Rules and Mechanism for the Oxidation of Lignin-based Aromatic Aldehyde under Alkaline Wet Oxygen

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To explore the extensive oxidative mechanism of syringaldehyde, vanillin, and *p*-hydroxybenzaldehyde during the alkaline wet oxidation process (AWOP), the yield of these aromatic aldehydes from AWOP at various temperatures and reaction times was studied. The results showed that the aromatic aldehydes could not be converted into the corresponding aromatic acids during the AWOP, and that the aromatic aldehyde was stable when subjected to the oxygen-free AWOP. However, as the reaction temperature increased or the number of methoxyl groups on the aromatic ring increased, the yield of aromatic aldehyde sharply decreased during the AWOP. The reason for the decreased yield was that the aromatic aldehyde underwent ring-opening reactions. The possible mechanism of the degradation indicated that the number of methoxyl groups on the phenolic ring determined the stability of the key intermediate of this reaction. The conversion of isoeugenol to vanillin during the AWOP at 60 ºC was > 99%, and the vanillin yield and selectivity were both 69.8%, indicating that the decrease in yield of the product from this degradation of lignin substrate and the product can be reduced or avoided in the AWOP at suitable temperature.

INTRODUCTION

With the shortage of petroleum resources, the preparation of fuels and chemicals using renewable lignocellulosic biomass resources has become a hot research topic (Liao *et al*. 2018; Duas *et al*. 2019). The conversion of lignin into high value-added products is in line with the concept of biorefining, which calls for the utilization of the three major lignocellulosic components (cellulose, hemicelluloses, and lignin) efficiently (Ragauskas *et al*. 2014; Anderson *et al*. 2016; Beckham *et al*. 2016; Rinaldi *et al*. 2016). At present, the application research of lignin is mainly divided into two categories: one class examines lignin macromolecules for modification and utilization; and the other class examines the decomposition of lignin into small molecules that are used as high value-added chemicals (Deng *et al*. 2008a; Milczarek and Inganas 2012). The chemical methods of lignin depolymerization mainly include acid hydrolysis, alcoholysis, hydrogenolysis, pyrolysis, oxidation, enzymatic hydrolysis, *etc*. The most studied methods are pyrolysis, hydrogenolysis, and oxidation of lignin (Deng *et al*. 2008a; Zakzeski *et al*. 2010; He *et al*. 2012; Ma *et al*. 2014; Asatryan *et al*. 2017; Thanh *et al*. 2017).

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Three main commercial aromatic aldehydes, such as syringaldehyde, vanillin, and *p*-hydroxybenzaldehyde, can be obtained from the alkaline wet oxidation process (AWOP) treatment of lignin using oxygen. These aromatic aldehyde compounds are widely used as spices, medicine, and chemical intermediates (Bjorsvik 1999; Sales *et al.* 2004, 2006; Deng *et al.* 2008b). Conventionally, the aromatic aldehyde is directly obtained from lignin under a basic oxygen atmosphere of 120 to 160 °C (Sales *et al.* 2004, 2006, Wu and Heitz 1995). The process starts with the formation of an enol ether intermediate, *i.e.* lignin-based α-olefin by the cleavage of the α-OH or α-O-4 ether bond during AWOP. After the enol ether intermediate is formed, a dioxetane intermediate will be formed to trigger the cleavage between Cα-Cβ to generate an aromatic aldehyde and an ester derived from the β-O-4 ether (Gierer 1982; Gierer and Nilvebrant 1986, Tarabanko et al. 1995a-b, 2000). It is clear that this ester is easily hydrolyzed under alkaline conditions, leading to the cleavage of the β-O-4 bond. The mechanism of lignin oxidation to aromatic aldehydes is described in detail at Fig. 4 in the discussion section of this article. The reason of the temperature of AWOP at 120 to 160 °C may be that this temperature can reach the activation energy of the cleavage of the α-OH or α-O-4 ether bond to generate a double bond.

During the oxidation of lignin to form the aromatic aldehyde, the degree of condensation of lignin from different sources has a significant impact on the yield of aromatic aldehyde produced by lignin (Pinto *et al.* 2011). The condensation of lignin comes mainly from the following two aspects: one comes from the process of its biosynthesis inside the biomass; the other comes from the process of separating lignin from the biomass. Obviously, the condensation during biosynthesis cannot be avoided, but the condensation during the extraction of lignin from biomass can be avoided or reduced (Li and Basudeb 2017).

Furthermore, the profiles of yield of these three aldehydes versus time from AWOP of lignin indicated that the yield shows an initial increase followed by a declining trend (Pacek *et al.* 2013; Pinto *et al.* 2011; Sales *et al.* 2004, 2006). This trend can be attributed to the fact that these three aldehydes are the result of the equilibrium between the formation of the aldehydes from lignin and the extensive oxidative degradation of the three aldehydes themselves (Pinto *et al.* 2011, Sales *et al.* 2004, 2006). The reason for the trend to increase in the initial period can be attributed to the fact that the rate of formation of aromatic aldehydes from lignin by oxidation is greater than the degradation rate of aromatic aldehydes. The trend of decline in the later period maybe because the degradation rate of aromatic aldehydes is greater than its formation rate.

The extensive oxidative degradation of the aromatic aldehyde and even the degradation of lignin substrate before conversion to aromatic aldehydes affect the yield of aromatic aldehydes by affecting this balance, and the products of the degradation are acid, carbon dioxide, and water, which are formed from the ring-opening reaction of the aromatic ring (Sales *et al.* 2004, 2006). The yield of aromatic aldehyde from lignin by alkaline nitrobenzene oxidation (NO) of is 5 to 10 times that from the same lignin by the AWOP (Tarabanko *et al.* 2004).

Although no one has proposed the reason for the huge difference between AWOP and NO, it can be speculated that there is no such degradation in the NO process or very little if any. At least this huge gap gives the possibility and potential to improve the yield of aromatic aldehydes by AWOP.

Based on the above analysis, the condensation of lignin generated during the extraction and the extensive oxidative degradation of the lignin substrate and the aromatic aldehyde product during the AWOP seriously hinders the possibility of achieving high

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yield of aromatic aldehyde from AWOP. 4-methylguaiacol, one of the products of hydrogenolysis of lignin, can be oxidized to vanillin (Zhao 2010; Ma et al. 2017). This process can reach a conversion of 100% and selectivity of 90% by Co-salt/NaOH catalytic system (Liu *et al.* 2017) at 80 °C. This shows that finding the right conditions can reduce or avoid this extensive oxidative ring-open degradation. It can be seen from the above mechanism (Fig. 4 in dicussion section) that the aromatic aldehydes are all converted from the α-olefin intermediate of the lignin side chain (Tarabanko *et al.* 1995a-b, 2000). And these degradations were caused by the ring opening of aromatic rings, as speculated (Sales *et al.* 2004, 2006). It is clear that the aromatic ring is more stable than the α-olefin intermediate of the lignin side chain. Therefore, finding an appropriate temperature in the AWOP of the lignin monomer with α-olefin in the side chain has the possibility to ensure that this temperature can provide the activation energy for the oxidation of the side chain and is lower than the activation energy for the ring-opening degradation of the aromatic ring.

To conclude, the old method of coupling of the conversion of lignin to lignin-based α-olefin and the oxidation of the α-olefin to aromatic aldehydes at 120 to 160 °C have been shown to be unable to avoid the extensive oxidative degradation. Therefore, even the use of natural lignin in AWOP cannot avoid the reduction in yield caused by its extensive oxidative degradation. However, Li *et al.* (2016) reported a method for extracting uncondensed lignin with FA stabilization during extracting process, and nearly 50% monomers can be obtained through hydrogenolysis from this lignin. The compounds 4-ethylguaiacol, 4-ethylphenol, 4-ethylsyringol, 4-propylguaiacol, 4-propylphenol, 4-propylsyringol, dihydrocoumarol, dihydroconiferol, and dihydrosinolate are major hydrogenolysis products (Li *et al.* 2016).

These monomers have the potential to be converted to lignin monomers with α-olefin in the side chains. Therefore, the conversion of monomers obtained from the hydrogenolysis of uncondensed lignin into monomers of lignin-based α-olefin in side chain as lignin substrate for AWOP has the possibility to avoid the reduction in yield caused by condensation and extensive oxidative degradation. Although the highly selective conversion of these lignin-based hydrogenolytic monomers to lignin-based α-olefins is a huge challenge, it is at least a tempting direction.

Therefore, it is important to study the extensive oxidative degradation of lignin or lignin analogs in AWOP. The three aldehydes were used as lignin models or lignin analogs. At the same time, iso-eugenol was used as a model to verify the availability that the structure of this lignin-based α-olefin can avoid extensive oxidative degradation and achieve a high yield of aromatic aldehydes in AWOP. This study will help the selective oxidation of lignin hydrogenolysis products to aromatic aldehydes, and reduce the yield reduction caused by ring-open degradation. At the same time, in many oxidation reactions of lignin, to avoid this degradation, the phenolic hydroxyl group is protected with a methylating agent and the methyl group is removed after the oxidation reaction is completed. This process is tedious (Rahimi *et al.* 2013, 2014; Wu *et al.* 2019). Therefore, this study has certain reference value for the direct oxidation of lignin or lignin analogs without the protection of the phenolic functional groups by methylation, which avoids the oxidative degradation of lignin itself.

EXPERIMENTAL

Materials

Syringaldehyde, vanillin, *p*-hydroxybenzaldehyde, and isoeugenol were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Other reagents were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China).

Methods

Various aldehydes in AWOP

The alkaline wet oxygen oxidation reaction of the aromatic aldehyde was completed in a 2-L stainless steel WHFSK-2 reactor (Weihai Auto Control Reactor Co., Ltd., WeiHai, China). The reaction conditions of the AWOP were as follows: the concentration of NaOH was 2 mol/L and the initial concentration of various aldehydes was 30 g/L. After adding 1500 mL of the reaction solution to the reaction vessel, the reaction vessel was closed and the mixer was started at 400 rpm. Then, the reactor was purged with a small amount of nitrogen, which was followed by the reactor being heated to the reaction temperature.

After reaching the reaction temperature, nitrogen was introduced to make the total pressure reach 1.5 MPa, which was then quickly increased to 2.0 MPa with oxygen addition; oxygen was continuously supplied during the reaction to maintain the total pressure (which kept the partial pressure of oxygen to approximately 0.5 MPa). The moment oxygen entered was calculated as the zero of the reaction. A 5 mL sample was taken at specific time intervals during the reaction, and 1 mL solution of these samples was added to a 100-mL volumetric flask. Then, a methanol solution containing 3% acetic acid was added to the flask to a volume of 100 mL. The sample after constant volume was then filtered through a 0.22-µm organic filter and detected by high-pressure liquid chromatography (HPLC). Each condition was repeated three times.

Various aldehydes in AWOP without oxygen addition

With the exception that no oxygen but nitrogen was introduced directly to 2 MPa during the reaction, other reaction conditions and procedures were the same as described in the previous section. The sample was not taken during the reaction, and the reaction was quenched by cooling the circulating water after the specified time elapsed. After the reactor was cooled, the liquid was removed from the reaction vessel and was placed in a 2000-mL volumetric flask that was diluted to a constant volume with the addition of purified water. The sample in the flask was then taken out, diluted, filtered, and detected by HPLC as stated earlier. Each condition was repeated three times.

Isoeugenol to vanillin in AWOP

With the exception that the sample was not taken during the reaction, other reaction conditions and procedures were the same as described earlier. The reaction was quenched by cooling the circulating water after the specified time elapsed. After the reactor was cooled, the liquid was removed from the reaction vessel and placed into a 2000-mL volumetric flask that was diluted to volume with purified water addition. The sample in the flask was then taken out, diluted, filtered, and detected by HPLC as that of the aromatic aldehydes described earlier. Each condition was repeated three times.

HPLC analysis

The HPLC analysis was performed using an Agilent 1200 series liquid chromatograph (Agilent Technologies, Santa Clara, CA, USA) equipped with a Wonda Cract ODS2 column (250×4.6 mm^2) (Shimadzu Corp., Kyoto, Japan) and an ultraviolet (UV) detector to qualitatively and quantitatively analyze each product. The mobile phase was a mixed solution of 3.0% aqueous acetic acid and methanol in an 85:15 ratio. The column temperature was set to 30 °C, and the UV detection wavelength was set to 280 nm. The flow rate of the mobile phase was set to 1.0 mL/min, and the sample injection amount was 10 μL.

RESULTS AND DISCUSSION

Yield Variation of Aromatic Aldehydes and Aromatic Acids in AWOP

Variation of p-hydroxybenzaldehyde and p-hydroxybenzoic acid in AWOP

The yields of *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid during the AWOP at various reaction temperatures varied with reaction time are shown in Fig. 1. As shown in Fig. 1, the yield of *p*-hydroxybenzaldehyde did not change at 80 ℃, 100 ℃, and 120 ℃, *i.e.*, the yield from the samples removed in each time interval of these reactions over 5 h did not substantially change. A small amount of yield change of hydroxybenzaldehyde occurred with the reaction time at 140 ℃ where the yield of hydroxybenzaldehyde decreased 10.5% after 5 h. The yield of *p*-hydroxybenzaldehyde decreased 14.5% after 3 h at 160 °C. Synchronous detection of *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid revealed that the yield of *p*-hydroxybenzoic acid was 0% at any time in AWOP; in other words, *p*-hydroxybenzaldehyde can't be oxidized to the corresponding *p*-hydroxybenzoic acid at any time under AWOP.

Variation of vanillin and vanillic acid in AWOP

The yields of vanillin and vanillic acid during the AWOP at various reaction temperatures varied with reaction time are shown in Fig. 2. The yield of vanillin taken at various times during the 5-h reaction at 80 °C and 100 °C did not substantially change. After 5 h, the yield of vanillin decreased 11.4% and 23.9% at 120 °C and 140 °C, respectively. The yield of vanillin decreased 29.8% after 3 h at 160 °C, which was larger than the 11.5% of *p*-hydroxybenzaldehyde at the same condition. As with *p*-hydroxybenzaldehyde, the simultaneous detection of vanillin and vanillic acid found that the yield of each aromatic aldehyde oxidized to the corresponding aromatic acid was 0% at any time in AWOP.

Variation of syringaldehyde and syringic acid in AWOP

The yields of syringaldehyde and syringic acid during the AWOP at various reaction temperatures varied with reaction time are shown in Fig. 3. As shown, the decrease of yield of syringaldehyde at various temperatures was more noteworthy than that of *p*-hydroxybenzaldehyde and vanillin at the same conditions. Syringaldehyde was reacted for 5 h at 80 ℃, 100 ℃, 120 ℃, and 140 ℃, and the yield of syringaldehyde decreased 22.1%, 42.7%, 58.6%, and 76.5%, respectively. The yield of syringaldehyde at 160 °C decreased more remarkably than that at the other temperatures; the yield of syringaldehyde decreased to 0 after 150 min.
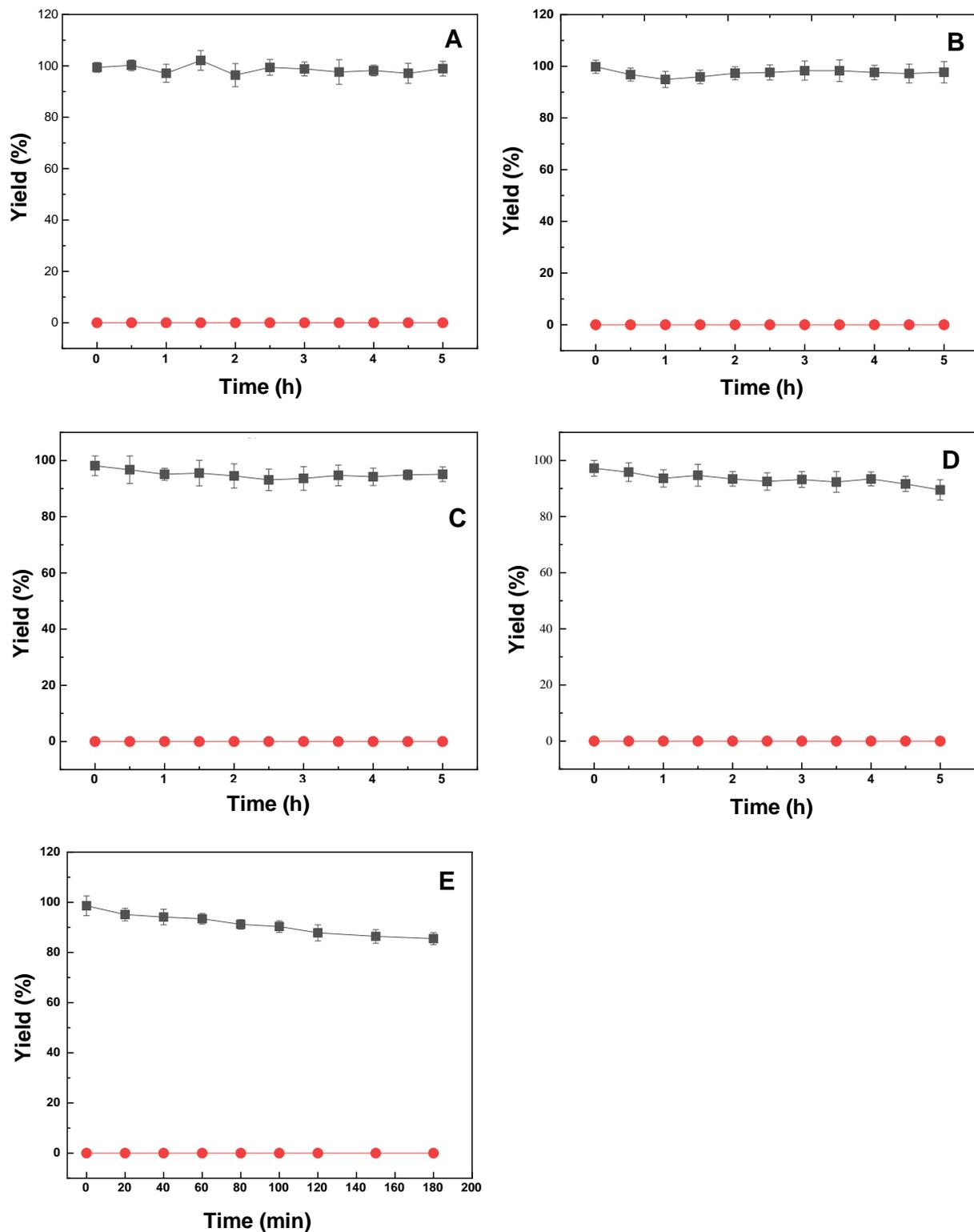
Fig. 1. The yield of *p*-hydroxybenzaldehyde (-■-) and *p*-hydroxybenzoic acid (-●-) at 80 °C (A), 100 °C (B), 120 °C (C), 140 °C (D), and 160 °C (E) *versus* reaction time for the oxidation of *p*-hydroxybenzaldehyde
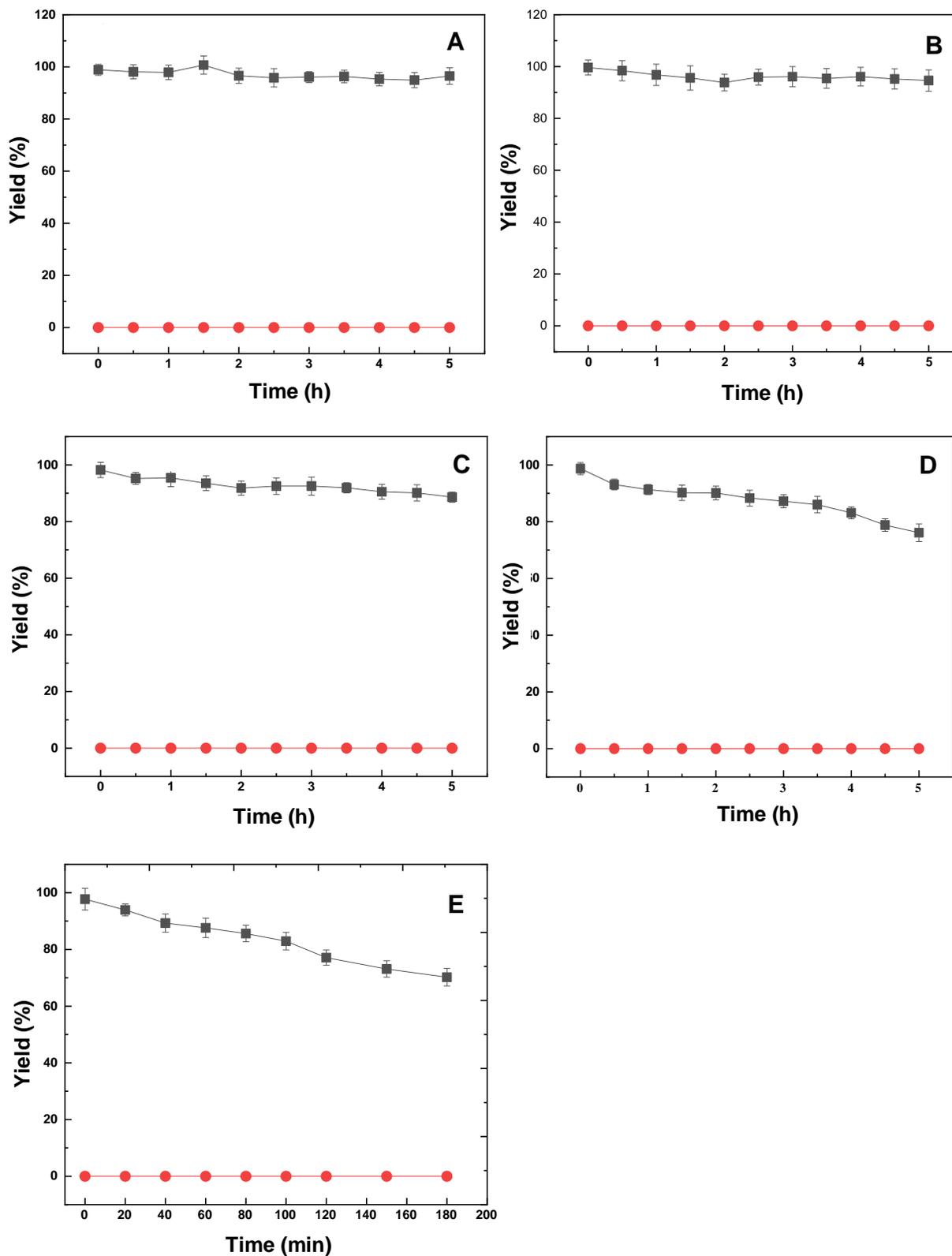
Fig. 2. The yield of vanillin (-■-) and vanillic acid (-●-) at 80 °C (A), 100 °C (B), 120 °C (C), 140 °C (D), and 160 °C (E) *versus* reaction time in the oxidation of vanillin

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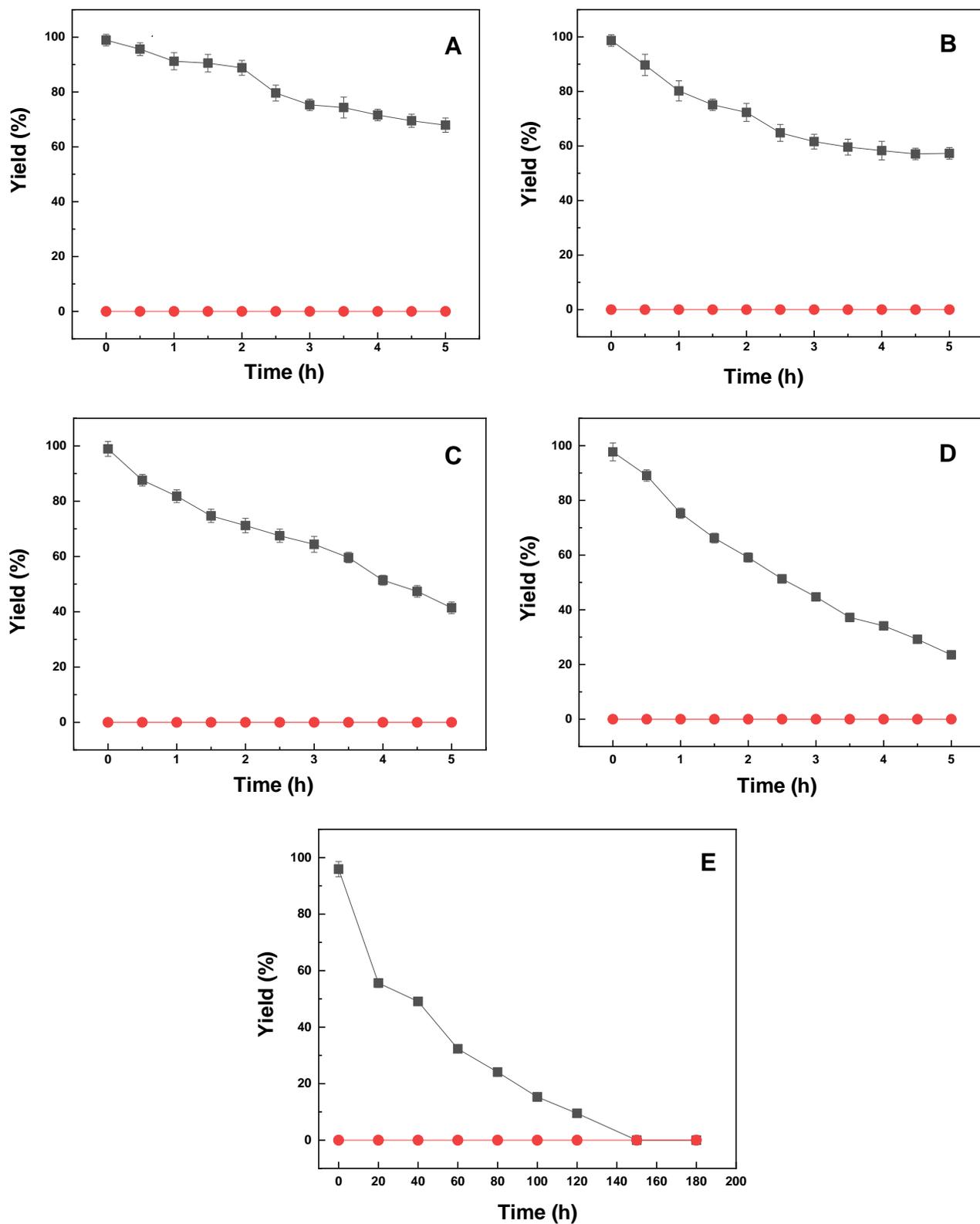
Fig. 3. The yield of syringaldehyde (-■-) and syringic acid (-●-) at 80 °C (A), 100 °C (B), 120 °C (C), 140 °C (D), and 160 °C (E) *versus* reaction time for the oxidation of syringaldehyde

As with *p*-hydroxybenzaldehyde and vanillin, the simultaneous detection of syringaldehyde and syringic acid failed to show the presence of any syringic acid, which further confirmed that the aromatic aldehydes could not be oxidized to the corresponding aromatic acids using this reaction system. This also indicated that the aromatic acid obtained by the oxidation of lignin might not be produced by the aromatic aldehyde intermediate.

Yield Variation of Aromatic Aldehydes during Oxygen-free AWOP

The *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde were subjected to oxygen-free AWOP for 5 h at 80 °C, 100 °C, 120 °C, and 140 °C or for 3 h at 160 °C (Table 1). The yields of various aldehydes did not change substantially in the absence of oxygen after 5 h or 3 h of the reaction (Table 1). To save the number of detections, the analysis was not taken at time intervals during each reaction, but the maximum time for each reaction time in Figs. 1 to 3 was selected as the reaction time of the blank reference experiment. These results indicated that these aldehydes were stable when subjected to oxygen-free AWOP. These results also indicated that these decreases of aromatic aldehydes in AWOP were themselves further oxidized by the addition of oxygen.

Table 1. Yield of Aromatic Aldehydes during Oxygen-free AWOP

T (ºC)	Yield (%)		
	p-Hydroxybenzaldehyde	Vanillin	Syringaldehydein
80	98.3 ± 2.3	98.8 ± 2.7	97.7 ± 2.6
100	98.7 ± 2.8	98.1 ± 2.9	96.9 ± 3.9
120	98.6 ± 2.3	97.2 ± 3.2	97.1 ± 4.2
140	99.1 ± 3.1	97.9 ± 2.1	96.2 ± 4.1
160[#]	97.3 ± 2.7	98.4 ± 3.3	94.7 ± 4.3

Note: The reaction time of the "[#]" labeled reaction was 3 h, whereas the reaction time of the other reactions in this table was 5 h. To save the number of detections, the analysis was not taken at time intervals during each reaction, but the maximum time for each reaction time in Figs. 1 to 3 was selected as the reaction time of the blank reference experiment.

Summary of the Laws of Various Aldehydes in AWOP

Reported mechanism for the oxidation of lignin to aromatic aldehydes in AWOP

At present, it is generally known that the AWOP of lignin to aromatic aldehyde is completed by the mechanism of free radicals as shown in Fig. 4(a), which includes a two-step single electron transfer (Gierer 1982; Gierer and Nilvebrant 1986; Tarabanko *et al.* 1995a-b, 2000). First, the lignin structural unit (1A) undergoes a dehydration reaction to obtain a phenolic anion of an enol ether (1B). The oxygen in the solution captures an electron of the phenolic anion (1B) to form an $^\bullet O_2^-$; while 1B is converted into a phenolic radical (1C), which is immediately rearranged to a quinone methide free radical (1D). This quinone methide free radical (1D) is easily attacked by $^\bullet O_2^-$ to produce a quinone methide peroxide anion (1E), which is rapidly converted into a phenolate dioxetane (1F). This dioxetane rapidly breaks at the C_α-C_β bond and the O-O bond simultaneously to obtain an aromatic aldehyde anion (1G) and an ester (1H) derived from the β-O-4 ether. It is clear that this ester is easily hydrolyzed under alkaline conditions, leading to the cleavage of the β-O-4 bond to yield an acid (1I) and a lignin monomer (1J). Throughout the course of the reaction, the formation of the quinone methide free radicals, 1C or 1D, and quinone methide hydroperoxide (1E) are the rate-determining steps throughout the reaction.

From the above mechanism in Fig. 4, it can be known that the β-O-4 ether bond is not directly broken but is broken by being oxidized to an ester and then saponified. This mechanism is based on the mechanism of oxygen bleaching of cellulose in alkaline media from the basis of Gierer's works (Gierer 1982; Gierer and Nilvebrant 1986; Tarabanko *et al.* 1995a-b, 2000). As is well known, industrial oxygen bleaching of cellulose is at 90 to 105 °C. By contrast, a typical AWOP occurs within the range 120 to 160 °C in a 2 mol/L sodium hydroxide solution. While β-O-4 ether is easily broken directly to yield lignin monomers in this system, meanwhile these monomers will repolymerize (Li and Basudeb 2017). The previous analysis shows that this condensation reaction will reduce the yield of aromatic aldehydes. However, the reduction in yield caused by the condensation produced during this AWOP has been ignored. To the best of the authors' efforts, such a study was not found. The above analysis again shows that the old method of coupling of the conversion of lignin to lignin-based α-olefin and the oxidation of the α-olefin to aromatic aldehydes hinders the achievement of high yield when obtaining aromatic aldehydes by AWOP.
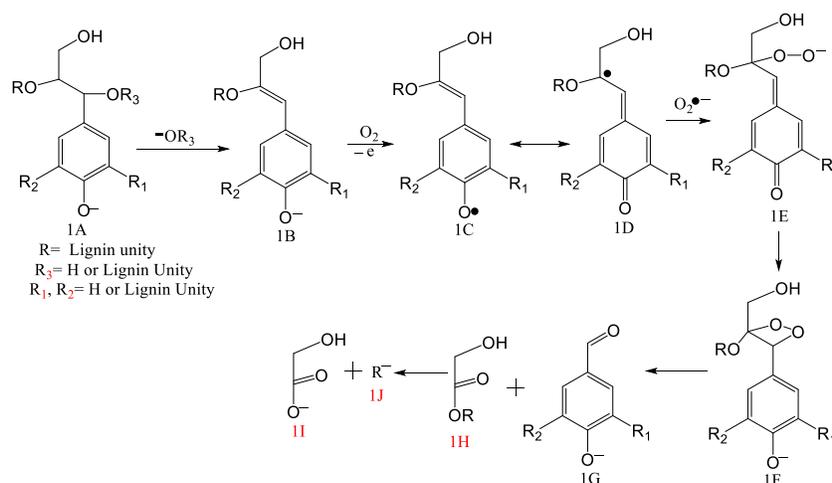
Fig. 4. The reported mechanism for the oxidation of lignin to aromatic aldehydes (Gierer 1982; Gierer and Nilvebrant 1986; Tarabanko *et al.* 1995a-b, 2000).

Reported mechanism of ring-opening degradation of lignin during AWOP

The yield of *p*-hydroxybenzaldehyde exhibited minimal change under the alkaline wet oxygen process at 80 °C, 100 °C, and 120 °C after 5 h. The same minimal change occurred during the oxygen process of vanillin at 80 °C and 100 °C after 5 h, while the yield of syringaldehyde decreased 38.4% at 80 °C after 5 h. The yield of *p*-hydroxybenzaldehyde and vanillin at 160 °C for 5 h decreased 14.5% and 29.8%, respectively. The syringaldehyde was completely degraded at 160 °C for 2.5 h, which was more noticeable than that of *p*-hydroxybenzaldehyde and vanillin. These results indicated that the order of stability was *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde at the same conditions as noted in Figs. 1 through 3; this observation was consistent with the results reported in the literature (Sales *et al.* 2004, 2006; Pinto *et al.* 2011; Pacek *et al.* 2013). However, the oxidation of the aromatic aldehyde did not result in the corresponding aromatic acid. Therefore, the extensive oxidation of the aromatic aldehyde under an oxygen atmosphere possibly occurred on the aromatic ring and not in the side chain.

However, the mechanism of oxygen bleaching of cellulose in alkaline media from Gierer revealed that the lignin-based substances, including the aromatic aldehydes obtained from the pathway of Fig. 4, would be degraded according to the mechanism shown in Fig. 5a (Gierer 1997). It can be seen from Fig. 5a that this degradation is carried out through two paths that respectively produce muconic compound (2F) or oxirans intermediate (2J). Since the mechanism of lignin to aromatic aldehydes is also derived from the Gierer's works, it is reasonable to adopt his mechanism for the degradation of lignin unit or analog (including aromatic aldehydes).
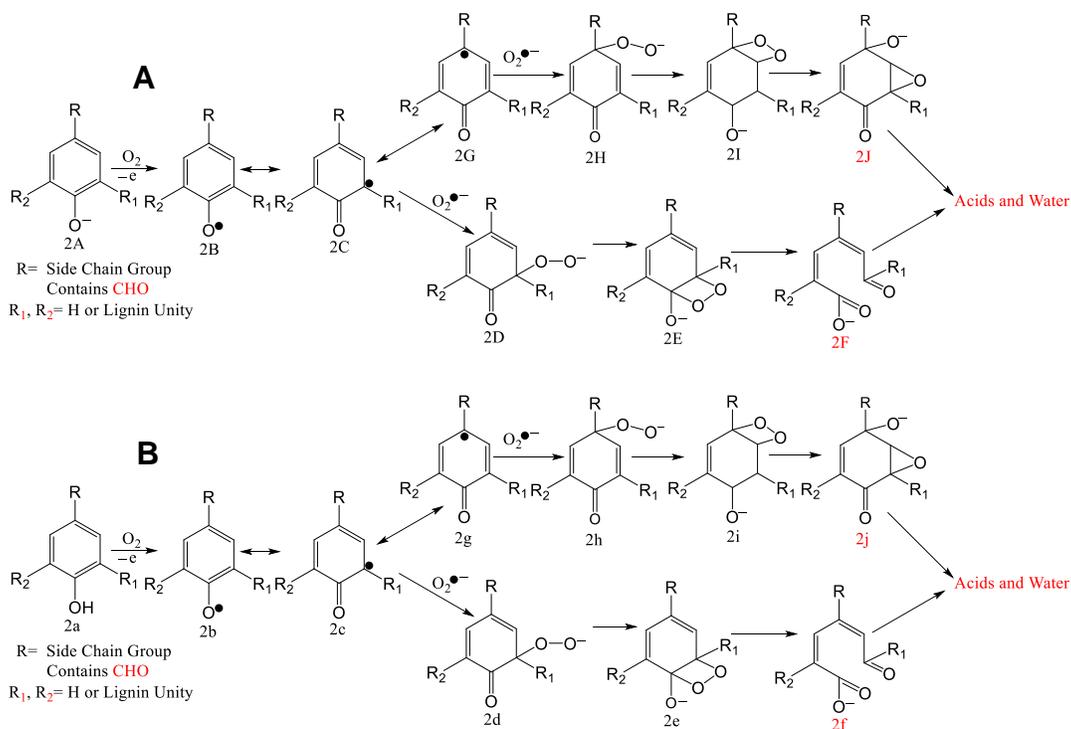
Fig. 5. The reported mechanism (Gierer 1997) for the extensive oxidation of aromatic aldehydes during AWOP (a), and the proposed mechanism by the author of the oxygen oxidation process of lignin under non-alkaline conditions (b). Note: to the best efforts of this study, the following has not been determined: why the phenolic group from lignin or its analog is protected by methoxyl groups during the oxygen oxidation process under non-alkaline conditions. It is speculated that the lignin will be degraded by oxidation according to the mechanism as shown in Fig. 5(b) during this process if the phenolic group is not protected.

This mechanism of Fig. 5a in detail is as followers. First, the lignin unit or analog including aromatic aldehyde is ionized as a phenolic anion (2A) in alkaline conditions. The phenolic anion (2A) is oxidized by oxygen in the solution through losing an electron to form a phenolic radical (2B), and the oxygen is converted to an $^\bullet O_2^-$ ion. The phenolic radical (2B) rapidly rearranges to mesomeric forms (2C) that are easily attacked by $^\bullet O_2^-$ ions to produce quinone peroxide anions (2D). 2D is rapidly converted into a dioxetane structure (2E) that rapidly decomposes both the C-C bond and the O-O bond to give an aromatic ring-opened muconic compound (2F). In addition, 2C can also be rapidly rearranged into 2G, which are easily attacked by $^\bullet O_2^-$ ions to produce quinone peroxide anion (2H). 2H is rapidly transformed into a dioxetane structure (2I), which is rapidly

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decomposed to form an oxirans intermediate (2J). Both intermediates 2F and 2J can be further degraded into small molecules of aliphatic acids and water.

According to the previous mechanism of lignin to aromatic aldehyde, it can be known that two intermediates, quinone methide free radicals and quinone methide hydroperoxide, are the decisive steps of the entire reaction. Therefore, it can also be speculated that the formation of phenolic radicals 2B or 2C and quinone peroxy anion (2D) is the determining step in the mucon (2F) route and that the decisive steps in the oxirans compound (2J) route are the generation of 2B or 2G and quinone peroxide anion (2H). The key factor for the generation of 2B, 2C, 2G, 2D, and 2E is the stability of the phenolic ortho-radical. It is clear that having more methoxyl groups leads to a higher electron density of the aromatic ring cloud, resulting in more stable free radical intermediate, and this makes the structure easier for the oxidative ring-opening degradation to occur.

It has not been determined why the phenolic group of lignin or lignin analog is protected by methoxyl groups during the oxygen oxidation process at non-alkaline conditions, as reported in the literature (Rahimi *et al.* 2013, 2014; Wu *et al.* 2019). It is speculated that the lignin will be degraded by oxidation according to the mechanism shown in Fig. 5(b) under this process if the phenolic group is not protected. The mechanism of Fig. 5(b) is similar to that in AWOP in Fig. 5(a) except that oxygen captures one electron from a hydrogen radical of the non-ionized phenolic group rather than from the ionized phenolate anion.

Because oxidative degradation begins with the capture of an electron from a phenolate anion or a hydrogen radical from a phenolic group, many lignin oxidation reactions protect the phenolic functional group by treating it with a methylating agent (Rahimi *et al.* 2013, 2014; Wu *et al.* 2019). Then, the oxidation reaction is completed, and an additional step of demethylation is required.

Application of Extensive Oxidation of Aromatic Aldehyde

Feasibility analysis of reducing or eliminating oxidation degradation of lignin or lignin analog

Based on the above analysis, it is important to obtain a high yield of product from lignin or lignin analog to reduce or avoid the ring-open degradation of the substrate and the product. It is clear the process of protection of the phenolic functional group by methylation is too cumbersome and requires a new non-protective phenolic direct oxidation process. The previous process analysis of yield of various from aldehydes in AWOP in Figs. 1 through 3 show that the lower the temperature, the less the product degrades. This indicates that the degradation of products and substrates can be reduced or avoid under certain conditions. The reason may be that the activation energy required for the oxidative ring-opening reaction is not reached at low temperatures. However, the oxidation of the side chain requires a certain temperature to reach its activation energy. Therefore, the following two conditions must be met to achieve this goal that the decrease of the yield of the product from the extensive oxidative degradation in the oxidation of the side chain of lignin or analog can be reduced or avoid: first, a specific substrate that the activation energy of the side chain oxidation of the lignin or lignin analog is less than that of ring-opening degradation from the substrate and the product, and second, the oxidation is at a temperature between the temperatures required for the activation energy of the two.

The conversion of isoeugenol to vanillin during AWOP can be performed by cobalt porphyrin as a catalyst at 50 °C and 24 h without alkali; the conversion, yield, and selectivity were > 99%, 72.0%, and 72.8%, respectively (Adilina *et al.* 2012). This

indicated that the activation energy for the oxidation of the side chain of this type of structure from lignin by cobalt porphyrin as a catalyst was lower than that of the oxidative ring opening of the aromatic structure of lignin. Although the catalyst can change the activation energy of the reaction, there is also the possibility that the activation energy for the oxidation of the side chain of this type of structure without catalyst is also lower than that of ring-opening degradation of lignin. According to the mechanism of Fig. 4, lignin compounds must be converted to compounds that form a double bond at the *α*, *β*-position of the side chain before the structure can be oxidized to aromatic aldehyde. This indicated that the activation energy for the oxidation of the side chain of this type of structure without catalyst can be reached at low temperatures to avoid ring-opening degradation of lignin.

Therefore, according to the above analysis, if lignin hydrogenolysis products are converted into compounds that form a double bond at the *α,β*-position of the side chain and then are oxidized to aromatic aldehydes at low temperature, it has the possibility to effectively reduce the yield reduction caused by the oxidation degradation. This mechanism was validated by examining isobutyl phenol as a substrate.

Isoeugenol to vanillin in AWOP to verify reducing or eliminating the oxidation degradation of lignin or lignin analog

The yield and selectivity of isoeugenol conversion to vanillin by the reaction at 60 °C for 3 h under an oxygen pressure of 1 MPa are shown in Table 2. It can be seen that the conversion can be as high as > 99%, and the vanillin yield and selectivity were both 69.8%. The results of Table 2 are in good agreement with the results reported by Adilina *et al.* (2012) through AWOP without alkaline. Isoeugenol is oxidized by oxygen to form a coupled dimer as shown in Fig. 6 (Drago *et al.* 1986); therefore, the reason why the selectivity of conversion of isoeugenol to vanillin by AWOP with or without alkaline is not 100% may be attributed to the conversion of isoeugenol to a dimerization reaction as shown in Fig. 6, instead of oxidative degradation of substrate and vanillin.

Table 2. Yield of Vanillin from the Alkaline Wet Oxygen of Isoeugenol

Temp. (ºC)	Conversion (%)	Yield (%)	Selectivity (%)
80	> 99	69.8 ± 1.3	69.8 ± 1.7

Because a small difference was found for the conversion and selectivity of vanillin between that of the reaction in Table 1 and that of the reaction from the reference of Adilina *et al.* (2012), this can confirm what the authors previously inferred, that the presence or absence of a catalyst does not change the activation energy of the oxidation of side chain and the ring opening of the aromatic structure of this compound. Therefore, this observation also confirmed that the activation energy for the oxidation of the side chain in lignin with this type of structure was lower than that of the oxidative ring-opening reaction. It could also be inferred that the conversion of the lignin degradation product to isoeugenol or its analog, which has an *α*-alkene at the *para* position of the phenolic group, can give a high yield of aromatic aldehyde during the AWOP at this temperature.
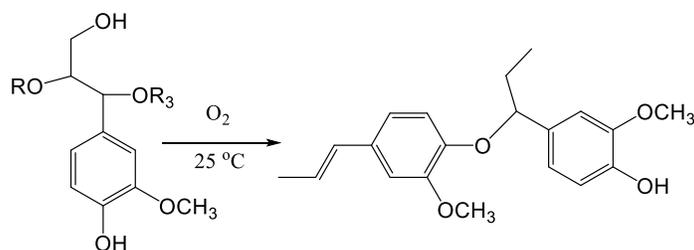
Fig. 6. Reported coupled dimer reaction occurring with the oxidation of isoeugenol (Drago *et al.* 1986)

CONCLUSIONS

1. The extensive oxidative ring-opening degradation of lignin-based substrate and the aromatic aldehyde product during the AWOP of lignin or analog can decrease the yield of aromatic aldehyde. This reduction in yield can be reduced or avoided if the following two conditions are met. First, a specific substrate of the activation energy of the side chain oxidation of the lignin or lignin analog should be less than that of ring-opening degradation from the substrate and the product. Second, the oxidation should occur at a temperature between the temperatures required for the activation energy of the two.

2. As the temperature increased or the number of methoxyl groups on the aromatic ring increased, the yield of aromatic aldehyde sharply decreased during alkaline wet oxidation reaction. The aromatic aldehyde was stable in AWOP without oxygen at the same conditions.

3. The reason for the decrease of yield was that the direct oxidation of the aromatic ring of lignin occurred instead of the conversion of an aromatic aldehyde into the corresponding aromatic acid. The aromatic acid obtained by oxygen oxidation of lignin was not through the intermediate of an aromatic aldehyde.

4. The possible mechanism of extensive oxidative ring-opening degradation of lignin-based substrate and the aromatic aldehyde product during the AWOP indicated that the number of methoxyl groups on the ring determined the stability of the key intermediate of this degradation reaction; *i.e.*, the more methoxy groups on the benzene ring, the more easily this degradation reaction occurs, and more of this degradation leads to a decrease in the yield of the aromatic aldehyde product.

5. The conversion of the reaction was > 99%, and the vanillin yield and selectivity were 69.8%, indicating that this lignin substrate that has *α*-alkene in the *para* position of the phenolic group can meet the structure of lignin substrate required for Conclusion 1.

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