Catalysis Science & Technology

PAPER

Catalytic Oxidation of Lignin-Acetoderivatives: A Potential New Recovery Route for Value-Added Aromatic Aldehydes from Acetoderivatives

Kissa R. Alunga[a], Yue-Yuan Ye[a*], Shui-Rong Li[a], Duo Wang[a], Yun-Quan Liu[a, b*],

Catalytic wet air oxidation (CWAO) of lignin and phenolic composition of waste water is a useful pathway towards the recovery of the valuable compounds. In this study, bamboo lignin was catalytically oxidized to aromatic aldehydes and acetoderivatives; similarly acetovanillone and acetosyringone were oxidized to vanillin and syringaldehyde respectively. A total product yield of 9.5% from bamboo lignin and a vanillin yield of 51% with greater than 90% selectivity from acetovanillone were achieved. The proposed reaction pathways suggest a two-step route towards the formation of value-added aromatic aldehydes from lignin via degradation of acetoderivatives. The kinetics study for the degradation of acetovanillone and formation of vanillin were reported for the first time over the temperature range of 120-150 °C, with the activation energies of 85.29 kJ/mol and 120.7 kJ/mol respectively. To date, CWAO breaks down the lignin polymer and toxic phenolic compounds reasonably and effectively, producing value-added aldehydes, which could become a potential new route for the recovery of value-added products.

Introduction

The world today is facing an all-time high demand for hydrocarbon-derived chemicals despite the recent oil price plummet due to the booming oil and gas production in the US [1]. It is reported that at some point in the near future, all non-renewable chemicals will become exhausted, necessitating a need for the development of alternative renewable sources so that a sustainable utilization of hydrocarbon resources can be achieved [2].

Lignocellulosic biomass, most especially lignin, is a promising renewable material, which is available at a relatively low cost for the production of a range of chemicals [3, 4]. The annual industrial production, mainly from the paper and pulp industry as a non-cellulosic waste, approximates 50 million tons [5, 6]. To date, however, only a limited amount of lignin has been effectively utilised with only 5% of the potentially available lignin being used in commercial applications as low value products, such as concrete additive or low grade fuel [5].

Lignin is a complex and recalcitrant phenolic macromolecule biosynthesized from the phenyl-propane building units of coniferyl, sinapyl and p-coumaryl alcohols [7]. These units are the precursors of guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H) moieties of the lignin structure, respectively [8].

Recently, the demand for the renewable aromatic aldehydes has rejuvenated the interest for the lignin route, most especially the production of vanillin (4-hydroxy-3-methoxybenzaldehyde, $C_8H_8O_3$), an important ingredient used in a variety of industries. In the cosmetology industry, it is applied as a fragrance ingredient in perfumes and creams; in the chemical industry, as an antifoaming agent, vulcanization inhibitor, and chemical precursor; in the pharmaceutical industry, as an odour-masking agent; in the agrochemical industries, as an ingredient in the pesticide formulations applied to the growing crops. In the food industry, it is used mainly as a flavouring agent in ice creams, soft drinks, chocolate, baked confectionery and cheap brandy and whisky, and also as a food preservative in sausages, seasonings, etc. It has also been suggested that vanillin (V) might have certain antioxidant and cancer prevention properties and that it is involved in bacterial cell-to-cell signalling, which potentially increases its value [9, 10, 11].

The synthetic production process of aromatic aldehydes accounts for about 15% from lignin oxidation [12]. However, the lignin oxidation process is characterized by other products besides aromatic aldehydes. They include acetovanillone (AV) and acetosyringone (AS) commonly referred to as acetoderivatives, arising from $C_β-C_γ$

bond cleavage of lignin [8]. Besides, AV is well considered as one of the most representative compounds in the phenolic fraction of the cork processing wastewater [13]. According to Harrison and Priest [14], AV is also particularly abundant in the peat infused whisky from Islay and Orkney in Scotland. Essentially, AV has been reported in the synthesis of AS [15] and V [16], as well as having anti-inflammatory capabilities [17].

CWAO of phenolic compounds and lignin is mostly preferred due to its mild conditions, good selectivity and short reaction time [5] with the application of molecular oxygen as an oxidant owing to its modest price, abundance and environmental friendliness [18]. Various catalysts, such as the homogeneous copper salts have been used in the catalytic oxidation reactions and wood delignification [19]. During the lignin oxidation, Cu(II) is reduced to Cu(I),which is oxidized back to Cu(II) species in the presence of molecular oxygen [20].

Very little in literature is available on the acetoderivative transformation into valuable aromatic aldehydes. The current study thus derives its interest in this regard to investigate their fate during CWAO with the goal of recovering value-added aldehydes. Therefore, the good understanding and appropriate control of acetoderivatives' behaviour during the oxidation process will not only get rid of them along the waste stream, but also enlighten the mechanism of lignin degradation into aromatic aldehydes as well as diversify biorefinery raw materials.

The aim of this work is to explore acetoderivative and bamboo lignin oxidative degradation in alkaline solution utilizing copper sulphate pentahydrate as a catalyst, so that a feasible process could be developed for future applications.

Experimental

Materials

Vanillin (99%), syringaldehyde (98%), acetovanillone (98%), ethyl vanillin (98%), and copper sulphate pentahydrate (99%) were all purchased from Aladdin Industrial Corporation. Acetosyringone (98%) was supplied by Shanghai Macklin Biochemical Co. Ltd. Hydrochloric acid (37%), sodium hydroxide (96%) and ethyl acetate (99.5%) were supplied by the local Lu Yin Co. Bamboo lignin was purchased from Geyi Energy Co. Ltd, which is an alkaline lignin (i.e. it was extracted with alkaline solution from the steam-treated bamboo, and the obtained black liquid was concentrated, and finally the reddish lignin powder was obtained by spray drying of the concentrated black liquid). Before use, the lignin was pretreated by dissolving it in demineralized water, then filtered to remove solid particles, precipitated with dilute HCl, washed several times till pH >5.0, and finally dried for 24 hrs at 55 ℃ in the oven. Pure acetovanillone and acetosyringone were used as model compounds to study their fate during the oxidation process. The oxygen and helium gases were supplied from Linde Gas Co. Ltd., Xiamen.

Methods

Procedures for Alkaline Oxidative Reaction

The batch experiments of lignin and acetoderivative oxidation were carried out in a stainless steel autoclave made by Parr (model 4848, 160 mL) equipped with an automatic temperature control system and mechanical stirring. About 1 g of lignin was dissolved in 30 mL of

alkaline solution (80 g/L of NaOH) by sonication. After full dissolution, the resultant mixture was diluted with alkaline solution until a final volume of 70 mL was reached in a reactor in the presence of catalyst (20% w/w on lignin). The reaction mixture was kept under agitation at 400 rpm. The reaction zone was temperature and pressure controlled. The reaction time started to count when the required temperature set point (170 ℃) was reached, and about 1.5 bars of oxygen was introduced to the reactor. The total pressure in the reactor was kept at 8.5 bars (This was made of two parts - the vapour (H_2O) pressure built up in the system, which is about 7.0 bars, and additional 1.5 bars of oxygen partial pressure filled in). This partial pressure was basically kept constant by the continuous supply of O_2 along the time of the reaction process. In all the experiments, pH remained above 13 after the reaction time. When AV was used as the starting material, similar treatments (Vol.=70 mL, T=170 ℃) were also followed, but with 0.05 g of the material each time.

GC-MS Analysis

Prior to the GC-MS analysis, the liquid in the reactor was collected in a beaker, then acidified to pH 1–2 with dilute HCl to enhance precipitation of non-oxidized lignin and allow recovery of organic compounds in the organic phase. The solid and liquid products were separated by a vacuum filter using a Millipore membrane (0.45 μm pore size). The liquid portion was extracted with an equal quantity of ethyl acetate (50 mL×3) forming two phases which were separated in a separatory funnel. The ethyl acetate solution obtained was dried over anhydrous sodium sulfate, filtered and evaporated at 45 ℃ in a vacuum rotary evaporator.

The ethyl acetate extract was redissolved in the same solvent; about 1.5 mL was obtained for injection into GC-MS for the identification and quantitative analysis. The identification and quantification of the isolated reaction products were carried out on a GC-MS (QP 2010 SE, Shimadzu, Japan) equipped with Rtx-5MS (30 m x 0.25 mm x 0.25 μm) capillary column. The volume of the sample injected was 1 μL with the split ratio of 10:1 and the flow rate of helium employed as carrier gas was 2 mL/min. The injection pressure and temperature were 120.5 kPa and 270 ℃, respectively. The capillary column was heated from 55 ℃, holding for 2 min, to 210 ℃ at a heating rate of 7 ℃/min. The temperature of ion source was 200 ℃, interface temperature was 275 ℃, solvent delay of 2.0 min, and mass scan range was from 35 to 500 m/z. The identification of detected compounds was carried out using the NIST database. Ethyl vanillin (98%) was added to the organic phase as an internal standard for GC-MS quantitative analysis (RRF-Relative Response Factor method).

Quantification of analytes was carried out using the following formulas;

$$Conc.A(g/L) = \frac{PA}{PB} \times \frac{1}{RRF} \times Conc.B \dots\dots\dots\dots\dots\dots(f.1)$$

$$\%Yield = \frac{Conc.A \times Vol.(ml) \times 100}{wt.A(g) \times 1000} \dots\dots\dots\dots\dots\dots(f.2)$$

Where PA and PB are the peak areas of unknown concentration of analyte (A) and known concentration of internal standard (B) respectively

Results and discussion

Bamboo lignin oxidation

$CuSO_4$ as a catalyst has been used in several laboratory lignin oxidation experiments including the commercial production of vanillin via air oxidation of lignosulfonates [21]. In our experiments, the aromatic aldehyde yields obtained were compared with those of the controlled experiments without catalyst as shown Fig. 1. It is clearly observed that there is an increase in the yields of V, AV, SY and AS in the presence of catalyst by about 45%, 60%, 25% and 10%, respectively; and the total product yield of aromatic aldehydes and acetoderivatives was improved from 6.75% to 9.5%, which represented an increase of about 30%.
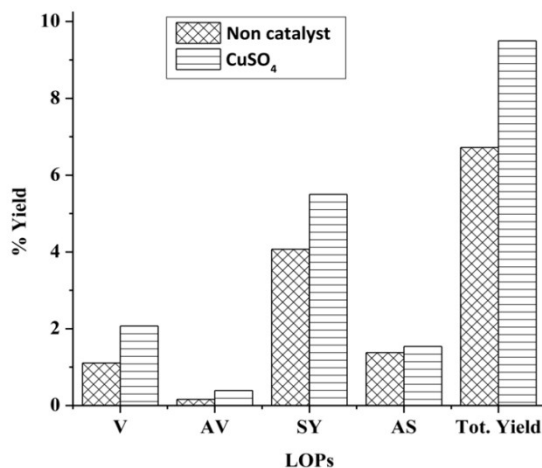

Fig. 1. Yields of aromatic aldehydes in non-catalyzed and $CuSO_4$ catalyzed oxidation of bamboo lignin with oxygen in NaOH solution.

These results indicated that $CuSO_4$ is an effective catalyst for the conversion of lignin into aromatic aldehydes. However, the effect of catalyst on lignin oxidation was rather moderate than that depicted in literature where copper salts used as catalysts are said to improve product yield and selectivity to as high as 100% [22]. This observation can be explained by the presence of impurities such as reducing sugars and protein residues in the bamboo lignin, which consume the active catalyst species as demonstrated by Santos et al. [23] and Boeriu et al. [24].

The significant differences in increment in the yields of lignin oxidized products (LOPs) can be interpreted in terms of the relative oxidation rates of S and G type units in lignin and the extent of secondary reactions of aromatic aldehydes. The oxidation of S units in lignin is much faster than that of G units, therefore, SY and its counterpart AS suffer stronger subsequent degradation than V and its counterpart AV [23]. These conclusions are in agreement with the knowledge of higher reactivity of S-type than G-type lignin units in reactions with oxygen in alkaline media [25]. AV content obtained is less than 1%, and similar results have also been reported by Pinto et al., [26], however, approximately 6.39% AV has been reported in literature [27]. The most probable reason for this is the structural changes due to the more intensive delignification process, lowering the reactive structures [8].

Catalytic oxidation of acetoderivatives to aromatic aldehydes

Under catalytic reactions, AV conversion (Fig. 2a), vanillin yield (Fig. 2b) and catalyst selectivity (Fig. 2d) were significantly enhanced in the catalytic process in a very short reaction time possible. For instance, the AV conversion reached almost 100% in less than 10 min of the reaction. A maximum yield of 30% for vanillin, which is about 4 times the amount obtained in the non-catalytic process, was reached in 5 min followed by a sharp decline to 0% in the next 30 min. However, despite the catalytic improvement in vanillin yield, the catalytic selectivity for the desired product remained low at about 33% with the rest of the product fraction of about 65% (Fig. 2c) unaccounted for.
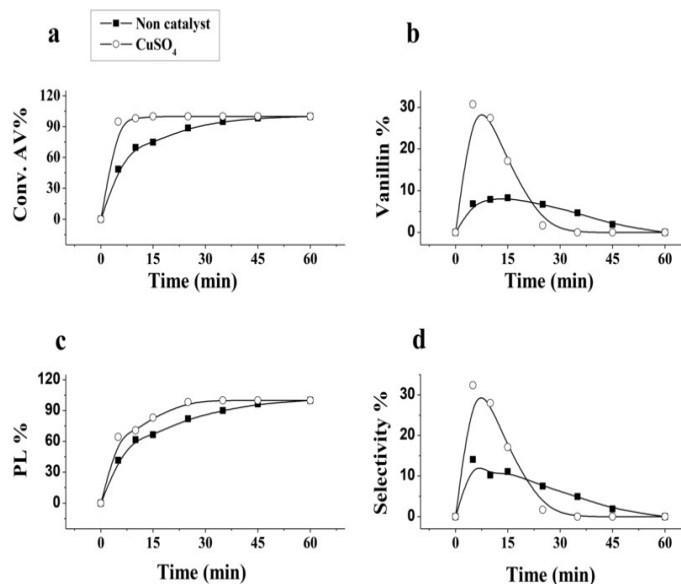

Fig. 2. Variation of acetovanillone conversion (a), vanillin yield (b), product loss (PL) (c), selectivity (d) with reaction time, in comparison to the non-catalyzed (■) and $CuSO_4$ catalyzed (○) processes at conditions; T=170 ºC, C_{AV}=0.7 g/L, P_{O2}=1.5 bars, C_{NaOH}=2.0 mol/L and Catalyst weight=0.01g.

The behaviour of vanillin noticed after 5 min suggested its vulnerability under in situ reaction conditions. Furthermore, we were expecting that any decrease in vanillin would be accompanied by a comparable increase in its oxidized counterpart vanillic acid, but that was not the case, actually vanillic acid was not detected by GC-MS. This suggested that it was also further degraded into low molecular carboxylic acids or oxidized into gases (trace amounts of CO_2 identified by GC).

Generally, the high AV conversion and product loss (unrecovered products) observed with and without catalytic reactions can be explained by the low acetovanillone concentration and by the degradative combined effects of temperature and pressure. Additionally, the observations reflect the occurrence of competitive reaction pathways or continual degradation pathways into low molecular compounds and gasification of compounds [28].

In the experimental reactions conducted without copper catalyst, only a maximum yield of 8% V could be attained. The low yield agrees well with Wu et al.'s [29] conclusion that poor selectivity towards aldehydes is observed in the presence of pure oxygen with no catalyst. Similar reaction conditions were carried out for AS

This journal is © The Royal Society of Chemistry 2015

Catal. Sci. Technol., 2015, **00**, 1-8 | **3**

oxidation, a single qualitative run indicated that there is a possibility of recovering SY from AS (see Fig. 3).
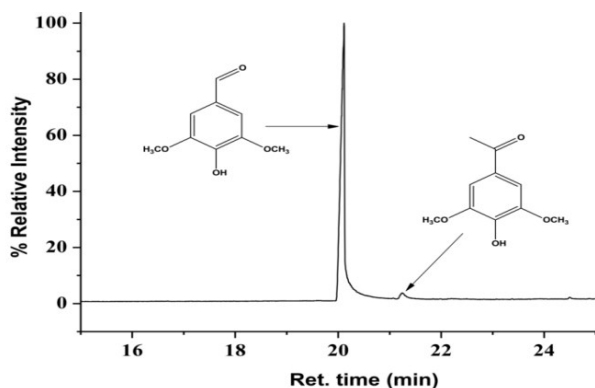

Fig. 3. The GC-MS images of AS and its oxidation product syringaldehyde

Effects of reaction conditions on acetovanillone oxidation

Effects of concentration of acetovanillone

The effects of AV concentration on the catalytic AV oxidation process were conducted by following the same experimental procedures with variation in AV concentration. Raw material concentration is said to play a crucial role as far as its conversion is concerned. Concentration effects of acetovanillone were thus evaluated on the acetovanillone parameters of interest.
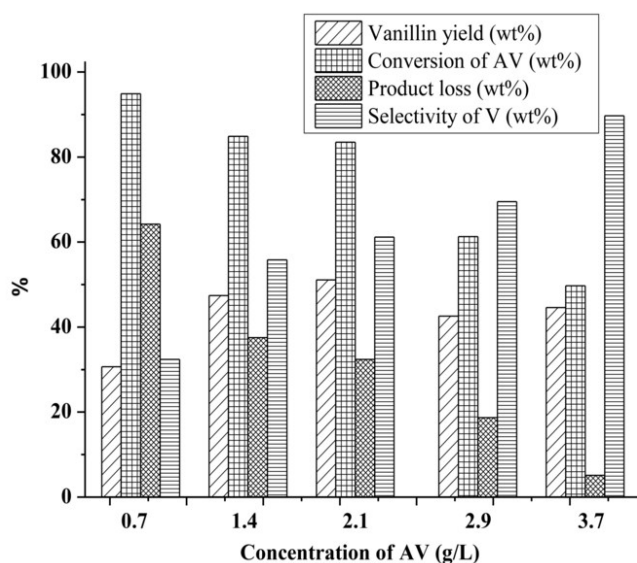

Fig. 4. Variation of vanillin yield, product loss, selectivity of vanillin and conversion of AV, with AV concentration at conditions; T=170 ℃, time=5 min, P_{O2}=1.5 bars, C_{NaOH}=2.0 mol/L and Catalyst amount=0.01g.

The vanillin yield and selectivity, and reduction in the product loss were significantly enhanced with increase in the AV concentration as shown in Fig. 4. In the presence of the catalyst, adjusting of acetovanillone concentration interestingly maneuvered all the parameters being investigated. Selectivity greater than 90% for the

desired product was noticed as compared to that of 33% obtained in Fig. 2d. Clearly, the product loss was significantly reduced from about 60% to 5.1% at a concentration of 3.7 g/L and the V yield increased markedly in proportion from 30% obtained in Fig. 2b to a maximum yield of 51%. On the other hand, the AV conversion was reduced to an acceptable value of approximately 50% from about 95% since much of the products were not recovered at a higher conversion.

Finally, we had successfully achieved two satisfactory process points based on the product yield, product loss and AV conversion. In Coulson and Richardson's Chemical and Biochemical & Process control book [30], if unreacted 'A' can be recovered from product mixture at a low cost and recycled economically, and the reaction can be probably operated economically at quite a low conversion per pass, then a relative yield of 44.6% V with a loss of 5.1% and AV conversion of 50% obtained at a concentration of 3.7 g/L would be preferred. However, if it cannot be recovered and no credit is allotted to it, the operational yield is more relevant and the reactor will probably have to operate at a high conversion per pass. For this case, a yield of 51% V, conversion of 80% AV, and a product loss of 32.4% obtained at a concentration of 2.1 g/L would be preferred.

Effects of alkaline concentration and oxygen partial pressure

The effects of alkaline concentration and O_2 partial pressure were shown in Fig. 5. Alkaline concentration effects were analysed by catalytically oxidizing AV under 0.5-2 mol/L concentrations of NaOH while keeping the other conditions constant. In Fig. 5a, a considerable increment of V was achieved by increasing the concentration of sodium hydroxide but a significant decline in the unreacted AV, implying that the concentration of alkaline solution has a greater influence on acetoderivative degradation. This implies that more phenolic hydroxyl groups in the lignin unit were ionized with increasing basic conditions as pointed out in literature [31]. Secondly, it demonstrated that acetovanillone was degraded into other products with the exception of vanillin.
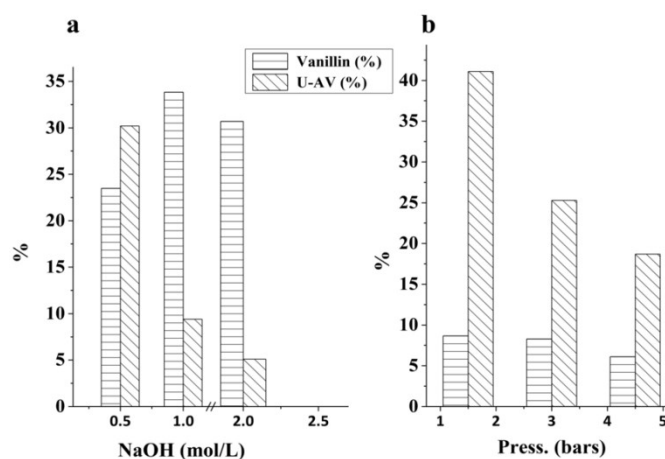

Fig. 5. Effects of alkaline concentration (a) and O_2 partial pressure (b) on the vanillin yield and unreacted acetovanillone (U-AV)

The effect of O_2 pressure was determined without a catalyst and three O_2 partial pressures (1.5, 3 and 4.5 bars) were tested at 170 ℃ for 5 min. Fig. 5b depicts the changes in vanillin and acetovanillone composition with the increasing oxygen partial pressure. A slow decreasing effect was noted on vanillin yield but a faster decline in acetovanillone degradation was observed, suggesting that a different

4 | *Catal. Sci. Technol.*, 2015, **00**, 1-8

This journal is © The Royal Society of Chemistry 2015

reaction mechanism could have operated in our oxidation system due to the higher oxygen solubility at high pressure [32].

The mechanism of acetovanillone oxidation

Several authors have stressed that a clear understanding of actual reaction pathways for lignin oxidation can only be explained by using model compounds for reactions. The possible mechanism proposed herein (see Fig. 6) for acetovanillone oxidation is based on our experimental observations and results, and what has been reported in literature. The phenolic and ring-conjugated structures of both lignin and its models are more reactive with oxygen. These oxidative reactions proceed essentially via radical reaction mechanism. The participating superoxide oxygen species (a.1) are formed during the stepwise and combined reactions of oxidative species formation during oxygen-based autoxidation reactions [31].

$$\cdot O\text{-}O\cdot \rightleftharpoons O_2^{\cdot -} \quad\text{.. (a.1)}$$
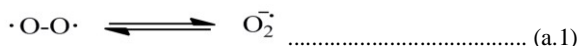
Since oxygen is a weak oxidizing agent in its normal state, the reaction needs basic conditions to ionize free phenolic hydroxyl group to form phenolate anion.

For reaction pathway A (Fig. 6A), a redox reaction is envisaged to be taking place, Cu^{2+} ion is reduced to Cu^{+} by superoxide radical anion, then oxidized back to Cu^{2+} in the presence of molecular oxygen (here, oxygen is activated by Cu^{+} ions [33]). We suspected the proceeding reactions as those proposed by Zhang et al. [33]. In their study, they described a chemo-selective oxidation cleavage of C(CO)-C(methyl) bond of methyl ketones that yields aldehydes through Copper-catalyzed reactions under oxygen in DMSO solvent.

The reaction pathway B in Fig. 6B may be explained by the following account. It has been pointed out several times in literature, for example, by Ma et al. [31], that the peroxy radical formed in eq. (a.1) grabs an electron from phenolate ions forming phenoxy radicals and peroxide anions. Simultaneously, protonation of peroxide anions rises to hydroperoxy radicals, which are known to behave as strong oxidants than molecular oxygen, reacting faster with AV/lignin units. Hydroperoxy radicals will attack carbon in the cyclohexadienone intermediate to form C-O-O-C cyclic peroxide structures. These cyclic structures are known to be unstable, leading to demethoxylation and aromatic ring opening. Consequently, dicarboxylic acids (DCAs) such as muconic acid, muconolactone, maleic acid, succinic acid, and malonic acid are formed [31].
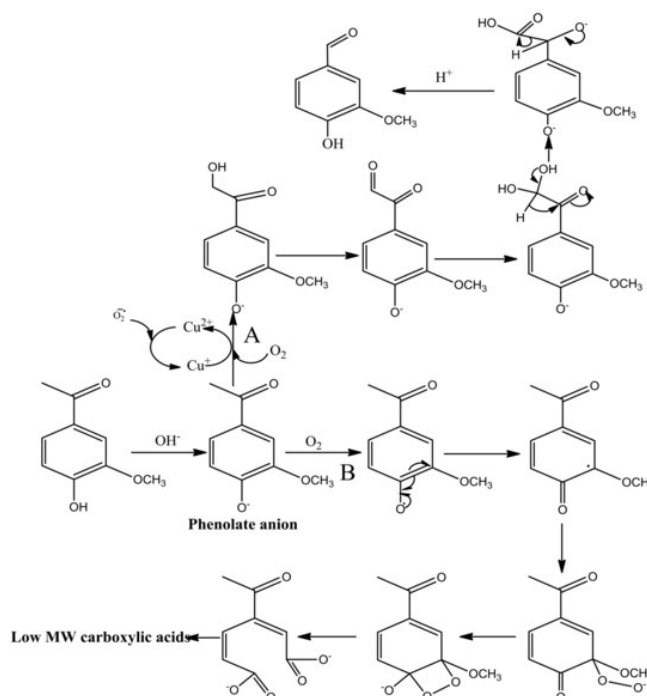

Fig. 6. Plausible reaction mechanisms of acetovanillone oxidation to vanillin

Kinetic studies

So far, we did not find any kinetic studies related to CWAO of AV to V, so we presume this study was reported for the first time. The influence of temperature on reaction rate was investigated in the range of 120-150 °C and initial AV concentration of 3.5 g/L, the other operation conditions were kept constant; 1.5 bars of oxygen pressure, catalyst weight 0.01 g and C_{NaOH}= 2.0 mol/L.

The effect of reaction temperature on AV degradation and V formation under CWAO process is depicted in Fig. 7. As expected, AV was degraded more rapidly as temperature increases. The rate of formation of V decreases as temperature decreases, as well as the time at which the maximum concentration appears i.e. the reaction time relating to the maximum yield of vanillin was systematically shorter as temperature rose.
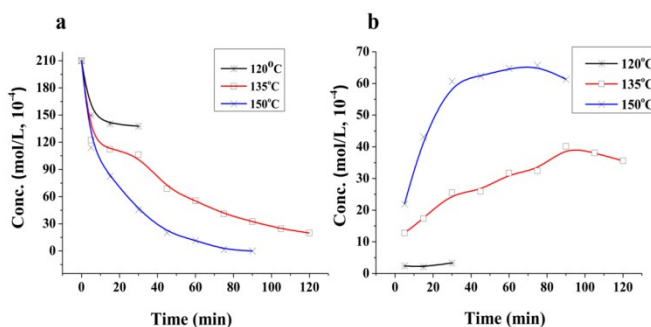

Fig. 7. Concentration-time profiles of AV degradation (a) and V formation (b) during the CWAO process at various temperatures; 120-150 °C

At 120 °C, the reaction was the slowest with maximum V concentration expected after a longer reaction time; at 135 °C, the reaction proceeded moderately, with a maximum V concentration of about 40×10^{-4} mol/L at 90 min; while at 150 °C, AV conversion is almost complete at the same reaction time. However, generally the formation of point $V_{maximum}$ for both temperatures was slow making it a little bit hard to tell the exact turning point.

The kinetics study was carried out under the optimal reaction conditions. These conditions had guaranteed a pseudo-constant alkalinity and oxygen supply along all periods of AV oxidation.

The oxidation of AV at temperature of 170 °C was too fast to hinder the assessment of kinetics study. The effective kinetic parameters were evaluated considering the oxidation of AV as a consecutive reaction, where the oxidation product (V) was assumed to undergo further degradation into low-molecular weight products (D); however, these end products were not detected by GC-MS system.

$$AV \xrightarrow{\ r_1(O_2,OH^{-1})\ } V \xrightarrow{\ r_2\ } D ....(1)$$
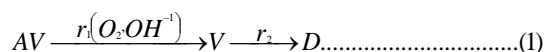
Since the oxidation of AV takes place under quasi-constant concentrations of base (sodium hydroxide) and oxygen, and assuming first order reaction kinetics, the reaction rate may be expressed as follows;

$$\frac{dC_{AV}}{dt} = -kC_{AV} ....(2)$$

To evaluate the order of reaction with respect to AV concentration, the experimental results of (Fig. 7a), were plotted in the form of eq. (3) by re-arranging and integrating eq. (2);

$$-\int_{C_{AV_o}}^{C_{AV}} \frac{dC_{AV}}{C_{AV}} = kt...................................(3)$$

The degradation kinetics of AV exhibited a pseudo-first order dependence on the AV concentration as demonstrated by the linear time-course plots of $\ln C_{AV}$ (Fig. 8a) with a slope equal to $(-k)$ and an intercept equal to $\ln C_{AVo}$, and $\ln (C_{AVo}/C_A)$ (Fig. 8b) passing through the origin, where C_{AVo} and C_{AV} is the initial concentration of AV and concentration of AV at different reaction times respectively. Similarly, this first order dependence has also been reported for phenol and substituted phenols elsewhere [34].

Taking into account that $r1 \gg r2$ and that $-dC_{AV}/dt \approx dC_V/dt$, the eq. (2) may be re-written as follows;

$$\frac{dC_V}{dt} = kC_{AV} ....(4)$$

Since $C_{AV} = C_{AVo} - C_V$ and $C_{AVo} \approx C_{V\infty}$, $C_{V\infty}$ is the concentration of vanillin at discontinuous reaction time, i.e., at 100% conversion of AV), eq. (4) may be re-written as follows;

$$\frac{dC_V}{dt} = k\left(C_{V_\infty} - C_V\right)...................................(5)$$

The integration of eq. (5) allows the expression for linear dependence of C_V and the reaction time, t;

$$\ln\left(C_{V_\infty} - C_V\right) = \ln C_{V_\infty} - kt...................................(6)$$

The observed reaction constant (k) for vanillin formation in (Fig. 7b) was calculated using the plots of $\ln (C_{V\infty} - C_V)$ against the reaction time for the temperature curves 135 °C and 150 °C (see Fig. 8c). Rather good linear correlations ($r^2 = 0.98$-0.99) were observed for the relatively short reaction times. The $C_{V\infty}$ value corresponded to the C_V at maximum yield (t) t_{max}.
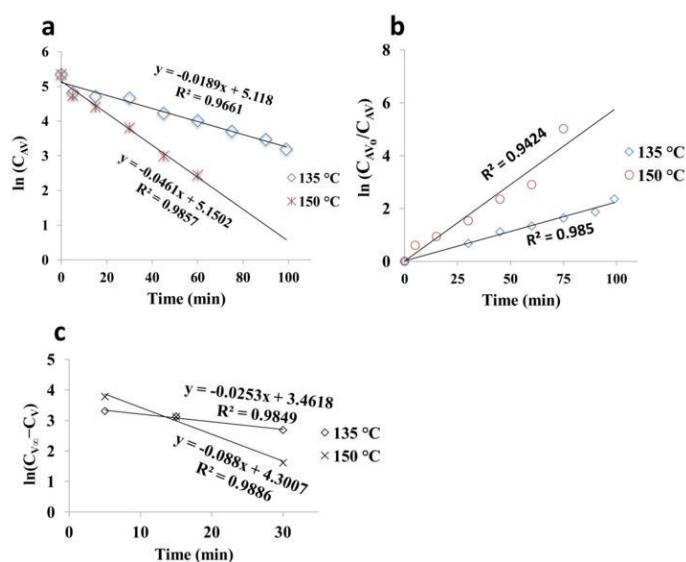

Fig. 8. Plots of first order kinetics with respect to AV concentration-plot of eq. (3) (a-b), and $\ln (C_{V\infty} - C_V)$ against the reaction time at 135 °C and 150 °C (c)

Consequently, assuming that the empirical kinetic constants followed Arrhenius dependence with temperature, the apparent activation energies were conveniently determined (see Tab. 1).

Tab. 1. The rate constants and activation energies for the AV degradation ($AV_{degrad.}$) and vanillin formation ($V_{form.}$)

	$AV_{degrad.}$	$V_{form.}$
Temp. (K)	k_i (min^{-1})	k_i (min^{-1})
408	0.0189	0.0253
423	0.0461	0.088
E_a/**kJ/mol**	85.29	120.7

The V formation was faster than AV degradation i.e. the rate constants for V formation were roughly twice of that for AV degradation. The activation energies reported here are higher than those reported in literature. The Ea values reported previously for the oxidation of different lignins to aromatic aldehydes under similar conditions are in the range of 50-70 kJ/mol. [23], this is probably due to the different pathways involved in the course of acetoderivatives oxidation to aromatic aldehydes. The fact that low oxygen partial pressure was used, the hypothesis that high activation

energy corresponds to a process with low oxygen excess appear to be confirmed [35].

The influence of temperature on the rate of AV degradation and V formation has been studied. As a consequence, the potential rate laws with reaction order 1 respect to AV have been proposed for the rate of AV disappearance and V formation at pH greater than 13. The resulting rate equations are;

$$-r_{AV} = A \exp\left(-\frac{10258}{T}\right) C_{AV} \quad \text{and}$$

$$r_{V} = A \exp\left(-\frac{14518}{T}\right)\left(C_{V_{\infty}} - C_{V}\right)$$

From the engineering perspective of lignin and its acetoderivative oxidation to valuable chemicals, the first stage in the scale-up of a chemical reaction from the laboratory to industry is the selection of the type of process, that is, batch or continuous and type of reactor. In terms of residence time, stirred vessels are more flexible than columns, and this is probably why investigations of the oxidation of lignin to aromatic aldehydes reported in the literature have mainly been performed in stirred vessels. Generally, the overall kinetics (chemistry and mass transfer) of oxidation are important in the reactor design [36].

Conclusions

Catalytic oxidation of bamboo lignin and acetovanillone under O_2 pressure yielded the expected aromatic aldehydes. The increase in the acetovanillone concentration improved the catalytic selectivity and product yield, and diminished the product loss, though acetovanillone conversion remained low. The yield of vanillin (51%) achieved from acetovanillone oxidation was higher than the 45% reported in a US patent [16], suggesting that a suitably prepared catalyst and optimized reaction conditions could enhance aldehyde recovery from acetoderivatives.

The AV degradation and vanillin formation kinetics were described for the first time over a temperature range of 120-150 °C, Cu (II) concentration of 5.72×10^{-4} mol/L, and oxygen pressure of 1.5 bars. The experimental results indicated that the reaction kinetics is first order with AV degradation with the characteristic activation energy of 85.29 kJ/mol and V formation with characteristic activation energy of 120.7 kJ/mol.

The proposed reaction mechanism needs further investigations to confirm and provide a clear understanding of the transformation of acetoderivatives degradation into aromatic aldehydes.

Acknowledgements

Notes and references

[a] College of Energy, Xiamen University, Xiamen, Fujian 361102, China
[b] iChEM, College of Chemistry & Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, China
* Corresponding authors: yq_liu@xmu.edu.cn, yyye@xmu.edu.cn

1. J. Gilmour, "Energy/Evironment," 28 October 2014. [Online]. Available: http://www.csmonitor.com/Environment. [Accessed 4 February 2015].

2. T.Nguyen, M.Maschietti, L.Amand, L.L.Olausson, S.Anderssona and R.Theliander, *Bioresour. Technol.,* 2014, **170**, 196–203.

3. M. David, G. Stephanie and A. James, *Chem. Soc. Rev.,* 2012, **41**, 8075-8098.

4. G. Rogers and D. Robin, *ACS Sustainable Chem. Eng.,* 2014, **2**, 322−339.

5. P. Gao, C. Li, H. Wang, X. Wang and A. Wang, *Chinese J. Catal.,* 2013, **34**, 1811–1815.

6. Z. Joseph, C. Pieter, L. Anna and M. Bert, *Chem. Rev.* 2010, **110**, 3552–3599.

7. C. Xu, R.A.D. Arancon, J. Labidi and R. Luque, *Chem. Soc. Rev.,* 2014, **43**, 7485-7500.

8. P.C.R. Pinto, C.E. Costa and A.E. Rodrigues, *Ind. Eng. Chem. Res.,* 2013, **52**, 4421−4428.

9. E.A. Borges de Silva, M. Zabkova, J.D. Araújo, C.A. Cateto, M.F. Barreiro, M.N. Belgacem and A.E. Rodrigues, *Chem. Eng. Res. Des.,* 2009, **87**, 1276–1292.

10. S.R. Rao and G.A. Ravishankar, *J. Sci. Food Agric.,* 2000, **80**, 289.

11. N. Mohamad, B. Sriprasanthi, A. Showkat and A. Farook, *BioRes.,* 2012, **7**, 4377-4399.

12. J.D.P. Araújo, C.A. Grande and A.E. Rodrigues, *chem. Eng. Res. Des.,* 2010, **88**, 1024–1032.

13. F.J. Benitez, F.J. Real, J.L. Acero, A.I. Leal and S. Cotilla, *J Environ Sci Health A Tox Hazard Subst Environ Eng.,* 2005, **40**, 2153-2169.

14. B.M. Harrison and F.G. Priest, *J Agric Food Chem.,* 2009, **57**, 2385-2391.

15. L. Crawford, E. Eaton and J. Pepper, *Can. J. Chem.,* 1956, **84**, 1562-1566.

16. B.S.K. Fung and B.F. Hrutfiord.US Patent 4691061, 1987.

17. K. Gonter, E. Takacs and L. Wojnarovits, *Radiat. Phys. Chem.,* 2012, **81**, 1495–1498.

18. N. Alison and S. Shannon, *Acc Chem Res.,* 2012, **45**, 851-863.

19. S. Dimitris, S. Miro and A. Leonid, *Ind. Eng. Chem. Res.,* 2004, **43**, 1200–1205.

20. K. Heikki, J. Pawel, L. Elina, R. Paul, L. Markku and R.Timo, *Eur J Inorg Chem.,* 2007, 2465–2471.

21. D.R. Walt, Applied Biochemistry and Biotechnology, B.H. Davison, J.D. McMillan and M. Finkelstein, Eds., Springer Science + Business Media, New York, 2001.

22. V. Tarabanko, D. Petukhov and G. Selyutin, *Kinet. Catal.,* 2004, **45**,569-577.

23. S.G. Santos, A.P. Marques, D.L.D. Lima, D.V. Evtuguin and V.I. Esteves, *Ind. Eng. Chem. Res.,* 2011, **50**, 291–298.

24. C.G. Boeriu, D. Bravo, R.J.A. Gosselink and J.E.G. van Dam, *Ind. Crop. Prod.,* 2004, **20**, 205–218.

25. D. W. Goheen, Low Molecular Weight Chemicals. In Lignins: Occurrence, Formation, Structure, and Reactions, K. W. Sarkanen and C. H. Ludwig, Eds., John Wiley & Sons, New York, 1971.

26. P.C.R. Pinto, E.A. Borges da Silva and A.E. Rodrigues, *Ind. Eng. Chem. Res.,* 2011, **50,** 741–748.

Catalysis Science & Technology Accepted Manuscript

27. Z. Wong, K. Chen and J. Li, *BioRes.,* 2010, **5,** 1509-1516.

28. L. Sayre and S. Jin, *J. Org. Chem.,* 1984, **49**, 3498–3503.

29. G. Wu, M. Heitz and C. Esteban, *Ind. Eng. Chem. Res.,* 1994, **33**, 718–723.

30. J. M. Coulson and J. F. Richardson, Chemical and Biochemical Reactors & Process Control, vol. 3, D. G. Peacock and J. F. Richardson, Eds., Butterworth–Heinemann, London, 1994.

31. R. Ma, Y. Xu and X. Zhang, *ChemSusChem.,* 2015, **8**, 24-51.

32. P. Chernavskii, A. Khodakov, G. Pankina, J. Girardon and E. Quinet, *Appl. Catal.,* 2006, **306**, 108–119.

33. L. Zhang, X. Bi, X. Guan, X. Li, Q. Liu, B. Barry and P. Liao, *Angew. Chem. Int. Ed.,* 2013, **52**, 11303 –11307.

34. V. Mishra and V.M.J. Joshi, *Ind. Eng. Chem. Res.,* 1995, 2–48.

35. S. Lefevre, O. Boutin, J.H. Farrasse, L. Malleret, R. Faucherand and A. Viand, *Chemosphere,* 2011 , **84**, 1208-1215.

36. A.W. Pacek, P. Ding, M. Garrett, G. Sheldrake and A.W. Nienow, *Ind. Eng. Chem. Res.,* 2013, **52**, 8361−8372.