Acid-Catalyzed Direct Synthesis of Methyl Levulinate from Paper Sludge in Methanol Medium

Lincai Peng,[a,c,]* Lu Lin,[b,]* Hui Li,[a] and Keli Chen [a]

A direct synthesis of methyl levulinate from the degradation of paper sludge in a methanol medium at moderate temperatures (≤ 230 °C) was performed using low-concentration sulfuric acid (≤ 0.05 mol/L) as the catalyst. Response surface methodology with a four-factor, five-level central composite rotatable design was employed to optimize the process conditions for maximized methyl levulinate production under the condition of controlling the dehydration of methanol to dimethyl ether. The yields of methyl levulinate and dimethyl ether as a function of the process variables were fitted to second-order polynomial models through application of multiple regression analyses. A good agreement between the experimental and modeled data was obtained. When the controlled yield of dimethyl ether was less than 20%, a maximum methyl levulinate yield of 54.8% was achieved, corresponding to 27.7% (w/w) overall yield for dry paper sludge. The findings indicated that paper sludge can act as a potential biomass material for upgrading and converting into high value-added chemicals.

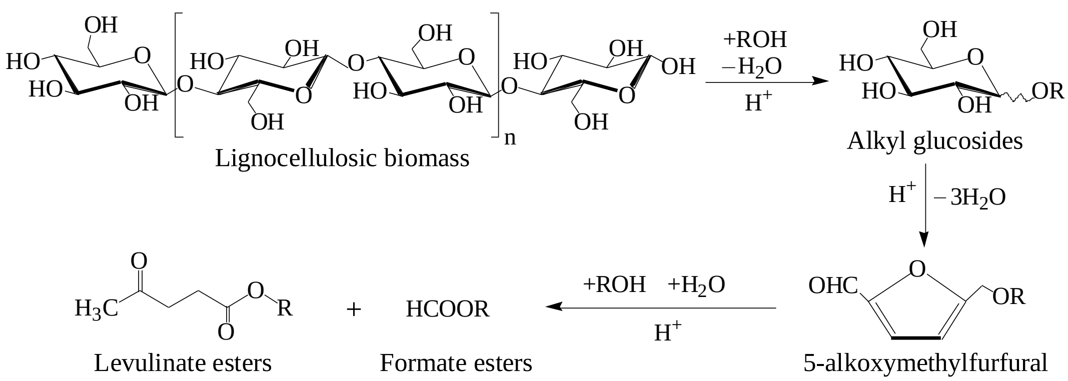
Keywords: Paper sludge; Alcoholysis; Response surface methodology; Methyl levulinate; Dimethyl ether

*Contact information: a: Faculty of Chemical Engineering, Kunming University of Science and Technology, Kunming 650500, China; b: School of Energy Research, Xiamen University, Xiamen 361005, China; c: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China; *Corresponding authors: penglincai8@163.com; lulin@xmu.edu.cn*

INTRODUCTION

Paper sludge is a solid by-product of the pulp and papermaking industries. The amount of paper sludge produced every year is enormous, and its disposal has been identified as posing a substantial problem for the paper mill industry (Hu *et al*. 2012). Currently, the bulk of paper sludge is disposed of in landfills or burned, which not only wastes potentially valuable resources but also pollutes the environment. However, many types of paper sludge are potentially attractive raw materials for the production of bio-fuel and chemicals (Xu and Lancaster 2008; Peng and Chen 2011; Kang *et al*. 2012). Paper sludge basically contains insoluble fibres, filler, flocculant, and other impurities. Compared to other lignocellulosic feedstocks, the composition of paper sludge is not typical (carbohydrate composition varies from 20 to 80%) (Budhavaram and Fan 2009). With regard to the paper sludge with high lignocellulosic content, it offers an excellent opportunity as biomass feedstock for upgrading of paper sludge.

In recent years, the direct synthesis of levulinate esters from acid-catalyzed reactions of lignocellulosic biomass or biomass-derived sugars and alcohols has attracted considerable interest as part of a bio-refinery. The generally accepted reaction pathway is schematically given in Scheme 1 (Peng *et al*. 2011). An advantage of this technology is that the synthetic technique is simple, wastewater is minimized, and higher-grade products are easily isolated by fractionation. Levulinate esters are versatile chemical feedstocks that have extensive industrial applications either in the fragrances and flavors industry or as diesel miscible bio-fuels (Hayes 2009; Joshi *et al*. 2011; Wang *et al*. 2012). There have been some reports on the direct production of levulinate esters from carbohydrates such as cellulose, sucrose, glucose, and fructose, and of biomass feedstocks including wood, bagasse, and wheat straw (Peng *et al*. 2011; Tominaga *et al*. 2011; Chang *et al*. 2012; Saravanamurugan and Riisager 2012). However, to our knowledge, less attention has been paid to the synthesis of levulinate esters from paper sludge. To improve the value of paper sludge, the direct conversion of paper sludge with high lignocellulosic content into levulinate esters might be a novel alternative method. On the other hand, the previous studies mainly focused on the optimization of levulinate esters yield. They took no account of the side reaction involving the formation of undesired diether from the acid-catalyzed inter-molecular dehydration of alcohols medium, a reaction that must be seen as to some extent unavoidable under the experimental conditions (Mascal and Nikitin 2010). If diether production could be minimized, it would be very favorable for the recycling of alcohols on an industrial scale.



Scheme 1. Reaction pathway for the direct synthesis of levulinate esters from acid-catalyzed reactions of lignocellulosic biomass and alcohols

The aim of this study was to identify whether paper sludge can be a useful biomass source for the acid-catalyzed direct synthesis of levulinate esters. Here, methanol was selected as a reaction medium to be explored. The chemical composition of the paper sludge was determined, followed by comprehensive studies using response surface methodology (RSM) to optimise the yield of methyl levulinate under the condition of controlling the dehydration of methanol to dimethyl ether by altering the process variables (H_2SO_4 concentration, temperature, stirring rate, and time).

EXPERIMENTAL

Materials and Chemicals

The paper sludge employed in this study was obtained from a toilet paper mill and was produced from bleached kraft wood pulp (Zhongshun Paper Co., Ltd, Guangdong, China). The paper sludge contained calcium carbonate that rendered the resulting suspensions alkaline. Therefore, prior to experiments, the paper sludge was neutralized with a 1.0 M sulfuric acid aqueous solution, cleaned with distilled water, then air-dried and crushed. The methyl levulinate (99% purity) used for calibration was obtained from Alfa Aesar (Tianjin, China). The other reagents and chemicals were all of analytical grade, purchased from Sinopharm Chemical Reagent (Shanghai, China), and used without further purification or treatment.

Equipment and Experimental Procedures

All experiments were conducted in a 100-mL cylindrical stainless steel pressurized reactor made by Parr Instruments, USA. The reactor was heated in an adjustable electric oven. The temperature of the reactor contents was monitored by a thermocouple connected to the reactor. In accordance with previous experimental findings and the related literature (Chang *et al*. 2012; Peng *et al*. 2012), four key process variables, including H_2SO_4 concentration, temperature, stirring rate, and time, were selected as the experimental design factors to be studied. For each experiment, 2.5 g of paper sludge and a 50-mL portion of a solution of sulfuric acid in methanol were added to the reactor, which was then brought to the desired temperature by about 25 min of external heating, which both heated the system and generated stirring for the reaction. After a certain reaction time, the reactor was taken from the oven, quenched in an ice water bath to terminate the reaction, and fully depressurized. Then, the sample taken from the reactor was filtered and the liquid-phase products were collected for further analyses.

Analytical Approach

The paper sludge was dried to constant weight at 90 °C, cooled in a desiccator, and weighed. The cellulose, hemicelluloses, and lignin contents of the dried paper sludge were determined by a two-step quantitative hydrolysis using sulfuric acid and based on the method described by Yamashita *et al*. (2008). The ash content was determined by heating the dried paper sludge in a muffle furnace at 600 °C. The elemental composition of ash was analyzed *via* X-ray photoelectron spectroscopy (XPS). The XPS measurement was made on a Kratos Ultra system employing an Al Kα radiation source with 1 eV per step for a survey spectrum over a binding energy range of 0 to 1100 eV.

The amount of methyl levulinate (MLA) was determined on a GC (Agilent 6890 instrument) equipped with an HP-5 capillary column with dimensions of 30.0 m × 320 μm × 0.25 μm and a flame ionization detector (FID) operating at 270 °C. The MLA yield on a molar basis according to reaction stoichiometry was calculated using Equation (1).

$$\text{MLA yield}(\%) = \frac{\text{Amount of MLA after reaction (mol)} \times 100}{\text{Amount of glucose monomer in paper sludge (mol)}} \tag{1}$$

Equation (2) was used to calculate the overall yield for the conversion of paper sludge (dry matter basis) into methyl levulinate.

$$\text{Overall yield (\%, w/w)} = \frac{\text{Weight of MLA after reaction (g)} \times 100}{\text{Weight of dry paper sludge (g)}} \tag{2}$$

Due to the fact that dimethyl ether (DME) formed from the dehydration of the methanol medium was discharged in gaseous form when the reactor was deflated after the reaction and no other gas was generated from reactants during the reaction, the yield of dimethyl ether was calculated using Equation (3) according to the weight loss of the reactants before and after the reaction (Carr *et al*. 2011).

$$\text{DME yield (\%)} = \frac{\text{Weight loss of reactants before and after reaction (g)} \times 64 \times 100}{\text{Weight of methanol before reaction (g)} \times 46} \quad (3)$$

Experimental Design for Optimization

Response surface methodology (RSM) with a four-factor, five-level central composite rotatable design (CCRD) was employed to study the effects of the reaction conditions on the response variables and to optimize the process conditions in the conversion of paper sludge to MLA. For the statistical calculations, the relationship between the coded values and real values is described by Equation (4),

$$X_i = (x_i - x_0)/\Delta x \quad (4)$$

where X_i is a coded value of the independent variable, x_i is the real value of the independent variable, x_0 is the real value of the independent variable at the center point, and Δx is the step change of the independent variable. In this study, the independent variables and their corresponding ranges that were selected for the synthesis of MLA in a methanol medium were as follows: H_2SO_4 concentration, x_1 (0.01 to 0.05 M); temperature, x_2 (170 to 230 °C); stirring rate, x_3 (0 to 800 rpm), and time, x_4 (50 to 250 min). The levels of the variables for the CCRD are presented in Table 1.

Table 1. Range of Variables and their Corresponding Levels for the CCRD

Variable	Levels				
	–2	–1	0	+1	+2
H_2SO_4 concentration, x_1 (M)	0.01	0.02	0.03	0.04	0.05
Temperature, x_2 (°C)	170	185	200	215	230
Stirring rate, x_3 (rpm)	0	200	400	600	800
Time, x_4 (min)	50	100	150	200	250

The total number of required experiments (*N*) was 30, as obtained by use of Equation (5),

$$N = 2^K + 2k + n_0 \quad (5)$$

where *k* is the number of independent variables and n_0 is the number of replicated center points. The fractional factorial design was composed of 16 factorial points, 8 axial points, and 6 center points. The center point was repeated six times to give a good estimate of the experimental error (Mohammad *et al*. 2006). The applied experimental design is shown in Table 2.

All the experiments were performed in triplicate. MLA from the transformation of cellulose in paper sludge was selected as the target product, and MLA yield (Y_1) was taken as the major dependent variable or response. In this reaction process, another concern was the formation of undesired DME due to the acid-catalyzed inter-molecular dehydration of the methanol medium, a reaction that must be seen as to some extent unavoidable under the applied experimental conditions. Reducing DME production is very valuable, as it aids in the recycling of methanol and mitigates the security concerns related to its low boiling point (–24.9 °C) (Mascal and Nikitin 2010; Peng *et al*. 2012). For this reason, DME yield (Y_2) was considered to be the minor dependent variable or response in the determination of the optimal process conditions for the synthesis of MLA.

Table 2. Experimental Design and Results of the CCRD

No.	H_2SO_4 concentration (M)	Temperature (°C)	Stirring rate (rpm)	Time (min)	Actual MLA yield (%)	Actual DME yield (%)
1	0.02	185	200	100	2.5	1.3
2	0.04	185	200	100	29.6	4.3
3	0.02	215	200	100	21.1	2.1
4	0.04	215	200	100	51.4	21.8
5	0.02	185	600	100	2.7	1.5
6	0.04	185	600	100	30.2	4.4
7	0.02	215	600	100	20.3	2.1
8	0.04	215	600	100	51.9	22.5
9	0.02	185	200	200	6.5	1.8
10	0.04	185	200	200	33.8	4.8
11	0.02	215	200	200	30.2	2.5
12	0.04	215	200	200	56.5	31.7
13	0.02	185	600	200	6.2	2.4
14	0.04	185	600	200	35.4	5.2
15	0.02	215	600	200	29.7	2.5
16	0.04	215	600	200	57.1	32.5
17	0.01	200	400	150	0.9	0.5
18	0.05	200	400	150	48.9	25.5
19	0.03	170	400	150	10.8	1.3
20	0.03	230	400	150	49.9	14.9
21	0.03	200	0	150	34.2	3.6
22	0.03	200	800	150	36.6	4.1
23	0.03	200	400	50	28.4	2.5
24	0.03	200	400	250	38.3	5.5
25	0.03	200	400	150	37.7	4.9
26	0.03	200	400	150	36.9	4.5
27	0.03	200	400	150	37.1	3.4
28	0.03	200	400	150	36.5	5.3
29	0.03	200	400	150	38.8	4.1
30	0.03	200	400	150	35.6	6.4

The Minitab statistical software package was used to fit the experimental data to a second-order polynomial model using the following equation,

$$Y = \beta_0 + \sum_{i=1}^{4}\beta_i X_i + \sum_{i=1}^{4}\beta_{ii} X_i^2 + \sum_{i=j}^{3}\sum_{j=i+1}^{4}\beta_{ij} X_i X_j \quad (6)$$

where Y is the dependent variable; X_i and X_j are the independent variables; and β_0, β_i, β_ii, and β_ij are the constant, linear coefficients, squared coefficients, and interaction coefficients, respectively. Analyses of variance (ANOVA) and R^2 (coefficient of determination) were used to check the adequacy of the developed models. The significance of each coefficient in the models was estimated using a *t*-test and *P*-value. The fitted polynomial equations were expressed as surface plots to visualize the relationship between the response variables and experimental levels of each factor. Under the condition of controlling the formation of DME, the optimal process variables for the synthesis of MLA were obtained using the software's numerical optimization function.

RESULTS AND DISCUSSION

Paper Sludge Composition

The paper sludge used in this study was primary sludge from a papermaking process that used wood pulp. The percent (w/w) composition of the paper sludge is presented in Table 3. The carbohydrate content was as high as 75.0% relative to the dry mass of the original sample. The cellulose content (60.8%) was particularly high compared to the average cellulose contents found in other reported studies (Nakasaki and Adachi 2003; Marques *et al*. 2008). In the previous reports, this paper sludge is believed to be one of the most promising biomass feedstocks for production of fermentation products such as ethanol and lactic acid due to its high cellulose content and fine structure, allowing enzyme accessibility for hydrolyzing to glucose. It will likely be an attractive raw material as well for the acid-catalyzed direct synthesis of levulinate esters.

The ash (10.7%) is not a degradable component during the reaction, and its element composition consisted of C (1.43%), O (4.72%), Fe (0.35%), Ca (0.79%), Si (1.38%), Al (1.52%), and Mg (0.51%). Mineral ions compositions are similar to the report of Yamashita *et al*. (2008). It was concluded that the ash mainly comes from inorganic substances added during the papermaking process, *i.e.*, calcium carbonate ($CaCO_3$), kaolin ($Al_2Si_2O_5(OH)_4$), and talc ($Mg_3Si_4O_{10}(OH)_2$).

Table 3. Paper Sludge Composition

Composition	Content (%-w/w)	
Moisture	4.3	
Carbohydrate	75.0	
Cellulose		60.8
Hemicelluloses		14.2
Lignin	8.4	
Acid soluble lignin		0.7
Acid insoluble lignin		7.7
Ash	10.7	
C		1.43
O		4.72
Fe		0.35
Ca		0.79
Si		1.38
Al		1.52
Mg		0.51
Others materials	1.6	
Total	100	

Models Fitting and Analyses of Variance (ANOVA)

Model for MLA yield

By applying multiple regression analyses to the experimental data of the MLA yield in Table 2, the following second-order polynomial equation was established to explain the relationship between MLA yield and the test variables based on the coded values,

$$Y_1 = 37.10 + 13.45X_1 + 10.40X_2 + 0.28X_3 + 2.73X_4 - 3.37X_1^2 - 2.01X_2^2 - 0.75X_3^2 - 1.26X_4^2 + 0.28X_1X_2 + 0.29X_1X_3 - 0.39X_1X_4 - 0.14X_2X_3 + 0.74X_2X_4 + 0.06X_3X_4 \quad (7)$$

where Y_1 is the MLA yield and X_1, X_2, X_3, and X_4 are the coded values of H_2SO_4 concentration, temperature, stirring rate, and time, respectively.

The ANOVA of the quadratic regression model indicated that the model is highly significant; a very low *P*-value (< 0.001) from the *F*-test showed that the model satisfactorily represents the real relationship among the process variables. Figure 1a shows the parity plot for the actual and predicted yields of MLA obtained from Eq. (7). A good linear distribution with a coefficient of determination (R^2) = 0.9915 can be observed, which was indicative of a close agreement between the actual and predicted values. These results implied that the regression model is very reliable as a predictor of MLA yield. The significance of the regression coefficients was determined by a *t*-test. The regression coefficients and corresponding *P*-values for the model of MLA yield are presented in Table 4. A *P*-value less than 0.05 indicated that the model term is significant. As can be seen from Table 4, the linear (X_1, X_2, X_4) and quadratic terms (X_1^2, X_2^2, X_4^2) had a significant effect on the yield of MLA.

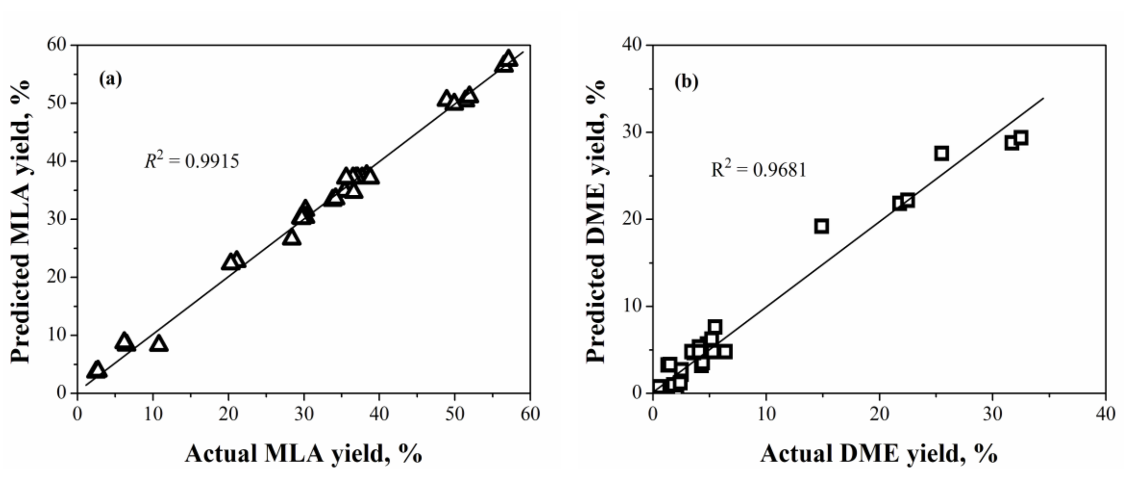


Fig. 1. Parity plots for the actual and predicted MLA yield (a) and DME yield (b)

Model for DME yield

Analogously, the fitting of the data describing DME yield in Table 2 produced the following second-order polynomial equation explaining the formation of DME from the dehydration of methanol,

$$Y_2 = 4.77 + 6.71X_1 + 4.97X_2 + 0.16X_3 + 1.23X_4 + 2.35X_1^2 + 1.12X_2^2 + 0.06X_3^2 + 0.10X_4^2 + 5.48X_1X_2 + 0.08X_1X_3 + 1.19X_1X_4 + 0.01X_2X_3 + 1.13X_2X_4 + 0.05X_3X_4 \quad (8)$$

where Y_2 is the DME yield and X_1, X_2, X_3, and X_4 are the coded values of H_2SO_4 concentration, temperature, stirring rate, and time, respectively, as in Eq. (7).

The ANOVA of the quadratic regression model demonstrated that the model is also highly significant, with a very small P-value (< 0.001). The parity plot for the actual and predicted yields of DME obtained from Eq. (8) is presented in Fig. 1b. A linear distribution with a coefficient of determination (R^2) = 0.9681 was obtained, which was indicative of a well-fit model. Table 4 shows the regression coefficients and corresponding P-values for the model of DME yield. The results showed that among the model term, the linear (X_1, X_2, X_4), quadratic (X_1^2, X_2^2), and interaction terms (X_1X_2) with P-values lower than 0.05 had a significant effect on DME yield.

Table 4. Significance Test of Regression Coefficient for Yields of MLA and DME

Model term	Parameter estimate		Standard error		*t*-value		*P*-value	
	MLA	DME	MLA	DME	MLA	DME	MLA	DME
Intercept	37.10	4.77	0.8444	0.9380	43.935	5.082	<0.001	<0.001
X_1	13.45	6.71	0.4222	0.4690	31.846	14.303	<0.001	<0.001
X_2	10.40	4.97	0.4222	0.4690	24.622	10.590	<0.001	<0.001
X_3	0.28	0.16	0.4222	0.4690	0.661	0.338	0.519	0.740
X_4	2.73	1.23	0.4222	0.4690	6.464	2.612	<0.001	0.020
X_1^2	–3.37	2.35	0.3949	0.4387	–8.538	5.347	<0.001	<0.001
X_2^2	–2.01	1.12	0.3949	0.4387	–5.088	2.555	<0.001	0.022
X_3^2	–0.75	0.06	0.3949	0.4387	–1.891	0.133	0.078	0.896
X_4^2	–1.26	0.10	0.3949	0.4387	–3.189	0.218	0.006	0.830
X_1X_2	0.28	5.48	0.5171	0.5744	0.544	9.532	0.595	<0.001
X_1X_3	0.29	0.08	0.5171	0.5744	0.568	0.131	0.578	0.898
X_1X_4	–0.39	1.19	0.5171	0.5744	–0.761	2.067	0.458	0.056
X_2X_3	–0.14	0.01	0.5171	0.5744	–0.278	0.022	0.785	0.983
X_2X_4	0.74	1.13	0.5171	0.5744	1.438	1.959	0.171	0.069
X_3X_4	0.06	0.05	0.5171	0.5744	0.109	0.087	0.915	0.932

Effects of Process Variables on the Response Variables

The effects of the four independent variables on the synthesis of MLA from the degradation of paper sludge and on the formation of DME from the dehydration of methanol are shown in Fig. 2. One variable was varied while the others were kept constant at their center points. The H_2SO_4 concentration was found to significantly affect the response variables (Fig. 2a). When the H_2SO_4 concentration was 0.01 M, the reaction did not proceed effectively and very little MLA was formed. However, previous research has determined that a H_2SO_4 concentration of 0.01 M could offer enough acid sites for the transformation of glucose and cellulose to MLA (Peng *et al*. 2012). A possible explanation for this difference is that the inorganic cations in paper sludge play an important role in the neutralization of acid sites, by causing the acidity of the reaction system to decrease (Springer and Harris 1985). In addition, the hemicelluloses and lignin existing in paper sludge can weaken the dissociation of acid and increase the difficulty of degradation (Maloney *et al*. 1985). When the H_2SO_4 concentration was increased to 0.03

M, a MLA yield of 38% was achieved. The yield of MLA increased accordingly with further augmentations of the acid concentration, but the variation trend thereafter slowed down. However, the side reaction involving the dehydration of methanol to DME became severe as the acid concentration was increased. When the H_2SO_4 concentration was 0.05 M, the rate of dehydration of methanol to DME was as high as 26%. Hence, a higher H_2SO_4 concentration was also unfavorable for the whole process. As can be seen from Fig. 2b, the yield of MLA improved when higher temperatures were employed. Meanwhile, the formation of DME showed an almost linearly increasing trend with the augmentation of temperature. A MLA yield of around 50% could be obtained with a H_2SO_4 concentration of 0.03 M at 230 °C or with a H_2SO_4 concentration of 0.05 M at 200 °C. However, the comparison revealed that the rate of dehydration of methanol to DME for the former (about 15%) was clearly lower than that for the latter (about 26%), implying that elevation of temperature is more favorable for the whole process than is high H_2SO_4 concentration. The stirring rate had little influence on the response variables (Fig. 2c). Even without stirring, the reaction progressed in the same manner, indicating that the interfacial mass transfer resistance between the paper sludge surface and the liquid phase was negligible. After a certain period of reaction time, any further extension of time was not able to effectively enhance the yield of MLA and had only a small influence on the dehydration of methanol to DME (Fig. 2d).

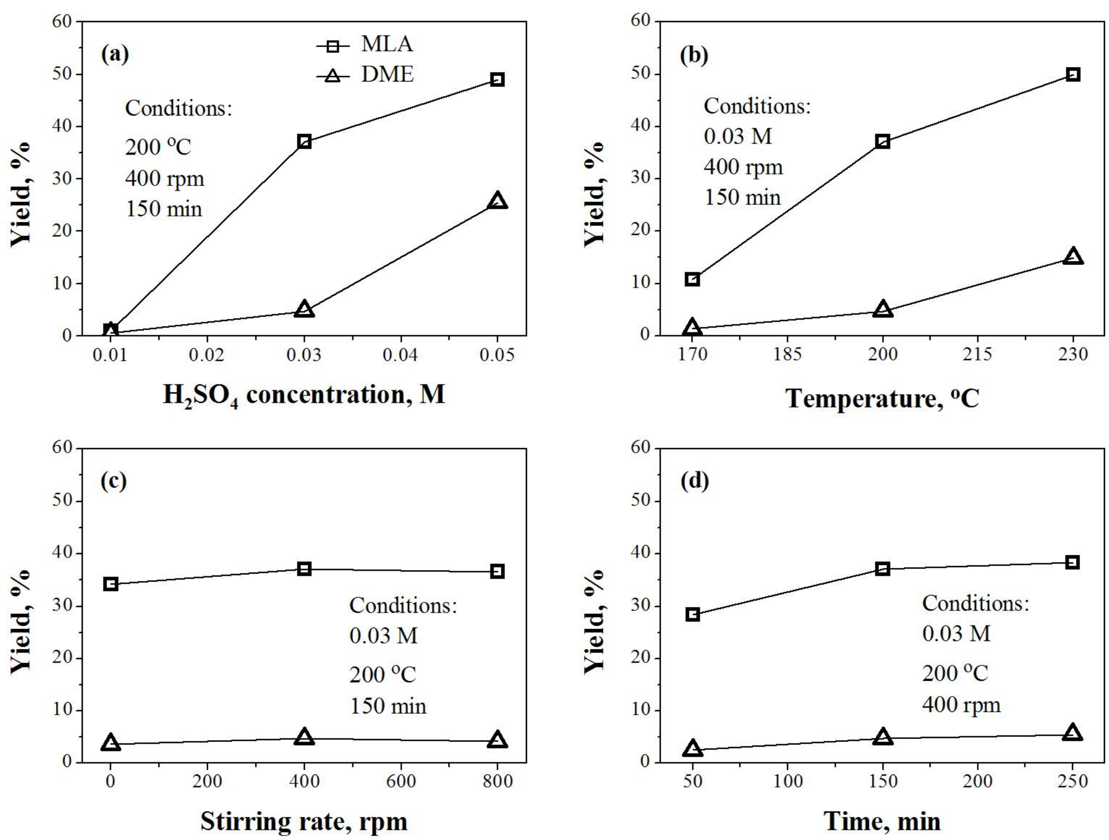


Fig. 2. Effects of different individual variables, *i.e.*, H_2SO_4 concentration (a), temperature (b), stirring rate (c), and time (d), on the yields of MLA and DME

The results derived from ANOVA indicated that H_2SO_4 concentration, temperature, and time were the key three parameters among the test variables for their effects on the response variables. The three-dimensional response surfaces were plotted to show the interaction effects of any two parameters on the yields of MLA and DME (Fig. 3), which further explains the results of the statistical analyses. Each figure presents the effect of two variables, while the remaining variables are held at center points.

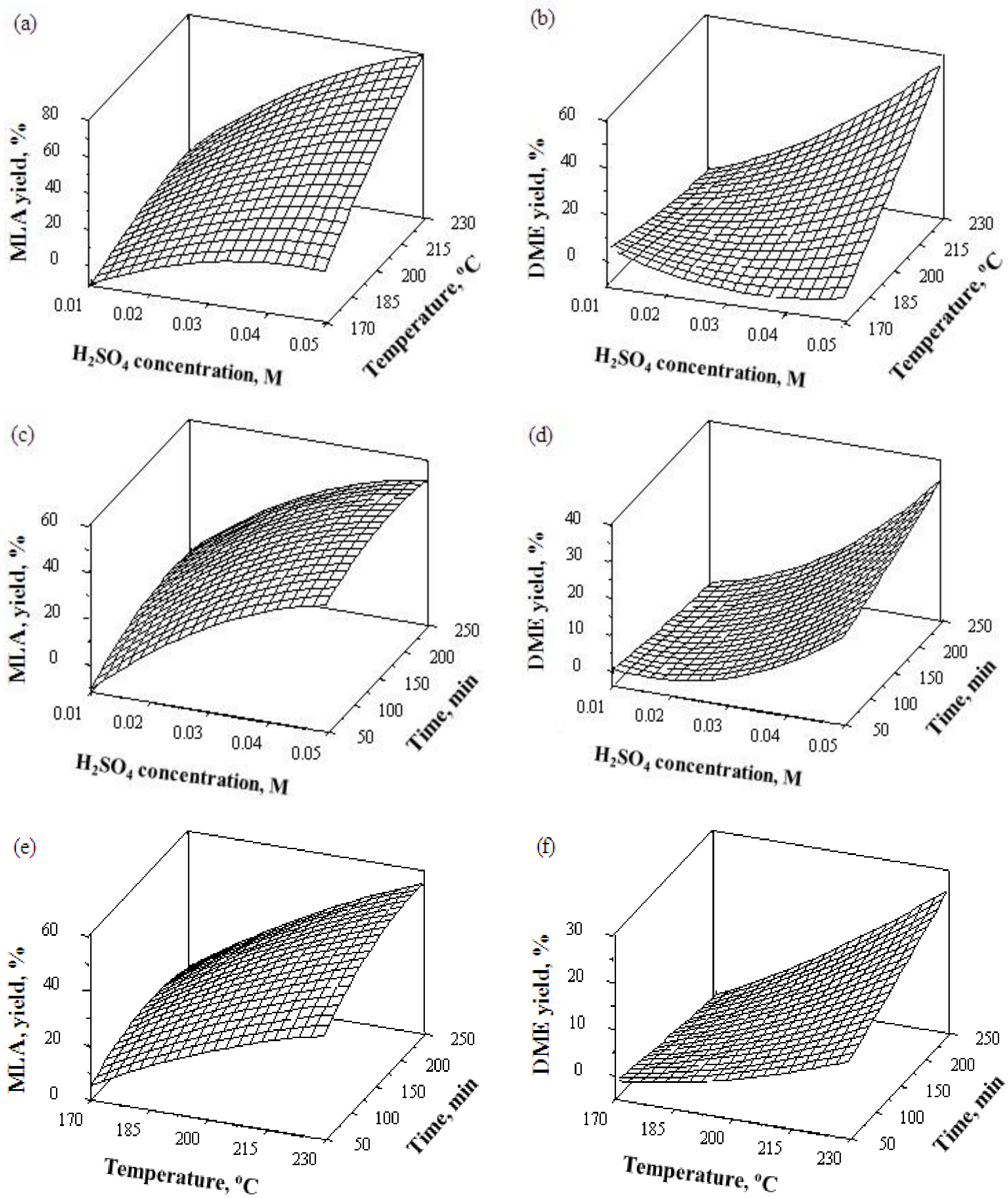


Fig. 3. Response surface plots showing the effects of the interaction between H_2SO_4 concentration, temperature, and time on the yields of MLA and DME

Figures 3a and b indicate no significant effects of the interaction between H_2SO_4 concentration and temperature on the yield of MLA. However, they were found to be interdependent on the yield of DME, meaning that the effect of H_2SO_4 concentration on the yield of DME was dependent on the level of temperature. As the H_2SO_4 concentration and temperature increased, the yield of MLA gradually increased, and the side reaction of the dehydration of methanol to DME intensified accordingly. When the controlled DME yield was less than 5%, the highest MLA yield of about 35% was reached; when the desired MLA yield was higher than 60%, around 40% of the methanol was dehydrated to DME. As can be observed from Figs. 3c, d, e, and f, there were no positive interactions between H_2SO_4 concentration and time or between temperature and time. At a fixed H_2SO_4 concentration and temperature, the yield of MLA increased with increasing time until it reached the optimum, after which there was no corresponding increase with a further increase in time, suggesting that the equilibrium conversion had been achieved. Nevertheless, at higher H_2SO_4 concentrations and temperatures, a nearly linear increase in DME yield with time was found. Therefore, it was determined that longer reaction times are not necessary and can even have negative effects.

Process Control and Optimization

Under the condition of controlling the formation of DME, the value of each parameter that produced the highest MLA yield was predicted based on Eqs. (7) and (8) using the software's numerical optimization function. The optimal combinations of parameters are shown in Table 5. When the controlled DME yields were less than 20%, 10%, 5%, and 1%, the highest predicted MLA yields reached 52.2%, 45.1%, 37.6%, and 25.6%, respectively. It follows that the side reaction of the dehydration of methanol to DME could be effectively controlled by changing the reaction conditions, while the degradation of paper sludge is negatively affected, causing a lower MLA yield. Hence, MLA yield and the rate of dehydration of methanol to DME must be considered in practical application during the selection of the appropriate reaction conditions. To confirm the predicted results of the models, valid experiments were performed under the optimum conditions, the results of which are listed in Table 5. A good correlation between the predicted and measured values was found for all tests, indicating that the models are effective and feasible as predictors and optimizers of the synthesis of MLA from paper sludge under the condition of controlling the dehydration of methanol to DME.

Table 5. Optimum Conditions for the Direct Conversion of Paper Sludge to MLA

No.	H_2SO_4 concentration (M)	Temperature (°C)	Stirring rate (rpm)	Time (min)	Predicted MLA yield (%)	Actual MLA yield (%)	Controlled DME Yield (%)	Actual DME yield (%)
1	0.031	222	420	215	52.2	54.8	<20.0	19.1
2	0.032	208	436	155	45.1	44.5	<10.0	9.3
3	0.030	200	401	159	37.6	37.1	<5.0	4.6
4	0.019	230	347	103	25.6	23.9	<1.0	1.2

CONCLUSIONS

1. H_2SO_4 concentration and temperature have significant effects on the reaction process. The elevation of temperature is more favorable than is high H_2SO_4 concentration for increased MLA production and reduced DME formation. The interfacial mass transfer resistance between paper sludge surface and the liquid phase is negligible.
2. The side reaction of the dehydration of methanol to DME can be effectively controlled through manipulation of the process conditions. When the controlled DME yields were less than 20%, 10%, 5%, and 1%, the highest predicted MLA yields reached 52.2%, 45.1%, 37.6%, and 25.6%, respectively. Also, a good correlation between the experimental and predicted values was obtained.
3. The overall yield of 27.7% (w/w) for conversion of paper sludge (dry matter basis) into methyl levulinate was achieved, representing an actual methyl levulinate yield of 54.8%. This proposed pathway is facile and effective for the resource utilization and upgrading of certain types of paper sludge.

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