Optimal Synthesis of Aromatic Carbonyl Compounds by Electrooxidation of Soda Lignins on Stainless steel and TiMMO Anodes

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ABSTRACT: *Electrooxidation (EO) studies were conducted on Wheat Straw Soda Lignin (WSSL), and bagasse soda lignin (BSL) for the synthesis of aromatic carbonyl compounds (CO_{arom}). Stainless Steel (SS), and titanium mixed metal oxide (TiMMO) anodes were used for the purpose. Experiments were designed according to Box Behnken Design (BBD), and Central Composite Design (CCD). The process parameters, namely EO current density, and EO time, were optimized using Response Surface Methodology (RSM) to obtain the maximum yields of different CO_{arom}, individually as well as collectively. A maximum of 30% cumulative yield of CO_{arom}, based on the total amount of lignin, could be obtained from BSL under optimized conditions of 2.24 mA/cm^2 EO current density, and 18 h EO time using SS anode. Among individual compounds, vanillin was produced with the highest yield of 20% of starting BSL with EO current density, and EO time optimized to 5.87 mA/cm^2, and 18 h, respectively. In all cases, SS anode fares better than TiMMO anode.*

Keywords: *Electrooxidation; Soda lignin; Aromatic carbonyl compounds; Anode; Response Surface Methodology*.

INTRODUCTION

Keeping in view the dwindling reserves of fossils, it is imperative to look for renewable alternatives as feedstock for producing functional organic chemicals [1]. In this context, lignin deserves special mention as the most abundant aromatic polymer of vegetative origin [2, 3]. Attempts are therefore made for the isolation of lignin [4]. It is important to valorize lignin by converting it into value-added chemicals which will add to environmental sustainability [1, 5].

During pulping of lignocelluloses, high-temperature alkali treatment degrades and depolymerizes the lignin, making it hydrophilic and soluble in the reaction medium. The solid fraction consisting of cellulose fibers is separated from the reaction mass. The remaining liquid is called black liquor (BL) with lignin dissolved in it [2]. For a mill, this is both an asset and a liability. Large wood-based paper mills burn the BL after drying [6, 7], which is nevertheless unable to unlock the full potential of lignin valorization [8]. In small paper mills, mostly based on agro residues like wheat straw and bagasse, even this route of deriving energy from lignin is not viable due to economy of size constraints. BL from such industries, therefore, remains largely unutilized [6].

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Lignin finds use in several industries like leather tanning [9], carbon products like fibers, and activated carbons [10-12], and basic materials for polymer industries [13, 14]. Soda lignin from agro residues can be utilized to partially replace or supplement petrochemicals [15]. Lignin can be a potential source of aromatic chemicals such as Benzene, Toluene, Xylene (BTX), and phenols through thermochemical conversion [16-18]. It can be converted into low molecular weight aromatic compounds by depolymerization and fractionation [19]. *Villar et al.* oxidized lignin in the presence of cupric oxide to produce some phenolic derivatives [20]. Other studies on lignin oxidation have reported the production of vanillin [21-23], syringaldehyde [24-26], and p-hydroxybenzaldehyde [27, 28]. Phenolic aldehydes, like vanillin, are widely used as flavoring agents in the food, pharmaceutical, and cosmetic industries. There have been few attempts to degrade lignin with electrooxidation (EO) using different electrodes. These include studies on degradation mechanisms and bond cleavage in the lignin macromolecule [29-31]. Production of low molecular weight aromatics, including vanillin and apocynin, is also reported [32-34]. *Singh* and *Ghatak* examined the kinetics of lignin degradation and vanillin production during EO on Stainless Steel (SS) anode [2].

Many process parameters influence the outcome from the EO of lignin. Optimization of these parameters is desirable to get the best out of lignin EO. This requires a suitable Design of Experiments (DOE) followed by statistical analysis of experimental data to develop an appropriate mathematical model. DOE [35, 36] and statistical analysis tools [37, 38] are useful techniques for modeling and predicting the yield of EO products. The influence of interaction between factors on the yield is studied based on the analysis of variance (ANOVA). Box Behnken Design (BBD) and Central Composite Design (CCD) are two particularly suitable techniques to design experiments while RSM is a powerful mathematical tool for multivariable optimization [39]. EO process optimization for combining BBD or CCD with Response Surface Methodology (RSM) has been reported in the technical literature for the remediation of environmental pollutants [40-42].

The present study is devoted to RSM optimization of EO process parameters (thermochemical pre-treatment (TP) temperature, TP time, EO current density, and EO time) to derive the maximum yields of various aromatic carbonyl compounds (CO_{arom}) from agro residue lignins (Wheat Straw Soda Lignin (WSSL) and Bagasse Soda Lignin (BSL) using SS and TiMMO anodes.

EXPERIMENTAL SECTION

Materials

SS-304 sheet of 2 mm thickness was purchased from a local market and cut into electrodes of a specific size (contact area 44.7 cm^2) for EO experiments. Ti Anode Fabricators Pvt. Ltd., Chennai, India, supplied TiMMO anodes (thickness 1.5 mm, contact area 22.6 cm^2, with a coating of the electrocatalytic active layer of tantalum oxide and iridium oxide over titanium substrate).

Deionized water was prepared in the laboratory with Millipore RiOS 5 Century Synergy water purification system from Millipore India (Pvt.) Ltd., Mumbai, India, All HPLC, and analytical grade chemicals were obtained from Sigma-Aldrich, Bangalore, India.

Wheat straw was collected from a nearby farm while bagasse was obtained from a sugar crushing installation. After initial water washing, these were air-dried and stored. These raw materials were subjected to soda pulping to separate the lignin.

Lignin isolation

In each case, 150 g of raw material (wheat straw or bagasse) was taken in a 2 L reaction bomb. To this, we added 1 L solution of NaOH (29 g/L for wheat straw and 32 g/L for bagasse). Subsequently, the reaction bomb was heated for 150 min at 160^0 C. Lignin dissolved in the alkaline reaction medium leaving the cellulose fibers as pulp. To separate the BL, the pulp was hand squeezed on a 400-mesh wire screen. The black liquor characteristics were then estimated as per TAPPI standard method T-650 pm-84. To precipitate lignin from BL it was acidified to pH 2.5 and the resultant broth was thermally stabilized for 2 h at 70^0 C. Precipitated lignin was washed several times with deionized water and then dried in a laboratory oven.

EO experiments

For EO experiments 1 g lignin was dissolved into 100 mL of 10 g/L NaOH solution. A pair of electrodes (cathode SS-304, and anode SS-304 or TiMMO) was dipped into it and connected to Biologic make SP 150 Potentiostat Galvanostat running in galvanostatic mode. The system was controlled by the EC-Lab V10.33 software.

For experiments with Thermochemical Pre-treatment (TP) 1 g lignin, placed in a covered silica crucible, was heated in a muffle furnace (Banbros Engineering Pvt. Ltd., India) at desired TP temperature for the desired TP time. At the end of the heating, the residue from the crucible was transferred into a glass beaker containing 100 mL of 10 g/L NaOH solution and stirred for 1 h. The solution was then filtered through a glass filter and used for EO.

At the end of each EO run, the solution was acidified to pH 2.5 and kept for 2 h at 70°C to precipitate the unreacted lignin. Thereafter, the solution was filtered through a glass filter. The benzene extract of the clear liquid obtained was used for GC/MS analysis. The precipitated lignin was washed several times with deionized water and oven-dried. Lignin degradation was gravimetrically assayed.

Analytical methods

Reaction products were estimated by GC in the following manner

- Equipment. Shimadzu QP 2010 Ultra GCMS system.
- Column. RETEK RTX 5 Sil MS (range 50 – 500 m/z) 30 m x 250 µm capillary column.
- Carrier gas. Helium flowing at 1 $ml.min^{-1}$.
- Temperature program:
- 60 °C for 10 min.
- Heated to 280 °C at the rate of 10 °C min^{-1}.
- Held at 280 °C for 5 min.
- Transfer line temperature. 20°C.
- Ion source temperature. 250 °C.
- Solvent delay time. 2 min.
- Compound identification. Using the instrument's inbuilt NIST library.

Design of experiment

Experiments were designed using Design-Expert software, version 6.0.10 from Stat-Ease Inc., Minneapolis, USA. For optimizing four process parameters, viz. TP temperature, TP time, EO current density, and EO time, BBD resulted in a set of 29 experiments. A set of 13 experiments were desired from CCD to optimize two process parameters, EO current density, and EO time. The experiments were conducted at random to exclude the possibility of systematic bias. The amount of different CO_{arom} produced constituted the target response. All experiments were performed in duplicate and the mean results were used for analysis.

Process optimization

Our objective was to get the optimal combination of process conditions to maximize the yields of different CO_{arom}. For this, model equations were developed by regression by fitting the experimental data. Adequacy of the model was judged by analysis of variance (ANOVA) to establish their statistical significance. Regressed equations resulted in 3D contour plots. The statistically significant regression equation led to the optimized set of values to obtain the best yields of the value-added chemicals. Design expert software 6.0.10 was used for mathematical and graphical analyses.

RESULTS AND DISCUSSION

Selection of significant parameters

To begin with, four parameters, viz. thermochemical pre-treatment (TP) temperature (parameter A), TP time (parameter B), EO current density (parameter C), and EO time (parameter D), were chosen for optimization to maximize the yields of different CO_{arom}. Accordingly, optimization studies were conducted using BBD on WSSL by TP followed by EO. The objective was to maximize the yields of individual compounds, namely, vanillin, acetosyringone, apocynin, syringaldehyde, and benzaldehyde, as well as the combined yield of all CO_{arom}. Regression equations were worked out relating the product yields with the process parameters. For each combination of lignin type and anode material, individual CO_{arom} with reasonable yields were considered for statistical analyses. Accordingly, for SS anode, vanillin, acetosyringone, apocynin, and syringaldehyde are the compounds found to be formed with reasonable yields. On TiMMO anode these are vanillin, acetosyringone, apocynin, and benzaldehyde.

Table 1 shows the ANOVA statistics for the synthesis of different CO_{arom} on SS anode. For the combined yield of all CO_{arom} the terms containing C^2, BC, and CD are significant as they have p values less than 0.05. However, the interaction term BC has a high negative coefficient so it would suppress the yield of CO_{arom}. For vanillin yield, the terms containing C, D, $D^{2,}$ and AC are significant in the regression equation owing to p values less than 0.05. However, in comparison to the other three terms, the p value for the interaction term AC is an order of magnitude lower and carries a very low coefficient. It, therefore, would have a negligible effect on vanillin yield. p values were less than 0.05 for the terms C, D, C^2, D^2, AB, and BC

Table 1: ANOVA statistics using BBD for synthesis of different CO_{arom} from WSSL on SS anode.

Parameter	CO_{arom}		Vanillin		Acetosyringone		Apocynin		Syringaldehyde	
	P value	coefficient	P value	coefficient	P value	coefficient	P value	coefficient	P value	coefficient
		2.834E+005		60209.48		147601.8		43390		13980.21
A	0.0887	2025.95	0.0758	96.41	0.0839	-721.13	0.1523	-317.61	0.2368	-560.55
B	0.8378	-5873.75	0.7389	-1188.22	0.5525	-3260.84	0.3365	-731.39	0.5265	-419.27
C	0.1647	2.890E+005	0.0001*	61458.32	0.0231*	150543.2	0.0664	44271.68	0.0365*	14152.28
D	0.3569	364.79	0.0054*	171.83	0.0041*	18.66	0.0985	110.39	0.4452	18.09
A*A	0.4481	-0.11	0.3742	2.51	0.0815	-1.47	0.3585	-1.33	0.8526	1.07
B*B	0.0717	41.19	0.8167	9.33	0.6548	20.99	0.6625	4.82	0.0956	5.41
C*C	0.0418*	73689.41	0.0987	15686.64	0.0422*	38390.23	0.0023*	11293.97	0.1253	3582.31
D*D	0.060	-60.38	0.0001*	-15.91	0.0248*	-26.43	0.031*	-6.94	0.2689	-5.45
A*B	0.084	-67.74	0.2357	-21.52	0.0489*	-26.85	0.3341	-6.03	0.3654	-10.32
A*C	0.059	-1016.24	0.0342*	55.76	0.7523	-361.14	0.0689	-161.1	0.4897	-284.32
A*D	0.0845	-3.10	0.0845	-1.11	0.8154	-1.28	0.0985	0	0.2653	-0.7
B*C	0.009*	-3002.63	0.0899	-607.78	0.0432*	-1665.62	0.0421*	-374.73	0.2988	-214.61
B*D	0.1352	-13.42	0.0637	-4.57	0.2354	-6.08	0.0658	1.08	0.0852	-1.55
C*D	0.0466*	180.14	0.5628	85.92	0.0676	7.14	0.3625	56.06	0.0985	8.51
LOF	0.0001		0.0227		0.0008		0.0003		0.0032	
Significant Model Terms	C^2, BC, CD		C, D, D^2, AC		C, D, C^2, D^2, AB, BC		C^2, D^2, BC		C	

A – TP temperature, B – TP time, C – EO Current Density, D – EO time

* *denote most significant factors and interaction effects (P-value<0.05).*

in the ANOVA statistics to produce acetosyringone. These terms are, therefore, significant for synthesizing acetosyringone by EO. Among these, the terms C, D, and C^2 contribute positively to acetosyringone yield with the other terms, with negative coefficients, having a lowering effect. By the same reasoning, apocynin yield is significantly affected by the terms C^2, D^2, and BC in the regression equation but only C^2 has a significant positive contribution. Similarly, syringaldehyde yield is significantly affected only by parameter C. All the regression models based on four parameters show that the p value for Lack of Fit (LOF) is very less than the confidence level (less than 0.05) which is undesirable. In other words, there is significant LOF in the model.

Table 2 shows the ANOVA statistics for the synthesis of different CO_{arom} on TiMMO anode. For the combined yield of all CO_{arom} the terms containing D, C^2, AC, and AD have p values less than 0.05. These terms are, therefore, significant. But the interaction terms AC and AD would suppress the CO_{arom} yield due to their negative coefficients. The terms C, C^2, D^2, AC, and AD are significant in the regression equation for vanillin yield. But the interactions AC and AD would tend to drag down the vanillin yield as they have negative coefficients. The yield of apocynin is significantly affected in a positive sense only by terms C, D, C^2, and CD (p values less than 0.05 and positive coefficients) while the interaction terms AC, and AD, though significant, would have a lowering effect on yield due to their negative coefficients. For maximizing the yield of benzaldehyde, the terms C, D, and C^2 are significant in the regression equation. For acetosyringone synthesis, only D, and C^2 have positive significance. Other significant terms in the regression equation, D^2, AC, and AD negatively influence the yield. Here also, all the regression models based on four parameters show that the p value for LOF is very less than the confidence level (less than 0.05) which is undesirable. In other words, there is significant LOF in the model.

Table 2: ANOVA statistics using BBD for the synthesis of different COarom from WSSL on TiMMO anode.

Parameter	CO_{arom}		Vanillin		Apocynin		Benzaldehyde		Acetosyringone	
	P value	coefficient	P value	coefficient	P value	coefficient	P value	coefficient	P value	coefficient
		5.47		1.45		0.17		0.24		3.48
A	0.7529	-26.80	0.6875	-10.10	0.287	-1.60	0.3288	0.23	0.4458	-13.95
B	0.8549	-0.27	0.4656	0.33	0.134	-0.20	0.4592	0.19	0.3181	-0.60
C	0.259	1.73	0.0263*	1.04	0.0178*	0.31	0.0069*	0.12	0.5501	0.36
D	0.0034*	5.19	0.1407	0.71	0.0001*	0.63	0.0311*	0.094	0.0011*	2.37
A*A	0.5268	26.42	0.7277	10.10	0.3599	1.79	0.0146	0.15	0.4851	13.03
B*B	0.3044	-2.14	0.2587	-0.63	0.068	-0.40	0.0708	0.12	0.9857	-0.50
C*C	0.0253*	5.01	< 0.0001*	2.98	0.0048*	0.58	0.0222*	0.12	0.0044*	2.46
D*D	0.0855	-3.71	0.0061*	-1.94	0.7964	0.24	0.0854	-0.089	0.0006*	-3.27
A*B	0.2683	2.94	0.0675	-0.72	0.0882	0.39	0.0001	0.60	0.0168	2.67
A*C	0.0016*	-9.92	< 0.0001*	-4.51	< 0.0001*	-1.21	0.0879	0.082	0.0002*	-4.60
A*D	0.0001*	-13.25	0.0211*	-2.11	< 0.0001*	-1.81	0.06152	0.069	0.0002*	-5.25
B*C	0.3353	2.55	0.5237	0.38	0.3258	0.052	0.2877	0.095	0.0617	2.02
B*D	0.964	0.12	0.3339	0.000	0.5244	-0.10	0.0975	0.038	0.0858	0.18
C*D	0.5124	-1.71	0.0596	-1.49	0.0078*	0.59	0.0947	+0.13	0.075	-0.63
LOF	<0.0001		0.0338		0.0005		0.0004		0.0043	
Significant Model Terms	D, C^2, AC, AD		C, C^2, D^2, AC, AD		C, D, C^2, AC, AD, CD		C, D, C^2		D, C^2, D^2, AC, AD	

A – TP temperature, B – TP time, C – EO Current Density, D – EO time

* *denote most significant factors and interaction effects (P-value<0.05).*

Based on the above discussion it is evident that TP is not recommended for electrochemical synthesis of CO_{arom} either for maximizing the cumulative yield or the yields of individual compounds. Hence, optimization studies were conducted using CCD with EO current density and EO time being process parameters.

Optimized synthesis of CO_{arom} from WSSL over SS anode

Cumulative yield:

The experimental data for the cumulative yield of CO_{arom} is fitted into the regression equation in terms of coded parameters as

$$CO_{arom}\ yield(mg) = 207.1 - 48.55C - 244.4D - 194.2D^2 + 43.77C^3 + 257.23D^3 \quad (1)$$

ANOVA statistics for the regression model, shown in Table 3, manifests the significance and satisfactory fit of the model as represented by p value of less than 0.05 and R^2 value of 0.96 respectively. As the adj. R^2 is very close to R^2 the model will fit well with new data. A value of 0.82 for pred. R^2 suggests that the model can predict a missing response with 82% confidence [43-45]. The LOF is insignificant as its p value at 0.9517 (almost approaching 1) is much higher than the confidence level [43]. F value is sufficiently large to make the regression significant. The normal plot of residuals (Fig. 1a) and the scatter plot of predicted data vs. experimental data (Fig. 1b) also lend support to the model. Fig. 1c shows the response surface generated by the regression equation. The cumulative yield of CO_{arom} has a strong dependence on EO time. With an increase in time, the yield increases attain its maximum and then drops with further increase in EO time. On the contrary, the effect of EO current density is less pronounced. One would expect a maximum of 277 mg of the cumulative yield of CO_{arom} for an EO current density of 3.3 $mA.cm^{-2}$ and 6.6 h EO time (Table 7). This is 27.7% of the original lignin amount.

Table 3: ANOVA statistics using CCD for the synthesis of different CO_{arom} from WSSL on SS anode.

Parameter	CO_{arom}	Vanillin	Acetosyringone	Apocynin	Syringaldehyde
SD	26.25	1.68	18.047	1.06	0.62
Mean	141.82	42.49	58.01	12.011	13.015
%CV	18.51	3.95	31.11	8.88	4.80
Press	8655	262	7622	154	86
R^2	0.96	0.99	0.92	0.99	0.99
Adj. R^2	0.93	0.99	0.86	0.98	0.99
Pred. R^2	0.82	0.85	0.71	0.86	0.81
Adequacy of prec.	14.33	57.15	10.26	35.19	54.64
Sum of squares	106436	10127.2	23779	1025.8	1061.2
Mean square	21287	2025.43	4755.7	170.97	176.86
F-value	30.88	716.37	14.60	149.97	452.07
P-value	0.0003	0.0001	0.0026	0.0001	0.0001
LOF (P-value)	0.9517	-[#]	-[#]	-[#]	-[#]
Significant Model terms	C, D, D^2, D^3	C, C^2, D^2, C^3, D^3	C, D, D^2, D^3	C, D, C^2 D^2, D^3	C, D, D^2, C^3, D^3

C – EO Current Density, D – EO time

[#] inadequate degree of freedom to calculate P-value of LOF

Vanillin yield

The experimental data for the cumulative yield of CO_{arom} is fitted into a regression equation in terms of coded parameters as

$$\text{Vanillin yield (mg)} = 66.68 - 73.07D - 5.29C^2 - 59.46D^2 + 1.27C^3 + 75.00D^3 \quad (2)$$

P value of 0.0001 (Table 3) is far less than 0.05 and the F value is sufficiently large, which shows that the regression model is significant. The fit of experimental data is very good with R^2 value of 0.99. The model is well adapted to fit new data and predict any missing response since the adj. R^2 and pred. R^2 are quite high. The model can fit new data and predict missing responses with 99% and 85% confidence, respectively. LOF is insignificant. The normal plot of residuals (Fig. 1a) and the scatter plot of predicted data vs. experimental data (Fig. 1b) is also supportive of the model. The response surface from the regression equation is shown in Fig. 1c. Parametric dependence is similar in trend to that for the cumulative yield of CO_{arom} with vanillin yield passing through a maximum with the increase in EO time. A maximum of 81 mg – 8.1% on initial lignin – could be obtained for EO current density of 4.77 mA/cm^2 and 5.9 h EO time (Table 7).

Acetosyringone yield

In terms of coded parameters, the yield of the target compound is represented by the following regression equation

$$\text{Acetosyringone yield (mg)} = 80.19 - 21.82C - 14D - 78.91D^2 + 23.102C^3 + 14.32D^3 \quad (3)$$

Here also, the model is significant with the good fit of experimental data as depicted by p value, F value, and R^2 values in Table 3. Adj. R^2 at 0.86 is not very less than R^2 and the model is suitable for fitting new data. Also, it can predict a missing response with 71% confidence as suggested by pred. R^2. LOF is insignificant. The normal plot of residuals and the scatter plot of predicted data vs. experimental data are also supportive of the model as shown in Fig. 1a, and Fig. 1b. Acetosyringone yield is largely dependent on EO time and less on EO current density as evident from the response surface shown in Fig. 1c. Similar to vanillin, the yield of acetosyringone

(a)

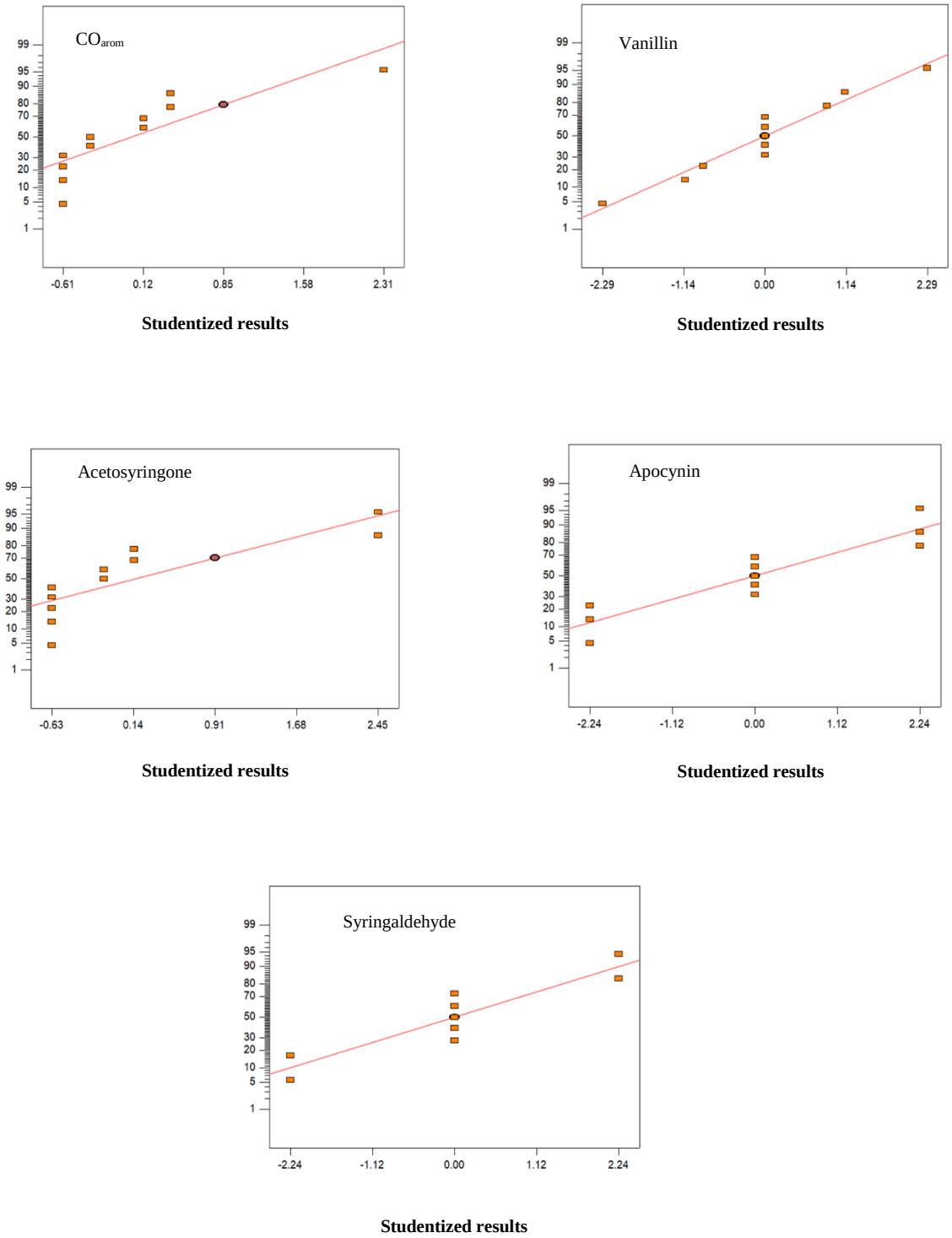
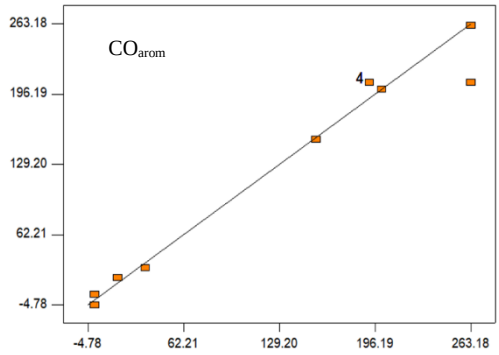


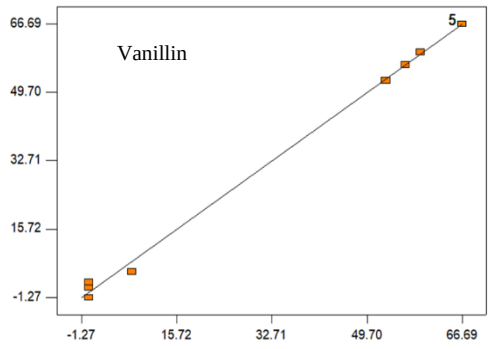
***Fig. 1 RSM optimization of WSSL EO on SS anode. (a) The normal plot of residuals*.**

(b)

Predicted data



Experimental data



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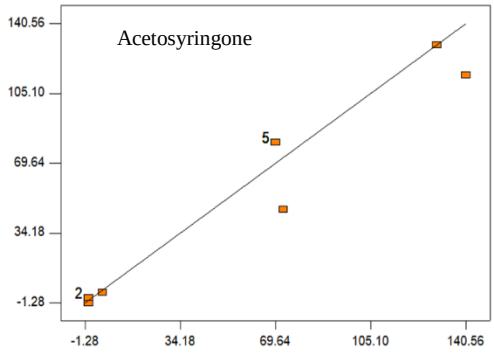

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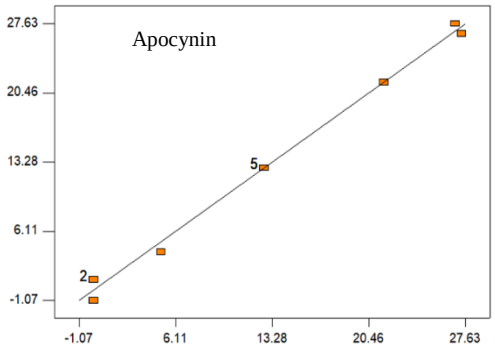

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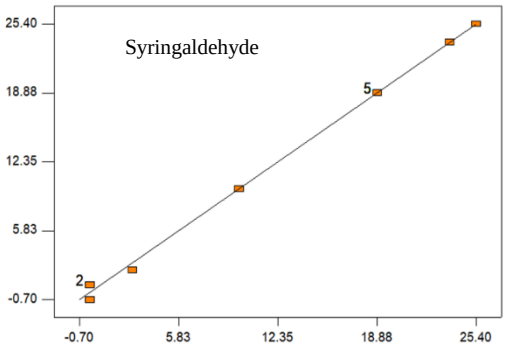


Experimental data

Fig. 1 RSM optimization of WSSL EO on SS anode. (b) Predicted vs. actual.

(c)

Amount (mg)

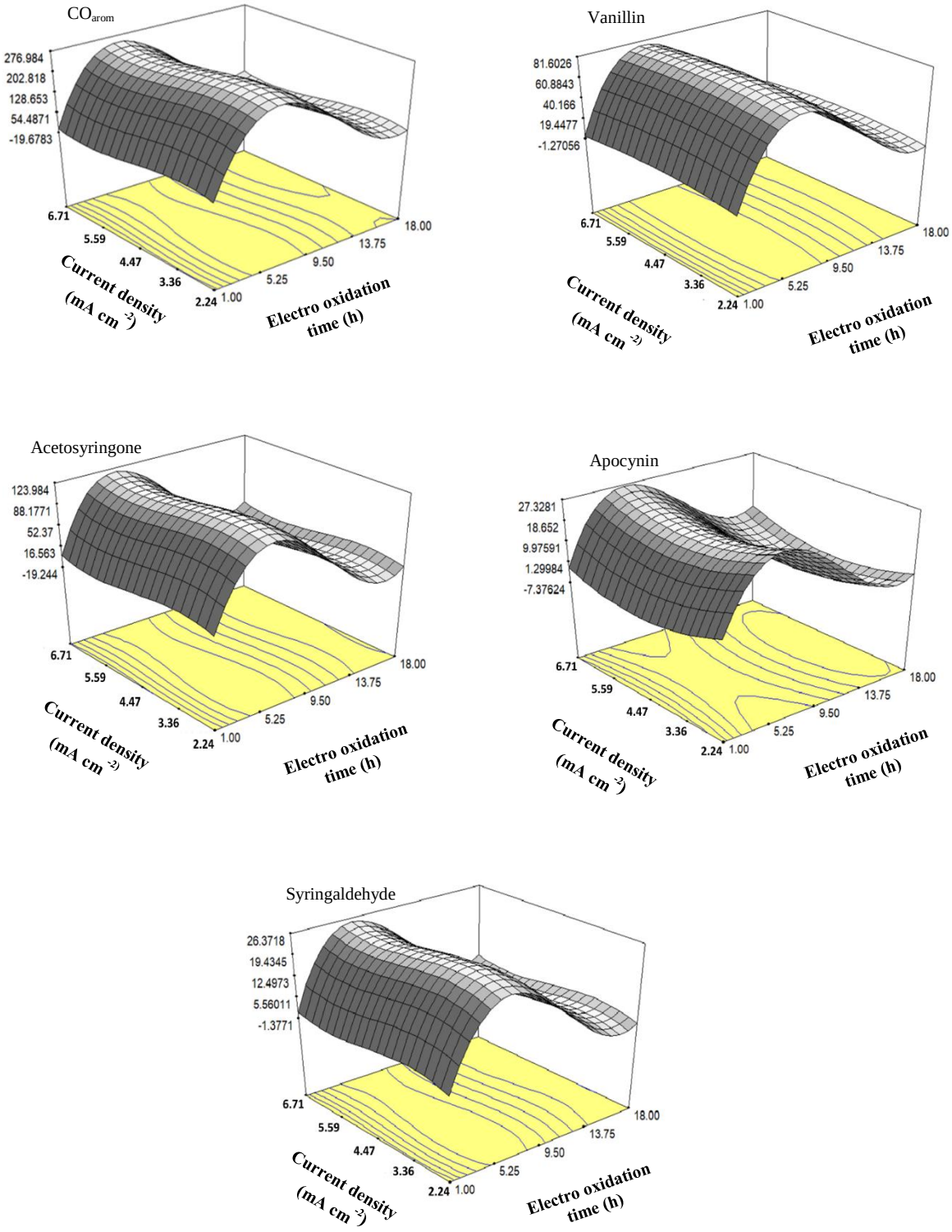


Fig. 1 RSM optimization of WSSL EO on SS anode. (c) Response surface.

Table 4: ANOVA statistics using CCD for the synthesis of different CO_{arom} from WSSL on TiMMO anode.

parameters	CO_{arom}	Vanillin	Acetosyringone	Benzaldehyde
SD	7.95	1.44	1.81	1.46
Mean	36.23	15.11	21.73	8.88
%CV	21.95	9.52	8.32	16.45
Press	304.8	251.67	5158.7	117.7
R^2	0.96	0.99	0.99	0.98
Adj. R^2	0.92	0.98	0.98	0.96
Pred. R^2	0.95	0.82	0.96	0.82
Adequacy of prec.	10.26	35.00	24.43	16.73
Sum of squares	8581.3	1440	2364.1	655.1
Mean square	1430.2	287.99	394.01	131.02
F-value	22.58	138.89	120.43	61.335
P-value	0.0018	0.0001	0.0001	0.0001
LOF (P-value)	0.8795	-[#]	-[#]	-[#]
Significant Model Terms	D, C^2, D^2, C^3, D^3	C, D, D^2, CD	C, D, C^2, D^2, CD, C^3	D, C^2, D^2

C – EO Current Density, D – EO time [#] *inadequate degree of freedom to calculate P-value LOF*

is maximum for a given EO time and drops on both sides of it. Optimized conditions of 3.22 $mA.cm^{-2}$ EO current density and 5.9 h EO time should give the maximum acetosyringone yield of 124 mg (Table 7) which is 12.4% of the starting amount of lignin.

Apocynin, and syringaldehyde yields:

Vanillin and acetosyringone are the two major CO_{arom} produced during EO of WSSL on SS anode. The other two compounds produced in lesser amounts are apocynin and syringaldehyde. Following are the regression equations for apocynin, and syringaldehyde yields, respectively.

$$\text{Apocynin yield (mg)} = 12.66 - 30.21D + 7.26C^2 - 16.68D^2 + 1.25CD + 0.18C^3 + 31.46D^3 \quad (4)$$

$$\text{Syringaldehyde yield (mg)} = 18.90 - 4.19C - 26.78D - 0.65C^2 - 17.55D^2 + 4.89C^3 + 27.48D^3 \quad (5)$$

From Table 3 the R^2, and p values show an excellent fit of experimental data and the significance of the respective models. F values – 150, and 452, respectively – are large enough for the model to be significant. LOF is insignificant. Adj. R^2 values are identical to R^2 showing that the statistical fit of the model to responses is unbiased and it can fit new data with a high degree of confidence. Pred. R^2 values suggest that missing responses can be predicted with 86% and 81% confidence, respectively. The normal plot of residuals and the scatter plot of predicted data vs. experimental data, shown in Fig. 1a, and Fig. 1b have good linear fits. Response surfaces in Fig. 1c are akin to those for vanillin and acetosyringone with yields of target compounds passing through maxima as the EO time is increased. From Table 7 the maximum yields of these two compounds are similar – 27 mg for apocynin and 26 mg for syringaldehyde. This amounts to 2.7%, and 2.6% on the initial lignin amount. However, the maximum yield of apocynin should occur at a lower EO current density and EO time compared to syringaldehyde (Table 7).

Optimized synthesis of CO_{arom} from WSSL over TiMMO anode

Cumulative yield:

The experimental data for the cumulative yield of CO_{arom} is fitted into the regression equation in terms of coded parameters as

$$CO_{arom}\ \text{yield (mg)} = 61.65 + 14.12C - 42.09D - 15.43C^2 - 42.16D^2 + 14.84C^3 + 46.15D^3 \quad (6)$$

ANOVA statistics are shown in Table 4. The low p value of 0.0018 (less than the confidence level of 0.05) and high F value of 22.58 makes the model significant. The LOF is insignificant as its p value is very high [43]. Experimental data fits well into the model as revealed by R^2 value of 0.96, the normal plot of residuals and the scatter plot of predicted data vs.

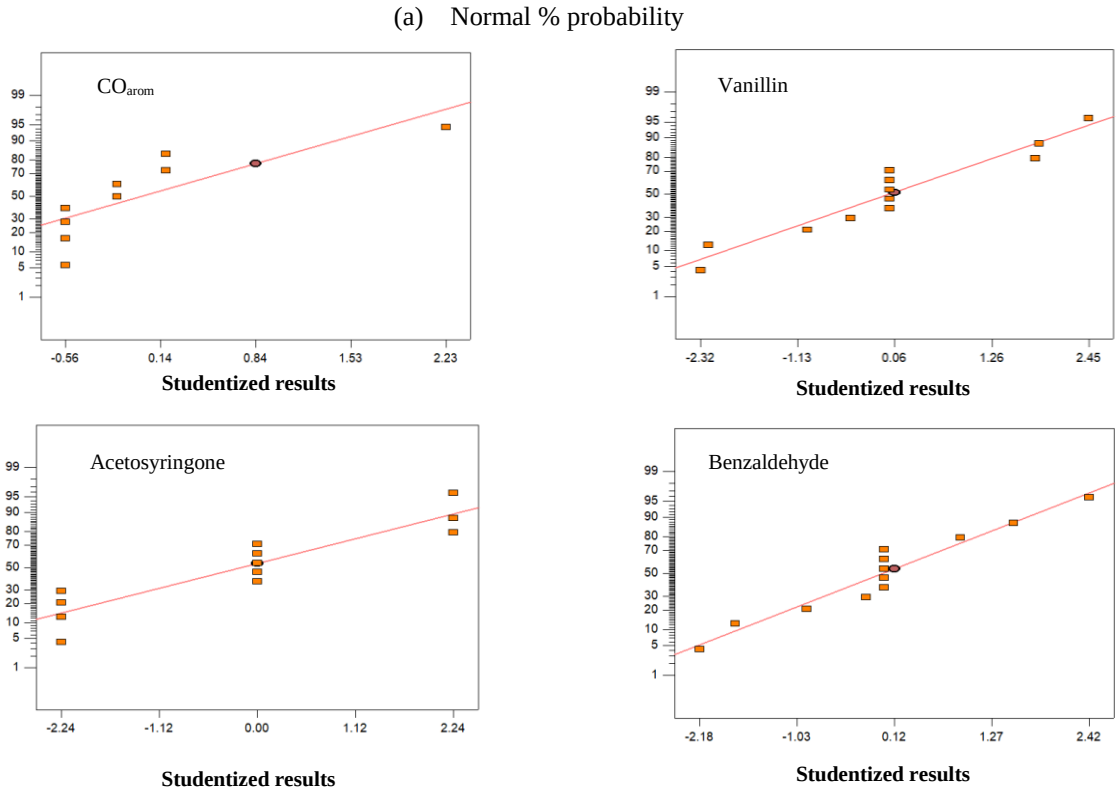


Fig. 2: RSM optimization of WSSL EO on TiMMO anode. (a) Normal plot of residuals, (b) Predicted vs. actual.

(c) Amount (mg)

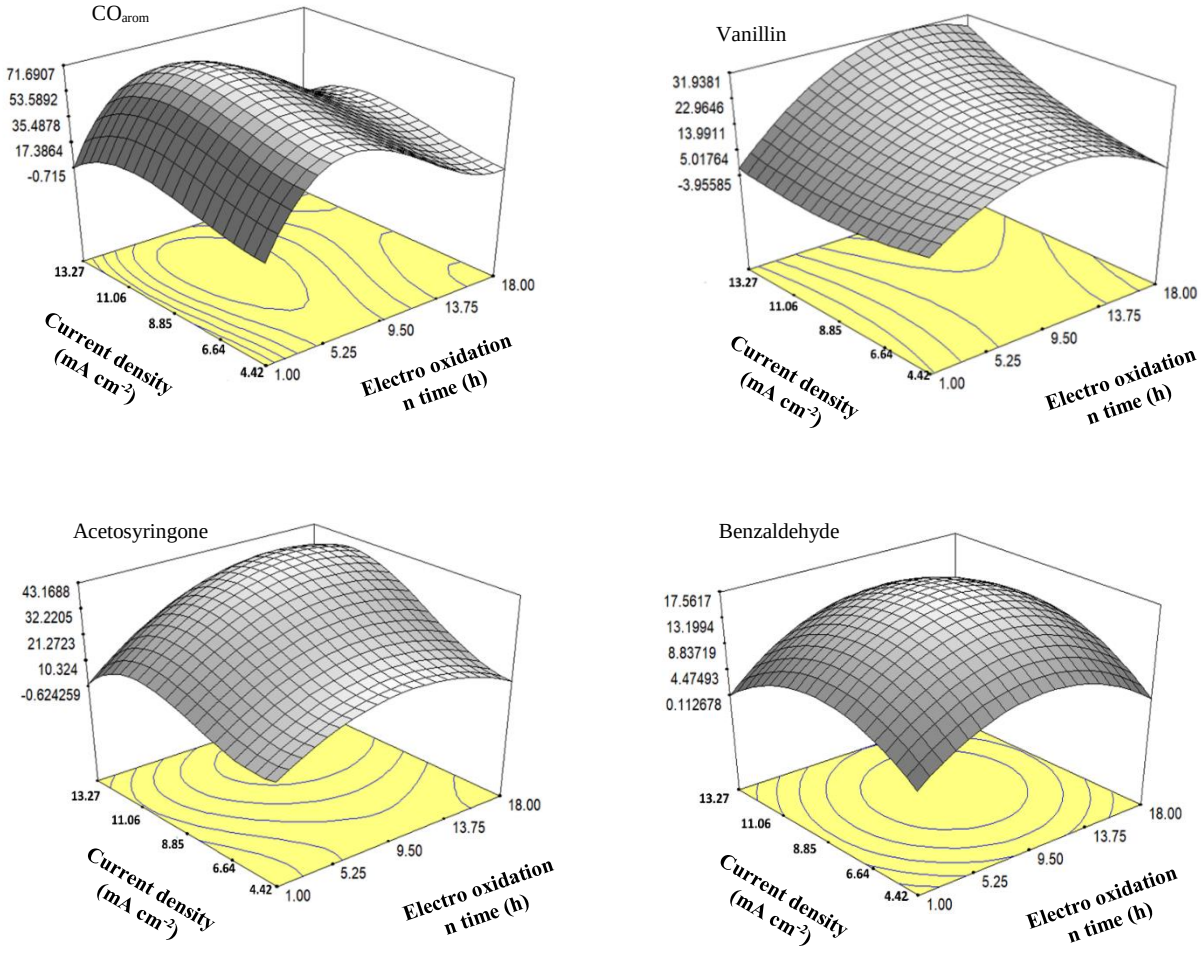


Fig. 2 RSM optimization of WSSL EO on TiMMO anode. (c) Response surface.

experimental data, shown in Fig. 2a, and Fig. 2b. Adj. R^2 and pred. R^2 is close to R^2 making the model unbiased. The model can fit new data with 92% confidence (adj. R^2 0.92) and predict missing responses with 95% confidence (pred. R^2 0.95). The response surface from the regressed equation is presented in Fig. 2c. Yield dependence on EO time resembles that for SS anode with the yield finding its maximum and then decreasing. But, with TiMMO anode the yield is also sensitive to EO current density with mid ranges of current densities particularly favoring the synthesis of CO_{arom}. The maximum yield of 72 mg of CO_{arom} is obtained under optimized conditions of 10.24 $mA.cm^{-2}$ EO current density and 6.73 h EO time, amounting to 7.2% on initial lignin.

Vanillin yield:

The regressed equation from experimental data is as follows

$$\text{Vanillin yield (mg)} = 19.16 + 5.41C - 7.99D + 3.80C^2 - 15.036D^2 + 6.63CD \quad (7)$$

From Table 4, the p value is much less than 0.05 with an R^2 value of 0.99. So, the regressed model is significant with the excellent fit of experimental data. F value at 138.9 is sufficiently high and LOF is insignificant. Adj. R^2 is almost identical to R^2 making the model capable of unbiased fitting of new responses with 98% confidence. It can predict missing responses with 82% confidence as indicated by pred. R^2. The normal plot of residuals

(Fig. 2a) and the scatter plot of predicted data vs. experimental data (Fig. 2b) have good linearity. From Fig. 2c – the response surface – the dependence of vanillin yield on EO time is on similar lines as for cumulative yield of CO_{arom}. But, the yield of vanillin is suppressed in the mid ranges of EO current density; a behavior not observed for other target compounds. The maximum yield of 32 mg of vanillin – 3.2% on original lignin – is obtained for 13.27 $mA.cm^{-2}$ EO current density and 13.64 h EO time.

Acetosyringone yield:

In terms of coded parameters, the yield of acetosyringone could be regressed into the following equation

$$\text{Acetosyringone yield (mg)} = 34.09 + 20.98C + 9.77D - 9.26C^2 - 14.7D^2 + 6.04CD - 14.94C^3 \quad (8)$$

p value, and R^2 from Table 4 shows that the model equation is significant and fits the data well. F value at 120.4 is sufficiently high. There is hardly any difference between R^2 and adj. R^2 suggests the unbiased fitting of new data by the model with 98% confidence. Pred. R^2 is also close to adj. R^2 and the model can predict any missing response with 96% confidence. A normal plot of residuals is linearly distributed and predicted values correspond well with those from the experiments (Fig. 2a, and Fig. 2b). The response surface for acetosyringone yield is shown in Fig. 2c. Both EO current density and EO time have an important bearing on the yield. An increase in current density, as well as time first, increases the yield. Once the maximum is attained, the synthesized amount drops with a further increase in current density or time. A maximum of 42 mg of acetosyringone is obtained (4.2% on lignin) at EO current density of 12 $mA.cm^{-2}$ for 10.2 h EO time.

Benzaldehyde yield:

The yield of benzaldehyde from EO of WSSL on TiMMO anode could be regressed into the following equation

$$\text{Benzaldehyde yield (mg)} = 17.40 + 1.03C + 1.94D - 7.10C^2 - 8.04D^2 + 1.22CD \quad (9)$$

p value, and R^2 value from ANOVA results (Table 4) indicate that the regressed model is significant and the data fits well into the equation. A high F value also lends support to the statistical significance of the model. Adj. R^2 at 0.96 is close to R^2 and the model is capable of unbiased fitting of new data with 96% confidence. It can predict missing responses with 82% confidence – pred. R^2 0.82. The normal plot of residuals (Fig. 2a) and the scatter plot of predicted data vs. experimental data (Fig. 2b) validate the model. The response surface is generated from the regression equation and presented in Fig. 2c. Yield dependence on EO current density and EO time is rather identical. 17.5 mg maximum yield of benzaldehyde (1.75% on lignin) results at 9 $mA.cm^{-2}$ EO current density and 10.8 h EO time. It is evident that benzaldehyde yield is less compared to vanillin and acetosyringone.

Optimized synthesis of CO_{arom} from BSL over SS anode

Cumulative yield

The experimental data for the cumulative yield of CO_{arom} is fitted into a regression equation in terms of coded parameters as

$$CO_{arom}\ \text{yield (mg)} = 205.591 + 12.7708C + 55.9153D - 1.89462C^2 - 40.2818D^2 - 15.109CD \quad (10)$$

ANOVA results for the regression model are shown in Table 5. The model is significant with a satisfactory fit as represented by p value of less than 0.05, a high F value of 34.5, and R^2 value of 0.97. LOF is insignificant. Adj. R^2 is close to R^2 suggesting that fit of experimental responses is not merely by chance. New data can be fitted by the model with 94% confidence. Prediction of missing response is achieved to 92% confidence as illustrated by pred. R^2. Model validity is further exemplified by the normal plot of residuals (Fig. 3a) and the scatter plot of predicted data vs. experimental data (Fig. 3b). The response surface generated by the regression equation is shown in Fig. 3c. It shows that EO time has a strong bearing on the cumulative yield of CO_{arom} with the yield increasing with increased EO time. The combined effect of EO current density and EO time is rather interesting. For short EO runs increasing current density increases the yield while at longer EO times there would be a marginal drop in yield with increased current density. A maximum of 306 mg of the cumulative yield of CO_{arom} would be obtained for the optimal conditions of 2.24 $mA.cm^{-2}$ EO current density and 18 h EO time (Table 7). The low EO current density requirement for maximizing the yield is also attractive from the point of view of energy consumption.

Table 5: ANOVA statistics using CCD for synthesis of different CO_{arom} from BSL on SS anode.

Parameters	CO_{arom}	Vanillin	Acetosyringone	Apocynin	Syringaldehyde
SD	10.49	10.93	1.06	0.68	4.30
Mean	221.61	128.22	19.75	4.90	79.03
%CV	4.73	8.53	5.37	14.04	5.44
Press	22086.3	20803	2108	1504	1015.3
R^2	0.97	0.97	0.99	0.97	0.95
Adj. R^2	0.94	0.94	0.96	0.96	0.91
Pred. R^2	0.92	0.88	0.89	0.51	0.58
Adequacy of prec.	18.31	21.99	29.39	20.49	14.22
Sum of squares	19040	24740	624.9	159.03	2323.8
Mean square	3808	4947.9	104.15	39.75	464.73
F-value	34.54	41.36	92.25	83.82	25.07
P-value	0.0007	0.0001	0.0001	0.0001	0.0006
LOF (P-value)	-[#]	-[#]	-[#]	-[#]	-[#]
Significant Model Terms	C, D, D^2, CD	C, D, D^2	C, D, C^2, D^2, D^3	D, C^2, D^2, D^3	C, D, C^2, D^2, CD

C – EO Current Density, D – EO time

[#] inadequate degree of freedom to calculate P-value LOF

Vanillin yield:

The experimental data for vanillin yield from EO of BSL on SS anode is fitted into regression equation in terms of coded parameters as

$$\text{Vanillin yield (mg)} = 121.48 + 27.52C + 59.03D - 7.14C^2 + 9.06D^2 - 16.11C^3 \quad (11)$$

p value of 0.0001, and R^2 value of 0.97 (ANOVA results, Table 5) denotes the significance of the model with a satisfactory fit. F value is sufficiently high as well to signify the model and LOF is insignificant. Adj. R^2 of 0.94 and pred. R^2 of 0.88 is close to R^2. The model can, therefore, fit new data with 94% confidence without bias and predict missing responses with 88% confidence. The normal plot of residuals and the scatter plot of predicted data vs. experimental data further lend credibility to the model as shown in Fig. 3a, and Fig. 3b, respectively. The response surface presented in Fig. 3c shows an almost monotonous increase in vanillin yield with EO time. Yield dependence on EO current density is less pronounced. The maximum vanillin yield is 200 mg at 5.87 $mA.cm^{-2}$ current density and 18 h EO time. This amounts to 20% of the initial lignin amount.

Syringaldehyde yield:

Another compound produced in significant quantity during EO of BSL on SS anode is syringaldehyde. In terms of coded parameters, the yield can be expressed as

$$\text{Syringaldehyde yield (mg)} = 69.5 + 5.76C - 5.76D + 11.13C^2 + 5.63D^2 - 15.04CD \quad (12)$$

Model significance and adequacy of fit are borne out by p, R^2, and F values (Table 5) as also by the normal plot of residuals, and the scatter plot of predicted data *vs.* experimental data (Fig. 3a, and Fig. 3b). Insignificant LOF lends credibility to the model. Adj. R^2 is 0.91 which is almost equal to R^2 showing an unbiased fit of data. The model is capable of fitting new data with 91% confidence. It can predict missing responses with 58% confidence as indicated by pred. R^2. The response surface, in this case, shown in Fig. 3c is quite interesting. At lower EO current density, the yield increases with increasing EO time. But the trend is reversed at higher current densities. Similarly, the yield increases with current density if EO time is less but decreases for EO times. The maximum yield of 112.8 mg – 11.3% of initial lignin amount – is achieved with 1 h EO time at 6.71 $mA.cm^{-2}$ EO current density.

(a)

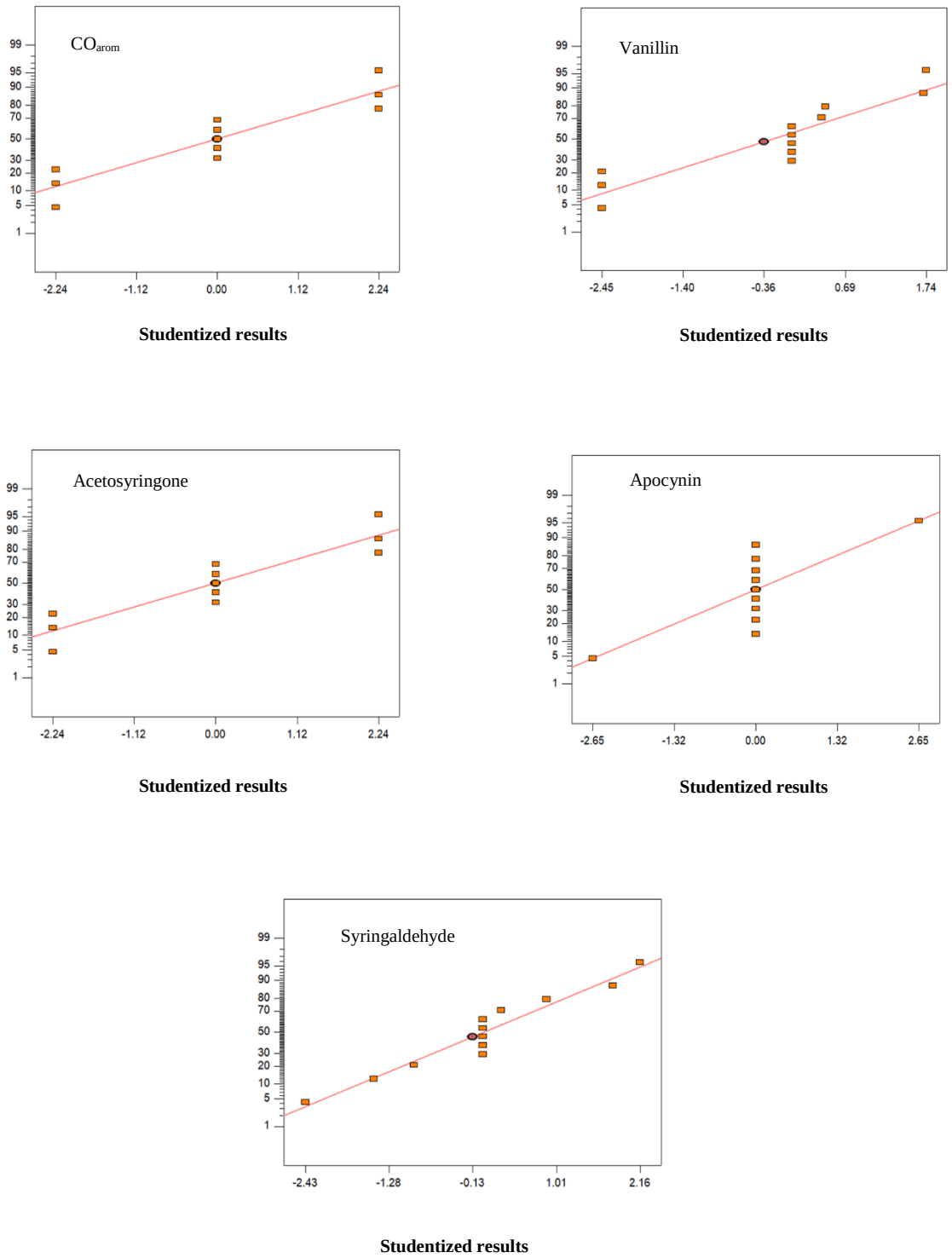


Fig. 3: RSM optimization of BSL EO on SS anode. (a) The normal plot of residuals.

(b)

Predicted data

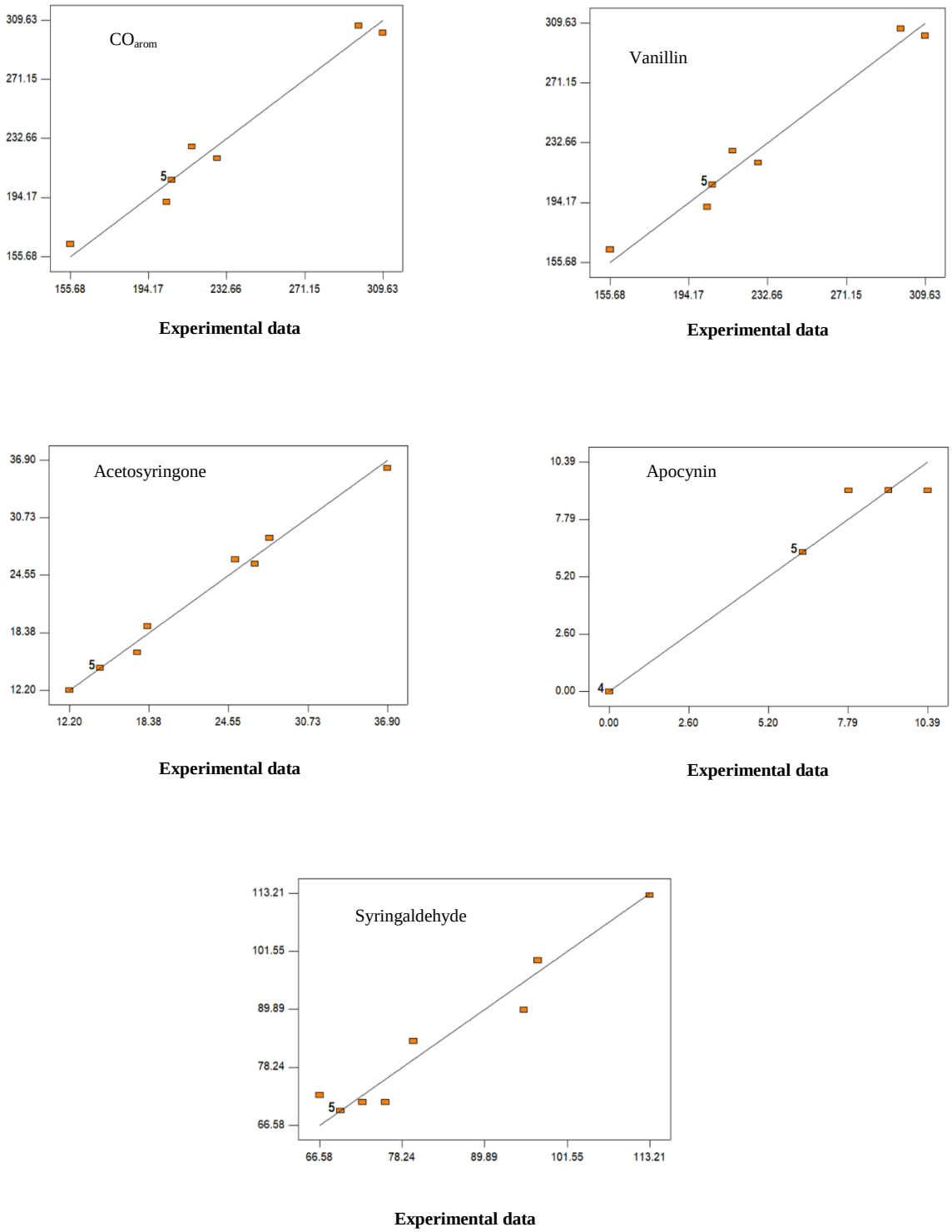


Fig. 3: RSM optimization of BSL EO on SS anode. (b) Predicted vs. actual.

(c)

Amount (mg)

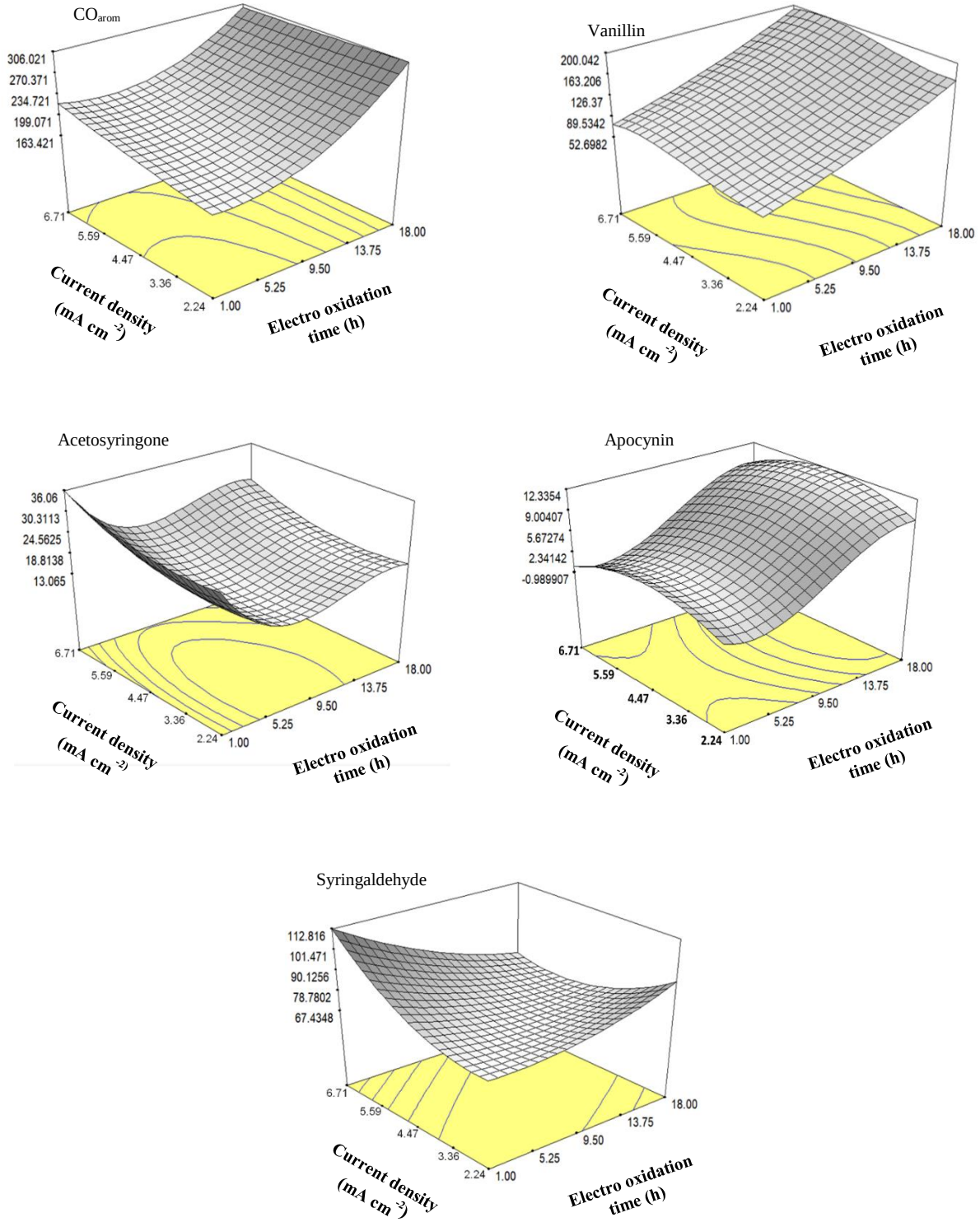


Fig. 3 RSM optimization of BSL EO on SS anode. (c) Response surface.

Table 6: ANOVA statistics using CCD for the synthesis of different CO_{arom} from BSL on TiMMO anode.

Parameters	CO_{arom}	Vanillin	Acetosyringone	Apocynin	Syringaldehyde
SD	8.44	5.70	3.23	6.94	3.03
Mean	144.12	59.99	18.84	5.98	65.28
%CV	5.85	9.51	17.15	116.08	4.65
Press	8690.31	3281.42	616.38	12255	1027.55
R^2	0.98	0.97	0.93	0.93	0.99
Adj. R^2	0.97	0.94	0.87	0.88	0.98
Pred. R^2	0.73	0.75	0.52	0.59	0.84
Adequacy of prec.	22.83	17.08	12.45	15.43	28.70
Sum of squares	32186.2	6453.72	851.68	4432.2	6436.28
Mean square	6437	1290.74	170.33	886.45	1287.26
F-value	90.33	39.62	16.29	18.39	139.52
P-value	0.0001	0.0002	0.0020	0.0014	0.0001
LOF (P-value)	-[#]	-[#]	-[#]	-[#]	-[#]
Significant Model Terms	C, D, C^2, CD	C, D, C^2, CD	D, C^2, CD	C, C^2, D^2, C^3	C, D, C^2, CD

C – EO Current Density, D – EO time
[#] *inadequate degree of freedom to calculate P-value LOF*

Acetosyringone and apocynin yields:

Regressed equations for acetosyringone, and apocynin, respectively, are

$$\text{Acetosyringone yield (mg)} = 14.58 + 3.53C + 5.11D + 3.35C^2 + 9.42D^2 - 0.21CD + 10.06D^3 \quad (13)$$

$$\text{Apocynin yield (mg)} = 6.30 + 9.12D - 3.17C^2 + 1.41D^2 - 4.57D^3 \quad (14)$$

ANOVA results from Table 5 and Fig. 3a, and Fig. 3b prove the models to be valid. R^2 and F values are high and LOF is insignificant. Adj. R^2 values are close to R^2 showing no bias in data fit. For acetosyringone pred. R^2 shows that missing responses are predicted by the model with 89% confidence. For apocynin, it is a shade lower at 51%. Fig. 3c presents the response surfaces. While the yield of acetosyringone is favored by less EO time, it is preferable to go for prolonged EO to increase the yield of apocynin. 36 mg is the highest acetosyringone yield (3.6% of the initial lignin amount) obtained at 6.71 $mA.cm^{-2}$ EO current density and 1 h EO time. The maximum apocynin yield obtained is 12 mg (1.2% of initial lignin amount) for 4.92 mA/cm^2 EO current density and 117.6 h EO time.

Optimized synthesis of CO_{arom} from BSL over TiMMO anode

Cumulative yield:

The cumulative yield of CO_{arom} could be represented by the following regression equation

$$\text{Cumulative yield (mg)} = 104.16 + 11.95C + 14.42D + 60.08C^2 - 3.35D^2 + 44.07CD \quad (15)$$

The model equation fits the experimental data well (R^2 0.98 in Table 6) and is significant (very low p value and high F value in Table 6). LOF is insignificant. The model is unbiased in fitting the data with 97% confidence depicted by adj. R^2. Pred. R^2 provides 73% Confidence in predicting missing responses by the model. The normal plot of residuals and the scatter plot of predicted data vs. experimental data have good linearity (Fig. 4a, and Fig. 4b). Fig. 4 c shows the response surface generated from the regression equation. At high EO current density increasing EO time yields more CO_{arom}. But the effect is almost masked at low current density. For all EO times, the mid ranges of current densities are to be avoided. The best yield of 231 mg could be achieved at 13.27 $mA.cm^{-2}$ EO current

(a)

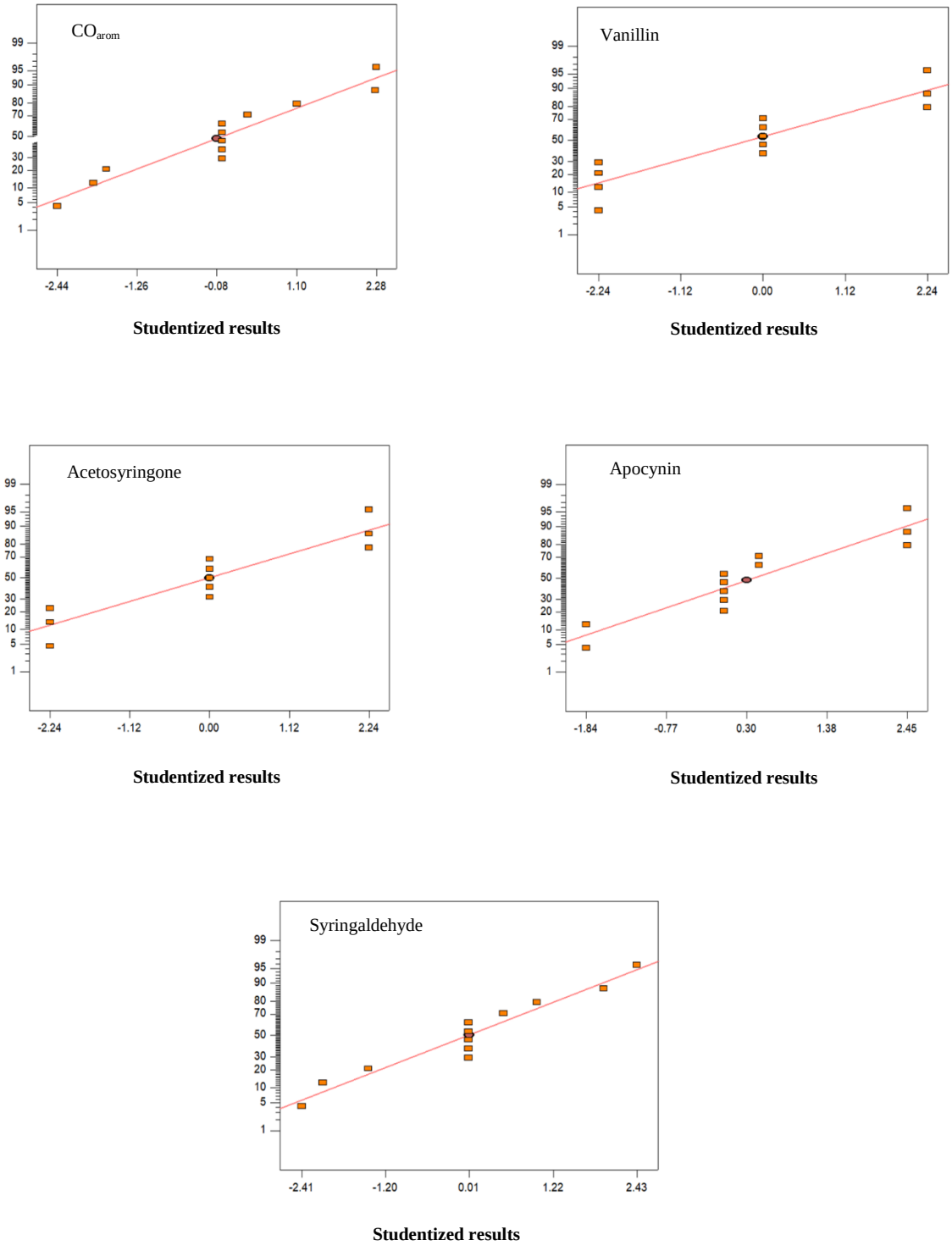
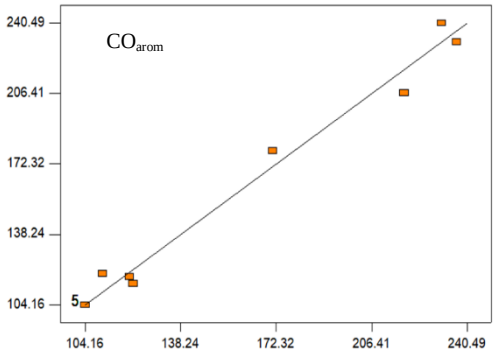


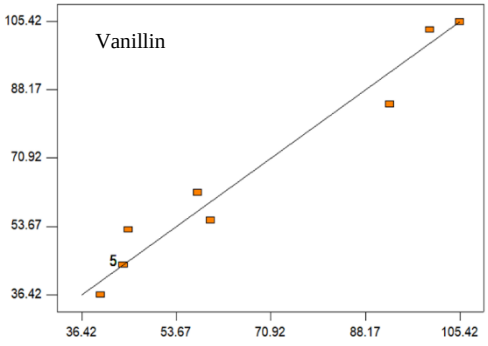
Fig. 4 RSM optimization of BSL EO on TiMMO anode. (a) The normal plot of residuals.

(b)

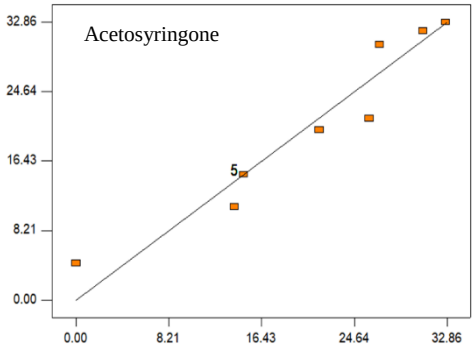
Predicted data



Experimental data



Experimental data



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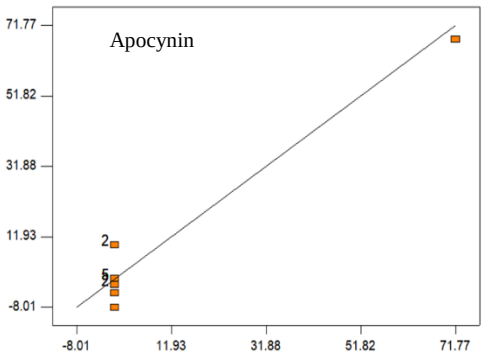
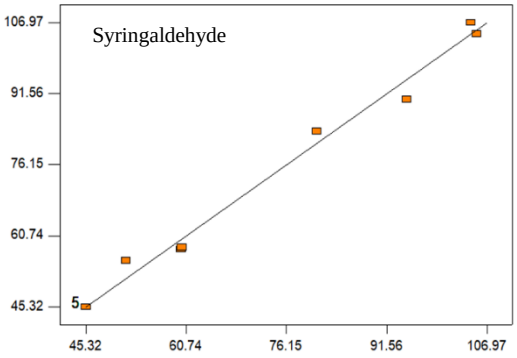


Experimental data



Experimental data

Fig. 4 RSM optimization of BSL EO on TiMMO anode. (b) Predicted vs. actual.

(c)

Amount (mg)

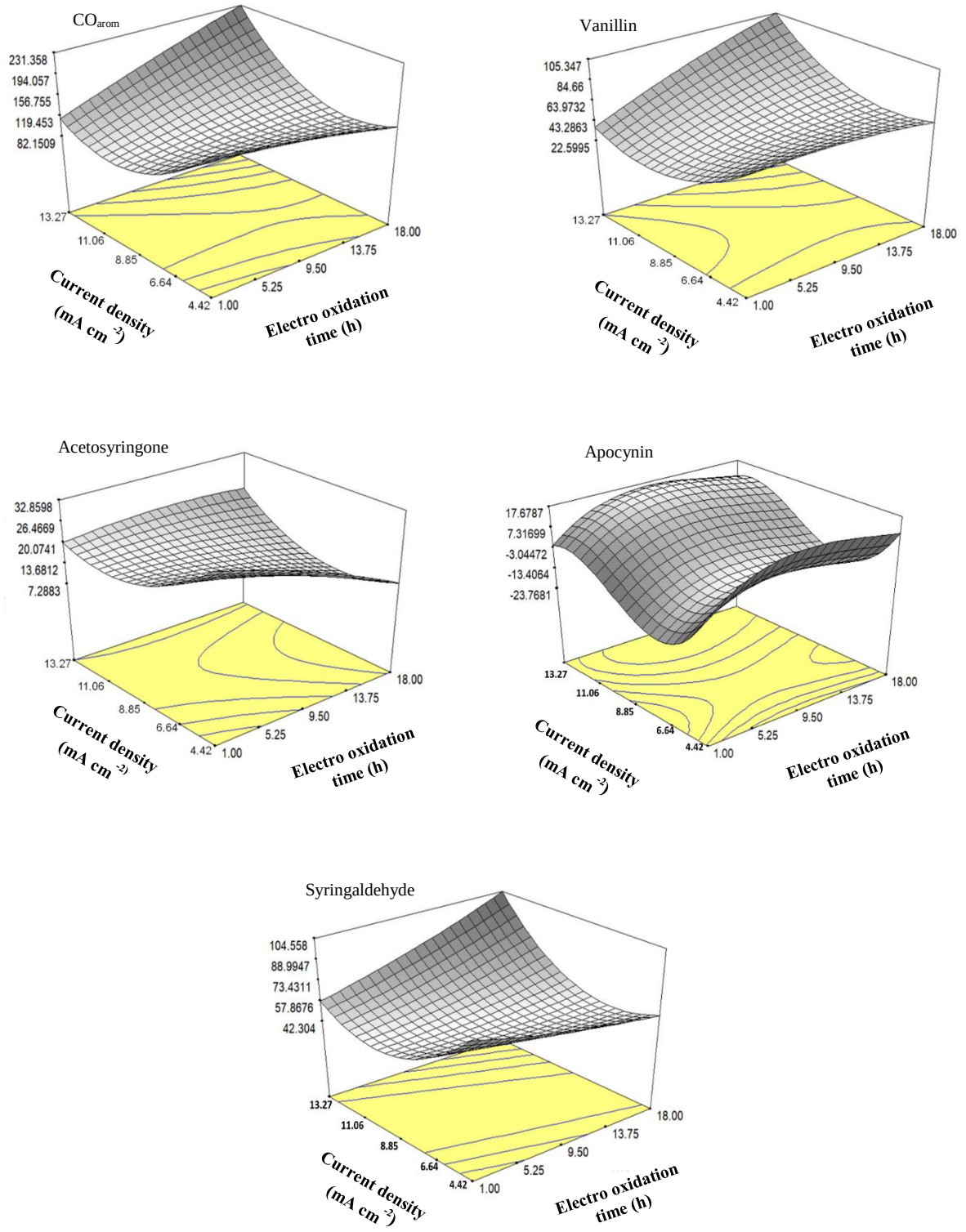


Fig. 4 RSM optimization of BSL EO on TiMMO anode. (c) Response surface.

density with EO carried out for 18 h, amounting to 23.1% of the initial lignin amount.

Vanillin yield:

The regressed equation – R^2 0.97, F value 39.6, p value 0.0002, and insignificant LOF from Table 6 – for vanillin yield comes out to be

$$\text{Vanillin yield (mg)} = 43.98 + 6.65C + 14.88 + 25.12C^2 - 4.88D^2 + 19.58CD \quad (16)$$

The model gives 94% confidence in the unbiased fitting of new data with adj. R^2 0.94. It can predict missing responses with 75% confidence, suggested by pred. R^2. The normal plot of residuals, and the scatter plot of predicted data vs. experimental data in Fig. 4a, and Fig. 4b have good linear distributions. Fig. 4c presents the regressed response surface. There is a slight increasing trend in yield with EO time which is more pronounced at high current density. The mid-range of current density is not conducive to vanillin yield, which is favoured by high EO current density and high EO time. The maximum yield is 105 mg (10.5% of lignin) achieved with 13.27 mA/cm^2 EO current density and 18 h EO time.

Syringaldehyde yield:

Syringaldehyde yield over TiMMO anode could be expressed in terms of coded parameters as

$$\text{Syringaldehyde yield (mg)} = 45.32 + 5.88C + 4.66D + 26.83C^2 + 3.13D^2 + 18.70CD \quad (17)$$

ANOVA results from Table 6 as well as the normal plot of residuals, and the scatter plot of predicted data vs. experimental data in Fig. 4a, and Fig. 4b support the significance of the model adequacy of fit. R^2 and F values are high and LOF is insignificant. Adj. R^2 is 0.98 and pred. R^2 is 0.84. The model, therefore, is unbiased to the extent of 98% confidence in fitting new data and predicts missing responses with 84% confidence. Response surface for yield as a function of EO current density and EO time is shown in Fig. 4c. When the current density is low, we expect a slight drop in yield with increasing EO time. But, at high current density increasing, EO time would increase the yield of syringaldehyde. The mid-range of current density is better avoided as it would lower the yield. The maximum obtainable yield is 104 mg at 13.27 mA/cm^2 EO current density and 18 h EO time, equivalent to 10.4% on initial lignin amount.

Acetosyringone and apocynin yields:

Regressed equations for acetosyringone, and apocynin, respectively, are

$$\text{Acetosyringone yield (mg)} = 14.85 - 0.57C - 5.12D + 8.12C^2 + 1.60D^2 + 5.78CD \quad (18)$$

$$\text{Apocynin yield (mg)} = 0.01 + 25.75C + 16.01C^2 - 12.02D^2 - 25.76C^3 + 5.66D^3 \quad (19)$$

Equations are significant and the data fit adequate as revealed by ANOVA results (low p values, high R^2, and F values, and insignificant LOF in Table 6), and error analysis (Fig. 4a, and Fig. 4b). Adj. R^2 does not differ much from R^2 showing that the data fit is reasonably unbiased. Like other compounds, the mid-range of current density is disadvantageous for yield. For acetosyringone, a slight drop in yield is expected with increasing EO time. However, with the increase in EO time, the apocynin yield first increases, attains a maximum, and decreases thereafter. 1 h EO at 4.44 mA.cm^{-2} current density yields a maximum of 33 mg acetosyringone (3.3% of lignin). To get the maximum of 18 mg apocynin (1.8% of lignin) the required conditions were 12.5 mA.cm^{-2} current density and 9.5 h EO time.

The results obtained for all value-added products compare favorably with that previously reported in the literature; however, these results were only for the formation of these value-added products from electro-oxidation of lignin [21-28, 32-34]. The optimal cumulative yield of CO_{arom} from RSM optimization varied between 7 – 30% while in literature it is 24.7 % with different anodic material [47]. For vanillin, the optimized yield by RSM varied between 3 – 20% in comparison to about 6 % reported in the literature with different types of anode [47, 48]. For other value-added products there is a lack of information in technical literature.

Effect of anode material and lignin source

A comparative account of optimal yields is given in Table 7. For the cumulative yield of CO_{arom} as well as the synthesis of vanillin, and acetosyringone, SS anode fares better than TiMMO. Optimal syringaldehyde yields are comparable for both the anodes. However, SS anode

Table 7: Optimal process conditions and yields for synthesis of different CO_{arom}

Materials	FAC.1[a] (Actual)	FAC.1[a] (Coded)	FAC.2[b] (Actual)	FAC.2[b] (Coded)	Compound	(mg)[c]	% Yield
SS_WS	3.3	-0.53	6.60	-0.34	CO_{arom}	276.82	27.7
	4.77	0.13	5.92	-0.42	Vanillin	81.22	8.1
	3.22	-0.56	5.92	-0.42	Acetosyringone	124.16	12.4
	2.24	-1.00	5.99	-0.41	Apocynin	27.33	2.7
	3.27	-0.54	6.33	-0.37	Syringaldehyde	26.32	2.6
TiMMO_WS	10.24	0.31	6.73	-0.33	CO_{arom}	71.75	7.2
	13.27	1	13.64	0.49	Vanillin	31.94	3.2
	12.01	0.71	10.20	0.50	Acetosyringone	42.27	4.2
	9.05	0.05	10.85	0.16	Benzaldehyde	17.55	1.8
SS_Bagasse	2.24	-1	18	1	CO_{arom}	306.02	30.6
	5.87	0.62	18	1	Vanillin	200.05	20
	6.71	1	1	-1	Acetosyringone	36.06	3.6
	4.92	0.20	17.62	0.91	Apocynin	12.21	1.2
	6.71	1	1	-1	Syringaldehyde	112.81	11.3
TiMMO_Bagasse	13.27	1	18	1	CO_{arom}	231.35	23.1
	13.27	1	18	1	vanillin	105.34	10.5
	4.44	-1	1.05	-0.99	Acetosyringone	32.74	3.3
	12.48	0.82	9.50	-0.00	Apocynin	17.69	1.8
	13.27	1	18	1	Syringaldehyde	104.55	10.5

[a]EO Current Density, [b]EO time, [c]Optimal Yield

requires lesser EO current density, and EO time, which would be economically advantageous. Interaction of lignin with iron during EO [46] could be the reason for these differences.

Vanillin is produced irrespective of lignin source and anode material. However, BSL yields significantly higher amounts of vanillin compared to WSSL. With WSSL acetosyringone is the predominant CO_{arom} during EO, but this compound is not produced in significant quantity with BSL. On the contrary, syringaldehyde is produced in significant quantities with EO of BSL, but this compound does not contribute much to the product mix of WSSL EO. Benzaldehyde is produced in modest yields only when WSSL is subjected to EO on TiMMO. With BSL, there is an overall predominance of aldehydes over ketones in the product mix. It is pertinent to note, however, that EO of lignin proceeds through an intricate set of series and parallel reactions [2], each with its kinetics. Predominant oxidant species reacting with the organic moieties is hydroxyl radical, which is nonselective due to its high reactivity. Hence, individual CO_{arom} compounds are not only formed but also subsequently react to transform into other compounds, and finally mineralize. All these are likely to influence the optimal yields of different CO_{arom} compounds.

CONCLUSIONS

EO process conditions could be optimized using RSM to get the highest possible yields of total CO_{arom} and individual compounds. The type of anode, and source of lignin, both affected the product mix and yields from EO. While vanillin was the main product, other aromatic aldehydes or ketones were formed and their maximized yields were dependent on optimal process conditions.

Important among these were acetosyringone, syringaldehyde, apocynin, and benzaldehyde. EO current density and EO time were the key parameters that affected the yields. As anode material, SS was found to be better than TiMMO for the synthesis of CO_{arom} compounds. BSL yielded higher amounts of CO_{arom} compounds compared to WSSL. The cumulative yield of CO_{arom} varied between 7 – 30% and that for vanillin varied between 3 – 20%.

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REFERENCES

[1] Ghatak H.R., Biorefineries from the Perspective of Sustainability: Feedstocks, Products, and Processes, *Renewable Sustainable Energy Rev.*, **15(8)**: 4042-4052 (2011).

[2] Singh S., Ghatak H.R., Vanillin Formation by Electrooxidation of Lignin on Stainless Steel Anode: Kinetics and By-Products, *J. Wood Chem. Technol.*, **37(6)**: 407-422 (2017).

[3] Tejado A., Pena C., Labidi J., Echeverria J.M., Mondragon I., Physico-chemical Characterization of Lignins from Different Sources for Use in Phenol–Formaldehyde Resin Synthesis, *Bioresour. Technol.*, **98(8)**: 1655-1663 (2007).

[4] Zhu W., Westman G., Theliander H., Investigation and Characterization of Lignin Precipitation in the Lignoboost Process, *J. Wood Chem. Technol.*, **34(2)**: 77-97 (2014).

[5] Aso T., Koda K., Kubo S., Yamada T., Nakajima I., Uraki Y., Preparation of Novel Lignin-Based Cement Dispersants from Isolated Lignins, *J. Wood Chem. Technol.*, **33(4)**: 286-298 (2013).

[6] Ghatak H.R., Spectroscopic Comparison of Lignin Separated by Electrolysis and Acid Precipitation of Wheat Straw Soda Black Liquor, *Ind. Crops Prod.*, **28(2)**: 206-212 (2008).

[7] da Silva E.B., Zabkova M., Araújo J.D., Cateto C.A., Barreiro M.F., Belgacem M. N., Rodrigues A.E., An Integrated Process to Produce Vanillin And Lignin-Based Polyurethanes from Kraft Lignin, *Chem. Eng. Res. Des.*, **87(9)**:1276-1292 (2009).

[8] Xiao C., Bolton R., Pan W.L., Lignin from Rice Straw Kraft Pulping: Effects on Soil Aggregation and Chemical Properties, *Bioresour. Technol.*, **98(7)**: 1482-1488 (2007).

[9] Suparno O., Covington A.D., Phillips P.S., Evans C.S., An Innovative New Application for Waste Phenolic Compounds: Use of Kraft Lignin And Naphthols In Leather Tanning, *Resour., Conserv. Recycl.*, **45(2)**: 114-127 (2005).

[10] Kadla J.F., Kubo S., Venditti R.A., Gilbert R.D., Compere A.L., Griffith W., Lignin-Based Carbon Fibers for Composite Fiber Applications, *Carbon*, **40(15)**: 2913-2920 (2002).

[11] Hayashi J.I., Muroyama K., Gomes V.G., Watkinson A.P., Fractal Dimensions of Activated Carbons Prepared from Llignin by Chemical Activation, *Carbon*, **40(4)**: 630-632 (2002).

[12] Fierro V., Torné-Fernández V., Celzard A., Kraft Lignin as a Precursor for Microporous Activated Carbons Prepared by Impregnation with Ortho-Phosphoric Acid: Synthesis and Textural Characterization, *Microporous Mesoporous Mater.*, **92(1-3)**:2 43-250 (2006).

[13] Pouteau C., Dole P., Cathala B., Averous L., Boquillon N., Antioxidant Properties of Lignin in Polypropylene, *Polym. Degrad. Stab.*, **81(1)**: 9-18 (2003).

[14] Pucciariello R., Villani V., Bonini C., D'Auria M., Vetere T., Physical Properties of Straw Lignin-Based Polymer Blends, *Polymer*, **45(12)**:4159-4169 (2004).

[15] Anglès M.N., Reguant J., Garcia-Valls R., Salvado J., Characteristics of Lignin Obtained from Steam-Exploded Softwood with Soda/Anthraquinone Pulping, *Wood Sci. Technol.*, **37(3-4)**: 309-320 (2003).

[16] Zheng Y., Chen D., Zhu X., Aromatic Hydrocarbon Production by the Online Catalytic Cracking of Lignin Fast Pyrolysis Vapors Using Mo_2N/γ-Al_2O_3, *J. Anal. Appl. Pyrolysis*, **104**: 514-520 (2013).

[17] Joffres B., Nguyen M.T., Laurenti D., Lorentz C., Souchon V., Charon N., Geantet C., Lignin Hydroconversion on MoS_2-Based Supported Catalyst: Comprehensive Analysis of Products and Reaction Scheme, *Appl. Catal., B*, **184**: 153-162 (2016).

[18] Stefanidis S.D., Karakoulia S.A., Kalogiannis K.G., Iliopoulou E.F., Delimitis A., Yiannoulakis H., Triantafyllidis K.S., Natural Magnesium Oxide (MgO) Catalysts: A Cost-Effective Sustainable Alternative to Acid Zeolites for the in Situ Upgrading of Biomass Fast Pyrolysis Oil, *Appl. Catal., B*, **196**:155-173 (2016).

[19] Liang S., Wan C., Biorefinery Lignin to Renewable Chemicals *Via* Sequential Fractionation and Depolymerisation, *Waste Biomass Valorization*, **8(2)**: 393-400 (2017).

[20] Villar J.C., Caperos A., Garcia-Ochoa F., Oxidation of Hardwood Kraft-Lignin to Phenolic Derivatives. Nitrobenzene and Copper Oxide as Oxidants, *J. Wood Chem. Technol*., **17(3)**: 259-285 (1997).

[21] Mathias A.L., Rodrigues A.E., Production of Vanillin by Oxidation of Pine Kraft Lignins with Oxygen, *Holzforschung*, **49(3)**: 273-278 (1995).

[22] Araújo J.D., Grande C.A., Rodrigues A.E., Vanillin Production from Lignin Oxidation in a Batch Reactor, *Chem. Eng. Res. Des.*, **88(8)**:1024-1032 (2010).

[23] Costa C.A.E., Pinto P.C.R., Rodrigues A.E., Radar Tool for Lignin Classification on the Perspective of its Valorization, *Ind. Eng. Chem. Res.*, **54(31)**: 7580-7590 (2015).

[24] Pinto P.C.R., Costa C.A.E., Rodrigues A.E., Oxidation of Lignin from Eucalyptus Globulus Pulping Liquors to Produce Syringaldehyde and Vanillin, *Ind. Eng. Chem. Res.*, **52(12)**: 4421-4428 (2013).

[25] Mota M.I.F., Pinto P.C.R., Loureiro J.M., Rodrigues A.E., Recovery of Vanillin and Syringaldehyde from Lignin Oxidation: A Review of Separation and Purification Processes, *Sep. Purif. Rev.*, **45(3)**:227-259 (2016).

[26] Mota M.I.F., Pinto P.C.R., Loureiro J.M., Rodrigues A.E., Successful Recovery and Concentration of Vanillin and Syringaldehyde onto a Polymeric Adsorbent with Ethanol/Water Solution *Chem. Eng. J. (Amsterdam, Neth.)*, **294**:73-82 (2016).

[27] Villar J.C., Caperos A., Garcia-Ochoa F., Oxidation of Hardwood Kraft-Lignin to Phenolic Derivatives with Oxygen as Oxidant, *Wood Sci. Technol.*, **35(3)**: 245-255 (2001).

[28] Sales F.G., Abreu C.A.M., Pereira J.A.F.R., Catalytic Wet-Air Oxidation of Lignin in a Three-Phase Reactor with Aromatic Aldehyde Production, *Braz. J. Chem. Eng.*, **21(2)**: 211-218 (2004).

[29] Shiraishi T., Takano T., Kamitakahara H., Nakatsubo F., Studies on Electrooxidation of Lignin and Lignin Model Compounds. Part 1: Direct Electrooxidation of Non-Phenolic Lignin Model Compounds, *Holzforschung*, **66(3)**: 303-309 (2012).

[30] Shiraishi T., Takano T., Kamitakahara H., Nakatsubo F., Studies on Electro-Oxidation of Lignin and Lignin Model Compounds. Part 2: N-Hydroxyphthalimide (NHPI)-Mediated Indirect Electro-Oxidation of Non-Phenolic Lignin Model Compounds, *Holzforschung*, **66(3)**: 311-315 (2012).

[31] Sannami Y., Kamitakahara H., Takano T., TEMPO-Mediated Electro-Oxidation Reactions of Non-Phenolic β-O-4-type Lignin Model Compounds, *Holzforschung*, **71(2)**:109-117 (2017).

[32] Zhang Y.M., Peng Y., Yin X.L., Liu Z.H., Li G., Degradation of Lignin to BHT by Electrochemical Catalysis on Pb/PbO_2 Anode in Alkaline Solution, *J. Chem. Technol. Biotechnol.*, **89**(12): 1954-1960 (2014).

[33] Ghahremani R., Staser J.A., Electrochemical Oxidation of Lignin for the Production of Value-Added Chemicals on Ni-Co Bimetallic Electrocatalysts, *Holzforschung*, **72(11)**: 951-960 (2018).

[34] Schmitt D., Regenbrecht C., Schubert M., Schollmeyer D., Waldvogel S.R., Treatment of Black Liquor (BL) by Adsorption on AE Resins and a Subsequent Electrochemical Degradation of BL to Obtain Vanillin, *Holzforschung*, **71(1)**:35-41 (2017).

[35] Abbasi S., Ekrami-Kakhki M.S., Tahari M., Modeling and Predicting the Photodecomposition o Methylene Blue via $ZnO–SnO_2$ Hybrids Using Design of Experiments (DOE), *J. Mater. Sci.: Mater. Electron.*, **28(20)**: 15306-15312 (2017).

[36] Abbasi, S., Hasanpour, M., Ekrami-Kakhki, M.-S., Removal Efficiency Optimization of Organic Pollutant (Methylene Blue) with Modified Multi-Walled Carbon Nanotubes Using Design of Experiments (DOE), *J. Mater. Sci.: Mater. Electron.*, **28(13)**: 9900–9910 (2017).

[37] Ekrami-Kakhki, M.-S., Abbasi, S., Farzaneh, N., Statistical Analysis of the Electrocatalytic Activity of Pt Nanoparticles Supported on Novel Functionalized Reduced Graphene Oxide-Chitosan for Methanol Electrooxidation, *Electron. Mater. Lett.*, **14(1)**:70–78 (2017).

[38] Ekrami-Kakhki, M.S., Abbasi, S. and Farzaneh, N., Design of Experiments Methodology to Investigate Methanol Electrooxidation on Pt Nanoparticles Supported Novel Functionalized Reduced Graphene Oxide, *Anal. Bioanal. Electrochem.*, **10(12)**: 1548-1561 (2018).

[39] Hinkelmann K., "Design and Analysis of Experiments, Volume 3: Special Designs and Applications", John Wiley & Sons, New York (2011).

[40] Rajkumar K., Muthukumar M., Optimization of Electro-Oxidation Process for the Treatment of Reactive Orange 107 Using Response Surface Methodology, *Environ. Sci. Pollut. Res.*, **19(1)**:148-160 (2012).

[41] Aleboyeh A., Daneshvar N., Kasiri M.B., Optimization of CI Acid Red 14 Azo Dye Removal by Electrocoagulation Batch Process with Response Surface Methodology, *Chem. Eng. Processing: Process Intensif.*, **47(5)**: 827-832 (2008).

[42] Körbahti B.K., Response Surface Optimization of Electrochemical Treatment of Textile Dye Wastewater, *J. Hazard. Mater.*, **145(1-2)**: 277-286 (2007).

[43] Abbasi, S., Photocatalytic Activity Study of Coated Anatase-Rutile Titania Nanoparticles with Nanocrystalline Tin Dioxide Based on the Statistical Analysis, *Environ. Monit. Assess.*, **191(4)** (2019).

[44] Abbasi S., Ahmadpoor F., Imani M., Ekrami-Kakhki M.-S., Synthesis of Magnetic Fe_3O_4@ZnO@graphene Oxide Nanocomposite for Photodegradation of Organic Dye Pollutant, *Int. J. Environ. Anal. Chem.*, 1-16 (2019).

[45] Abbasi, S., Adsorption of Dye Organic Pollutant Using Magnetic ZnO Embedded on the Surface of Graphene Oxide, *J. Inorg. Organomet. Polym. Mater.*, 1-11 (2019).

[46] Ghatak H.R., Iron Complexated Lignin from Electrolysis of Wheat Straw Soda Black Liquor and its Characterization, *Ind. Crops Prod.*, **43**: 738-744 (2013).

[47] Singh S., Ghatak H.R., Process Optimization of Lignin Conversion into Value Added Chemicals by Thermochemical Pretreatment and Electrooxidation on a Stainless Steel Anode, *Holzforschung*, **72(3)**: 187-199 (2018).

[48] Reichert E., Wintringer R., Volmer D.A., Hempelmann R., Electro-Catalytic Oxidative Cleavage of Lignin in a Protic Ionic Liquid, *Phys. Chem. Chem. Phys.*, **14(15)**: 5214-5221 (2012).