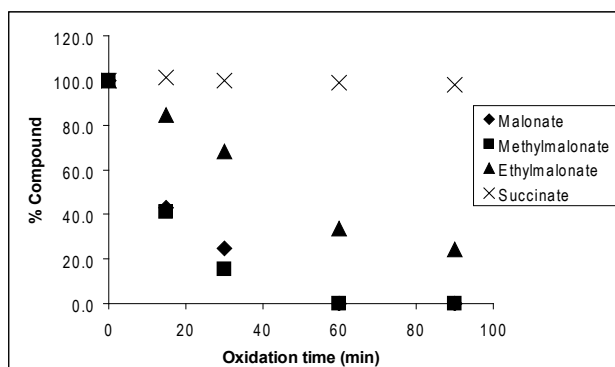


Figure 1. % malonate, methyl malonate, ethyl malonate and succinate versus time. Conditions: T=200 °C, synthetic Bayer liquor, [org] = 0.0096 M, PO<sub>2</sub> = 500 kPa, 800 rpm.

The reaction products identified after 90 minutes are given in Table 3. It can be seen that although malonate and ethyl malonate were both completely removed at approximately 60 minutes, they were not completely oxidised to CO<sub>2</sub> and H<sub>2</sub>O. The major products of malonate WAO were oxalate and carbonate. Formate was also identified during WAO of malonate, reaching a maximum concentration after 30 minutes. Formate is known to undergo appreciable WAO in isolation at lower temperatures than used in this study [Tardio 2002]. The major products of methyl malonate WAO were also carbonate and oxalate, however a significant amount of acetate was also produced. A test conducted on the WAO of acetate showed that it does not undergo appreciable oxidation under these conditions. A similar amount of formate to that observed in the malonate test was also observed for methyl malonate WAO with the maximum concentration again observed after 30 minutes. The major products identified from WAO of ethyl malonate were carbonate and oxalate, while significant amounts of formate and acetate were also identified. The greatest concentrations of acetate and formate were at the end of the 90 minutes, indicating that the rate of oxidation of formate was slower than its rate of production during this test. The major products identified for WAO of phenyl malonate were carbonate and oxalate. Small quantities of acetate and formate were also produced, with the greatest concentrations at the end of the 90 minutes. This is consistent with phenyl malonate not undergoing complete oxidation under the reaction conditions used.

Table 3. Product data for WAO of malonate, methyl malonate, ethyl malonate and phenyl malonate.

Organic compound	Concentration (g OC/L) of products identified after 90 min.				Carbon mass balance (%)
	Formate	Oxalate	Acetate		
Malonate	0.004	0.181	-	0.14	93
Methyl malonate	0.001	0.202	0.060	0.22	107
Ethyl malonate	0.023	0.165	0.102	0.24	120
Phenyl malonate	0.021	0.089	0.035	0.27	na*

Conditions: T=200 °C, synthetic Bayer liquor, [organic] = 0.0096 M, PO<sub>2</sub> = 500 kPa, 800 rpm.

\*Mass balance not available as [phenyl malonate] could not be measured by HPLC

### 3.2 Co-oxidation studies

The ability of malonate and the malonate derivatives to co-oxidise succinate was investigated using a 1:1 molar ratio of co-oxidizer to succinate. The results of these tests are presented in Figure 2. All of the malonate derivatives co-oxidised a significant amount of succinate. Malonate and methyl malonate were the most effective, both achieving a succinate removal of about 30%. Phenyl malonate co-oxidised about 22% and ethyl malonate about 17% of the succinate. The trend in extent of succinate oxidation for malonate, methyl malonate and ethyl malonate is consistent with the trend observed for the extent of oxidation observed for these three compounds when oxidised in isolation. These results for phenyl malonate indicate that the degree of phenyl malonate removal inferred from the measured reaction products in Section 3.1 was probably an under-estimate, and that there were other products of reaction that were not measured in the oxidation work described there.

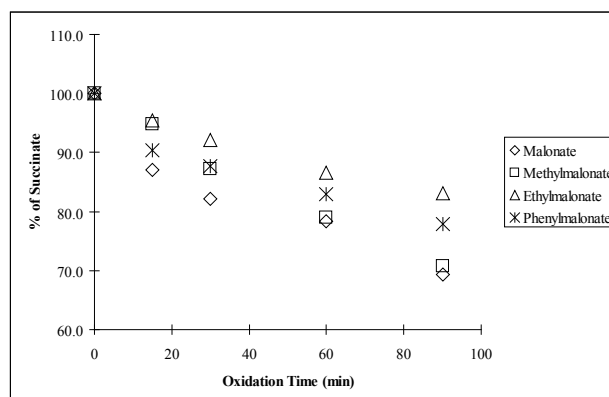


Figure 2. Effect of malonate derivatives on succinate. Conditions: T=200 °C, synthetic Bayer liquor, [malonate derivative] = 0.0096 M, [succinate] = 0.0096 M, PO<sub>2</sub> = 500 kPa, 800 rpm.

The extent of oxidation of the co-oxidant compounds in the co-oxidation tests is presented in Figure 3. From the data presented in Figure 3 it can be seen that the rate of oxidation of malonate, methyl malonate and ethyl malonate was significantly reduced in these tests. These results indicate that the oxidation of these compounds in isolation occurs at least partially by an auto-oxidation mechanism in which free radical intermediates that are produced initiate the oxidation of their parent compound, and that the oxidation of succinate consumes free radical intermediates that would otherwise react with the co-oxidant.

The extent of the decrease in extent of oxidation of the co-oxidant compounds during co-oxidation varies somewhat. After 90 minutes, the degree of oxidation of malonate, methyl malonate and ethyl malonate were about 20%, 30% and 50% less in the

presence of succinate than they were alone. The reduction in the rate of oxidation of the individual co-oxidants as influenced by succinate can be explained in terms of a competition between succinate and the parent co-oxidant for reaction with the free-radicals produced in the reaction of the co-oxidants with oxygen. The degree of reduction in oxidation of the co-oxidants between the parent co-oxidants is most likely related to the relative stabilities of the intermediates and their abilities to react with both the parent co-oxidant and succinate. The free radical intermediates produced from succinate would most likely be very similar to the intermediates shown in reaction scheme 1 and so can be expected to initiate the oxidation of other organic compounds via hydrogen abstraction. It is possible that reaction of succinate-based radical intermediates with methyl and ethyl malonate may be susceptible to a higher level of steric hindrance due to their larger size in relation to malonate, which could explain the decrease in the extent of oxidation for these compounds in comparison to malonate in the co-oxidation tests.

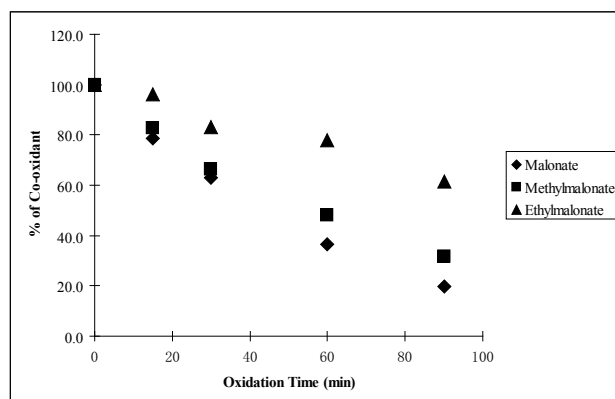


Figure 3. Effect of succinate on extent of oxidation of malonate and malonate derivatives. Conditions: T=200 °C, synthetic Bayer liquor, [malonate derivative] = 0.0096 M, [succinate] = 0.0096 M, PO<sub>2</sub> = 500 kPa, 800 rpm.

The rates of formation of reaction products identified from the co-oxidation tests were broadly similar to those observed in the tests on the co-oxidants alone. The main differences observed were the production of acetate and a higher amount of formate in the malonate / succinate test, and increased amounts of formate and acetate in the tests using the malonate derivatives. These results indicate that acetate and formate may be produced from the oxidation of succinate as well as from the co-oxidizers.

#### 4. Conclusions

Malonate, methyl malonate, ethyl malonate and phenyl malonate are oxidised quickly under Bayer like (highly alkaline) conditions using relatively mild WAO conditions (200 °C, p=500 kPa), whereas succinate does not undergo any appreciable oxidation under the same conditions. The ease of oxidation of malonate, methyl malonate, ethyl malonate and phenyl malonate is most likely due to these compounds containing one or more slightly acidic alpha hydrogen(s). WAO of malonate, methyl malonate, ethyl malonate and phenyl malonate produces highly reactive free radical intermediates capable of co-oxidising succinate. The extents of co-oxidation obtained using these co-oxidizer compounds are closely linked with the extent of oxidation of the co-oxidizer itself.

Further investigations focussing on the type(s) of free radical intermediates produced during WAO of malonate, methyl malonate, ethyl malonate and phenyl malonate would give a greater understanding of the chemistry of these intermediates. This knowledge is important in the development of WAO as an effective, economical process for removing organic contaminants from Bayer liquor.

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