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GRAPHICAL ABSTRACT

This work showcases an approach to convert lignocellulosic biomass into a potential biofuel as well as a bio-based platform chemical that could contribute in making such a process economically viable.
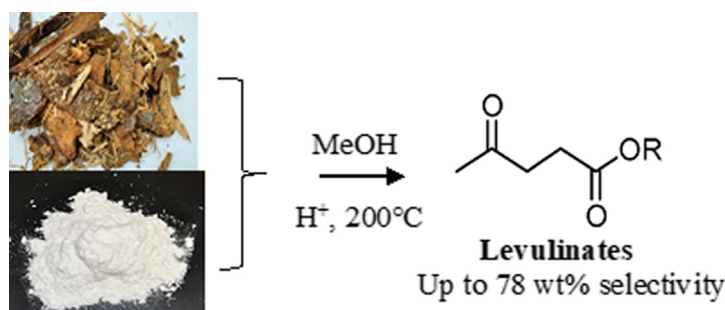
ABSTRACT

In this work, the direct production of levulinates from cheap residual lignocellulosic biomass was performed using an affordable homogeneous catalyst. A central composite design (CCD) using the response surface methodology (RSM) was applied to analyze the effects of the four selected factors (acid concentration, temperature, α-cellulose content, and reaction time) on the production of levulinates (levulinic acid derivatives). This optimization led to a total production of levulinates of 78 wt%, 72.5 wt%, 83 wt%, and 73 wt% using α-cellulose, poplar, sorghum, and softwood bark, respectively.

1. Introduction

The interest of producing alternative fuels and chemicals from renewable biomass has increased in the last decade in light of the global awareness on climate change, associated to the use of non-renewables [1]. Replacing part of the massive consumption of fossil fuel around the world requires different options, especially in the transportation sector, where the availability of large volumes of green carbon is of paramount importance.

In Canada, the lumbering industry produces large volumes of

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residues (such as bark, tree tops, and sawdust) and while some of it used to be integrated in the forest value-chain, the decline of the pulp and paper industry in the country has led to an accumulation of unused residues. The price of lignocellulosic residues generated from the forest sector is currently very low (often reaching as low as $5 per tonne for bark and $50 per tonne for white wood chips) and the fact that the pulping industry is not using as much biomass as it used to certainly represents an opportunity for the energy sector [2]. Therefore, now more than ever, conversion of lignocellulosic residues (forest or agricultural) could represent a low Carbon Intensity source for different fuels and chemicals.

Methyl levulinate is a short-chain ester that possesses properties that could, to a certain extent, be compared to fatty acid methyl esters (FAME). It has the potential to be used as biodiesel (as an additive) due to some of its properties (high lubricity, non-toxicity, and better flow properties under cold conditions) [3]. In addition, levulinate esters have shown many potential applications in the fragrance, flavoring, medicine, and energy sectors. For instance, another co-product obtained through the production of methyl levulinate is levulinic acid, a bio-based carboxylic acid containing two reactive functional groups (carboxylic acid and ketone) which, in turn, could be used as building blocks for numerous value-added compounds [4].

Literature shows that levulinate esters can be produced using homogeneous and heterogeneous catalysts. In the former case, diluted H_2SO_4 has often been considered for its affordability and capacity to provide sufficient protons (being a BrØnsted acid) to catalyze the reaction [5,34]. The production of methyl levulinate from glucose in acidified (H_2SO_4) methanol has been previously reported by Peng et al. 2012 [6] where the highest yield of methyl levulinate reported was of 50 wt% using 0.01 mol/L of H_2SO_4 and 0.3 mol/L of glucose at 200 °C for 4 h. Direct conversion of carbohydrates to levulinates avoids the recurrent problem of breaking the macromolecular structure of cellulose or hemicellulose in lignocellulosic biomass, which remains one of the biggest economical challenges of cellulosic-based chemicals and fuels. Wu et al., 2012 [7] adressed this situation and were able to convert microcrystalline cellulose to methyl levulinate at up to 55 wt% (using 20 g/L of the macromolecule and 0.02 mol/L of H_2SO_4, in 10 mL of methanol, at 190 °C for 5 h). Overall, no matter the type of catalyst used (either homogeneous or heterogeneous), a vast majority of research published in open literature either used glucose or cellulose as starting material for the production of levulinates, while lesser studies focused on raw residual forest or agricultural biomass. Using the latter would bring up additional challenges since the process would face interactions, not only with the carbohydrate-based macromolecules, but with lignin and secondary metabolites as well which could interfere with the different hydrolysis and dehydration mechanisms involved in the process.

In light of such reality, a central composite design (CCD) could contribute in reducing the number of experiments, overall helping reduce the cost and the duration of such investigation. Furthermore, response surface methodology (RSM) represents an excellent tool to analyze the influence of the factors on the response [8]. RSM is a collection of mathematical techniques that are used to obtain optimal conditions through regression methods [9]. Unfortunately, the developed response surface would be invalid for regions other than the studied ranges of factors.

This work aims at demonstrating the possibility of producing affordable methyl levulinate using low-cost residual forest and agricultural biomass. The objective here was to determine the effects of the different variables (acid concentration, temperature, α-cellulose content, and reaction time on methyl levulinate and levulinic acid yield as well as residue production) using a central composite design (CCD) under the response surface methodology (RSM).

Table 1
Factors (and levels) used in statistical model for direct conversion of cellulose to methyl levulinate and levulinic acid.

Factor	Symbol	Levels		
		−1	0	1
Acid concentration (mol/L)	x_1	0.04	0.122	0.24
Reaction time (h)	x_2	0.5	3.75	7
Cellulose content (wt%)	x_3	2.50	7.25	12
Temperature (°C)	x_4	180	190	200

2. Experimental

2.1. Chemicals and materials

α-Cellulose C8002, was purchased from Sigma, USA, and was dried at 105 °C for 24 h before utilization. Sulfuric acid (H_2SO_4, 98 wt%) was purchased from VWR Scientific Products, USA. Methyl levulinate (≥98 wt%) and levulinic acid (98 wt%) were obtained from Sigma-Aldrich, Germany. Methanol Optima (≥98 wt%) was purchased from Fisher Scientific, USA.

Sweet sorghum (*Sorghum bicolor* (L.) Moench) was collected at the CEROM research center in Saint-Mathieu-de-Beloeil (Québec, Canada, 45.58°N, 73.24°W). The free sugar content from this biomass was previously used for the production of ethanol by Damay, J. *et al.* 2018 [10]. The other biomass samples used in this work (poplar wood and softwood bark) were provided by ReSolve Energy Inc. and were produced from local sawmills in the Eastern Township region of Québec.

α-Cellulose, hemicellulose, and holocellulose contents were determined using the method reported by [11] while quantification of lignin was obtained according to the ASTM 1721-01 protocol [12] and ash content was done using the ASTM E1755-01 standard method [13]. Prior to analysis and reaction, biomass tissues were cryogenically grinded using liquid nitrogen (Freezer Mill, 6775 ATS Scientific, Canada) and dried for 24 h.

2.2. Equipment and experimental procedures

All the experiments were carried out in a 300 mL (total volume) cylindrical stainless steel (316 L) pressurized reactor (from PARR instrument company, USA) in which a 200 mL MONEL sleeve was introduced to prevent corrosion. α-Cellulose (or residual lignocellulosic biomass), methanol, and sulfuric acid were mixed in the reactor reaching a total reaction volume of 100 mL. The reactor was heated using an adjustable mantle and the temperature of the mixture inside the reactor was monitored using a G-type thermocouple. The reactions were carried out in the 180–200 °C temperature range using sulfuric acid concentrations varying from 0.04 to 0.24 mol/L, a reaction time ranging from 0.5 to 7 h and an α-cellulose (or biomass) content range of 2.5–12 wt%. Once the reaction completed, the reactor was removed from the mantle and placed in a cold-water bath to quench the reaction. The mixture was filtered to separate the undesired black insoluble polymeric particles and the unconverted α-cellulose (or biomass), which will further be referred to as "residues". The residues were vacuum-filtered using a 1.5 µm Glass Microfiber filter (VWR International, UK), after which residues were dried at 105 °C for 24 h and weighted. Equation (1) was used to calculate residue production (based on weight) at the end of the reaction.

$$\text{Residue production} = \frac{\text{Dry weight of solid residue(g)}}{\text{Dry weight of } \alpha - \text{cellulose before reaction (g)}} * 100\% \quad (1)$$

Table 2

Results of central composite design for production of methyl levulinate and levulinic acid from α-cellulose using H_2SO_4 as catalyst and methanol as solvent.

Run	Variables				Responses		
	x_1 Acid concentration (mol/L)	x_2 Reaction time (h)	x_3 Cellulose content (wt %)	x_4 Temperature (°C)	Y_1 ML yield (wt %)	Y_2 LA yield (wt %)	Y_3 Residues production (wt %)
1	0.04	0.5	2.5	180	38.2	0	0
2	0.04	0.5	2.5	200	42.9	15.4	0
3	0.04	0.5	12	180	53.6	2.1	0
4	0.04	0.5	12	200	17	12.7	1.1
5	0.04	7	2.5	180	9.9	48.1	5.4
6	0.04	7	2.5	200	6.9	59.2	9.5
7	0.04	7	12	180	17.7	32.3	2.9
8	0.04	7	12	200	18.9	45	7.8
9	0.24	0.5	2.5	180	10.4	23.6	0
10	0.24	0.5	2.5	200	5.7	58.2	8.7
11	0.24	0.5	12	180	15.1	16.6	1.0
12	0.24	0.5	12	200	14.5	45	3.9
13	0.24	7	2.5	180	10.2	46.3	9.9
14	0.24	7	2.5	200	7.8	47.6	12.8
15	0.24	7	12	180	20.9	46.9	9.0
16	0.24	7	12	200	21.9	31.8	14.8
17	0.04	3.75	7.25	190	9.3	38.9	4.1
18	0.24	3.75	7.25	190	16.3	47.7	6.8
19	0.122	0.5	7.25	190	9.8	20.7	1.3
20	0.122	7	7.25	190	15.2	45.5	12.0
21	0.122	3.75	2.5	190	4.5	61.2	10.0
22	0.122	3.75	12	190	20.1	50.3	7.3
23	0.122	3.75	7.25	180	12.9	47	5.4
24	0.122	3.75	7.25	200	12.5	49.9	14.0
25	0.122	3.75	7.25	190	12.9	44.7	11.1
26	0.122	3.75	7.25	190	13.5	47.4	9.1
27	0.122	3.75	7.25	190	12.4	46.6	9.3
28	0.122	3.75	7.25	190	12.5	47.8	9.6
29	0.122	3.75	7.25	190	14.6	47.2	11.1
30	0.122	3.75	7.25	190	11.9	48.3	10.3

Table 3

Significance of regression coefficient for methyl levulinate and levulinic acid yields and residue production for direct conversion of α-cellulose in methanol using H_2SO_4 as catalyst.

Coefficients	Methyl levulinate yield				Levulinic acid yield				Residue production			
	Regression coefficient	Stand error	t Value	P Value	Regression coefficient	Stand error	t Value	P Value	Regression coefficient	Stand error	t Value	P Value
β_0	47.90	1.85	25.84	< 0.0001*	9.39	0.59	15.83	< 0.0001*	11.83	2.26	5.22	0.0001*
β_1	6.11	1.40	4.34	0.0006*	2.01	0.45	4.47	0.0004*	−5.08	1.72	−2.96	0.0098*
β_2	11.57	1.40	8.23	< 0.0001*	3.79	0.45	8.43	< 0.0001*	−4.32	1.72	−2.51	0.0239*
β_3	−4.27	1.40	−3.04	0.0083*	−0.47	0.45	−1.06	0.3077	3.51	1.72	2.04	0.0593
β_4	5.66	1.40	4.02	0.0011*	2.17	0.45	4.82	0.0002*	−2.26	1.72	−1.32	0.2075
β_{12}	−7.82	1.49	−5.25	< 0.0001*	0.52	0.47	1.09	0.2924	7.08	1.82	3.88	0.0015*
β_{13}	−0.3	1.49	−0.20	0.8433	0.03	0.47	0.06	0.9508	1.81	1.82	0.99	0.3364
β_{23}	−1.52	1.49	−1.02	0.3229	−0.04	0.47	−0.10	0.9221	2.6	1.82	1.42	0.1748
β_{14}	−0.03	1.49	−0.03	0.9803	0.63	0.47	1.32	0.2070	1.68	1.82	0.92	0.3698
β_{24}	−4.93	1.49	−3.31	0.0048*	0.31	0.47	0.65	0.5229	2.12	1.82	1.16	0.2625
β_{34}	−1.61	1.49	−1.08	0.2968	−0.06	0.47	−0.13	0.8956	−1.85	1.82	−1.01	0.3268
β_{11}	−5.50	3.70	−1.48	0.1584	−3.17	1.18	−2.67	0.0174*	2.1	4.53	0.46	0.6500
β_{22}	−15.70	3.70	−4.24	0.0007*	−1.94	1.18	−1.64	0.1218	1.8	4.53	0.40	0.6971
β_{33}	6.94	3.70	1.87	0.0806	0.017	1.18	0.02	0.9881	1.6	4.53	0.35	0.7292
β_{44}	−0.35	3.70	−0.10	0.9253	1.07	1.18	0.90	0.3804	2	4.53	0.44	0.6655

2.3. Analytical methods

Methyl levulinate and levulinic acid concentrations were determined using a HPLC system (Agilent 1100 Series) equipped with a Rezex™ ROA-Organic acid H^+ (8%) 300 × 7.8 mm column (Phenomenex). The column temperature was maintained with an oven set at 65 °C. The mobile phase was a 2.5 mM aqueous sulfuric acid solution, which was operated at a 0.6 mL/min flow rate. 10 μL were injected and the detection was ensured by refractive index detector (RID). An external calibration curve was performed for each compound of interest. Methyl levulinate (ML) and levulinic acid (LA) yields were calculated (based on weight) using Eqs. (2)–(4):

$$\text{Yield of ML} = \frac{\text{grammes of ML produced}}{\text{Theoretical amount of ML produced(g)}} * 100\% \quad (2)$$

$$\text{Yield of LA} = \frac{\text{grammes of LA produced}}{\text{Theoretical amount of LA produced}} * 100\% \quad (3)$$

Table 4
Analysis of variance (ANOVA) of RSM regression analysis for methyl levulinate and levulinic acid yields and residue production for the conversion of α-cellulose using H_2SO_4 as catalyst in methanol.

Mode	SS	Df	MS	F-Value	P
Methyl levulinate model					
Regression	7201.55	14	514.397	14.44	< 0.0001
Error	534.12	15	35.609		
Total	7735.68	29			
R^2	0.9309				
Levulinic acid					
Regression	548.06	14	39.14	10.72	< 0.0001
Error	54.76	15	3.65		
Total	602.83	29			
R^2	0.9091				
Residues					
Regression	2574.73	14	189.90	3.45	0.0116
Error	799.49	15	53.3		
Total	3374.22	29			
R^2	0.7630				

SS, sum of squares; Df, degrees of freedom; MS, mean square

$$\text{Theoretical amount of levulinate} = \frac{\text{grammes of glucose in the feedstock} * \text{molecular weight of levulinate}}{\text{molecular weight of glucose}} \quad (4)$$

2.4. Response surface methodology

Under the response surface methodology (RSM), Central composite design (CCD) with four factors (acid concentration, cellulose content, reaction time, and temperature) was used to study ML and LA yields as well as the amount of residue produced in order to ultimately determine optimal reaction conditions. The statistical approach used in this work was inspired from previous work reported in open literature [10,27,28]. Three variable levels (-1, 0 and +1) of the x_1 (acid concentration), x_2 (reaction time), x_3 (cellulose content), and x_4 (temperature) are presented in Table 1.

The JMP 11 (SW) software was used for statistical analysis of the experimental data. According to central composite design (CCD) and response surface methodology (RSM) for four factors, a total of 30 sets of experiments needed to be carried out (Table 2).

Optimal reaction conditions for maximal methyl levulinate yield were obtained using the desirability function of the software from Eq. (5) which relies on the second order polynomial model:

$$Y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 \quad (5)$$

where Y_i are the response variables (ML yield, LA yield, and residue production); x_1, x_2, x_3, and x_4 are the factors; β_0 is the regression coefficient at the central point; β_1, β_2, β_3, and β_4 are the linear coefficients; β_{11}, β_{22}, β_{33}, and β_{44} are quadratic coefficients while β_{12}, β_{13}, β_{14}, β_{23}, β_{24}, and β_{34} are second-order interaction coefficients. Optimal conditions were determined using the desirability function of the software [14,26].

Following determination of optimal conditions for methyl levulinate and levulinic acid production, additional reactions using lignocellulosic biomass (softwood bark, residual poplar wood, and sorghum bagasse) were carried out.

3. Results and discussion

3.1. Model analysis

A response surface methodology and central composite design were used to study the relationship between factors and responses and to determine optimal conditions for methyl levulinate production. Methyl levulinate yield (Y_1), levulinic acid yield (Y_2), and residue production (Y_3) were correlated with tested variables : acid concentration (x_1), reaction time (x_2), cellulose content (x_3), and temperature (x_4).

The coefficients for the response models are shown in Table 3. The significance of each coefficient for the dependent variables is determined for the P-value. A smaller P-value shows that the coefficient is more significant [15,16]. Table 3 shows the significance of the regression coefficient for methyl levulinate and levulinic acid yields, as well as for residue wt%. The linear coefficient (x_2) has a highly significant effect on the smallest P-value (< 0.0001) as compared to other variables involved in methyl levulinate and levulinic acid yields. The linear coefficient (x_1) was significant for methyl levulinate, levulinic acid, and residue production, as depicted by the smallest P-value (0.0006, 0.0004, 0.0098 respectively).

The linear (x_3, x_4), the interactions ($x_1 x_2$, $x_2 x_4$) and the square coefficients (x_2^2) have a significant effect on the small P-value (< 0.01) observed in methyl levulinate yields. For levulinic acid yields, the linear effect (x_4) and square coefficient (x_1^2) were at 95%, a significant level at a small P-value (0.0002, 0.0174 respectively). In the case of residues, linear (x_2) and interaction coefficients ($x_1 x_2$) were found to be significant terms at a 5% response probability.

The analysis of variance (ANOVA) is presented in Table 4. The ANOVA of the quadratic regression model showed that the model was highly significant due to the low probability value (P < 0.0001) of methyl levulinate and levulinic acid yield. The analysis of variance demonstrated that the model for residue production was significant with a probability value of 0.01.

The determination coefficients (R^2) for methyl levulinate and levulinic acid models were 0.9309 and 0.9091 respectively and show an agreement between experimental and predicted values of methyl levulinate and levulinic acid yields. The determination coefficient for residue production was 0.7630, which is related to the difficulty of recovering residues at the end of the reaction, hence increasing the variability of this factor. A very small P-value (< 0.0001) and a suitable value of R^2 ($R^2 > 0.9$) can determine if the model is adequate for the estimation of the response value within conditions range [17].

3.2. Effects of reaction parameters

The response surface plots and the isoresponse curves of the RSM as function of two variables are shown in Figs. 1–3. The other two factors were fixed according to the results of the experimental design. The 3D response surface plots and isoresponse curves are helpful to understand the main effects as well as factors interaction [18,19]. As shown in Fig. 1a, as the cellulose content increased at lower temperature, a decrease was observed in methyl levulinate yields, indicating that increasing cellulose content at low temperature decreases the mass transfer affecting levulinate yields. The interaction between reaction time and acid concentration in Fig. 1b showed that methyl levulinate yields increased with acid concentration and reaction time until a maximum value was reached (acid concentration of 0.1785 mol/L and reaction time of 4 h). It indicates that sulfuric acid provides enough acid sites for the synthesis of methyl levulinate. Once the optimum acid concentration value was reached (0.1785 mol/L), methyl levulinate yields decreased due to the degradation of the products, potentially increasing residues production. As shown in Fig. 1c, at lower temperature (180 °C), methyl levulinate yields increased slowly with regards to reaction time. The same behavior was reported by [6] for the conversion of glucose using sulfuric acid as catalyst. Temperature and reaction time played a positive role on methyl levulinate yields until a maximum temperature (200 °C) and maximum reaction time (4 h) were reached. Increasing temperature could contribute to the acceleration of the chemical reaction rate while enhancing conversion efficiency [20]. Longer reaction time tended to increase methyl levulinate yields due to the transformation of polymer chains of cellulose into low molecular weight fragments, which were further converted into methyl levulinate [20,31,33].
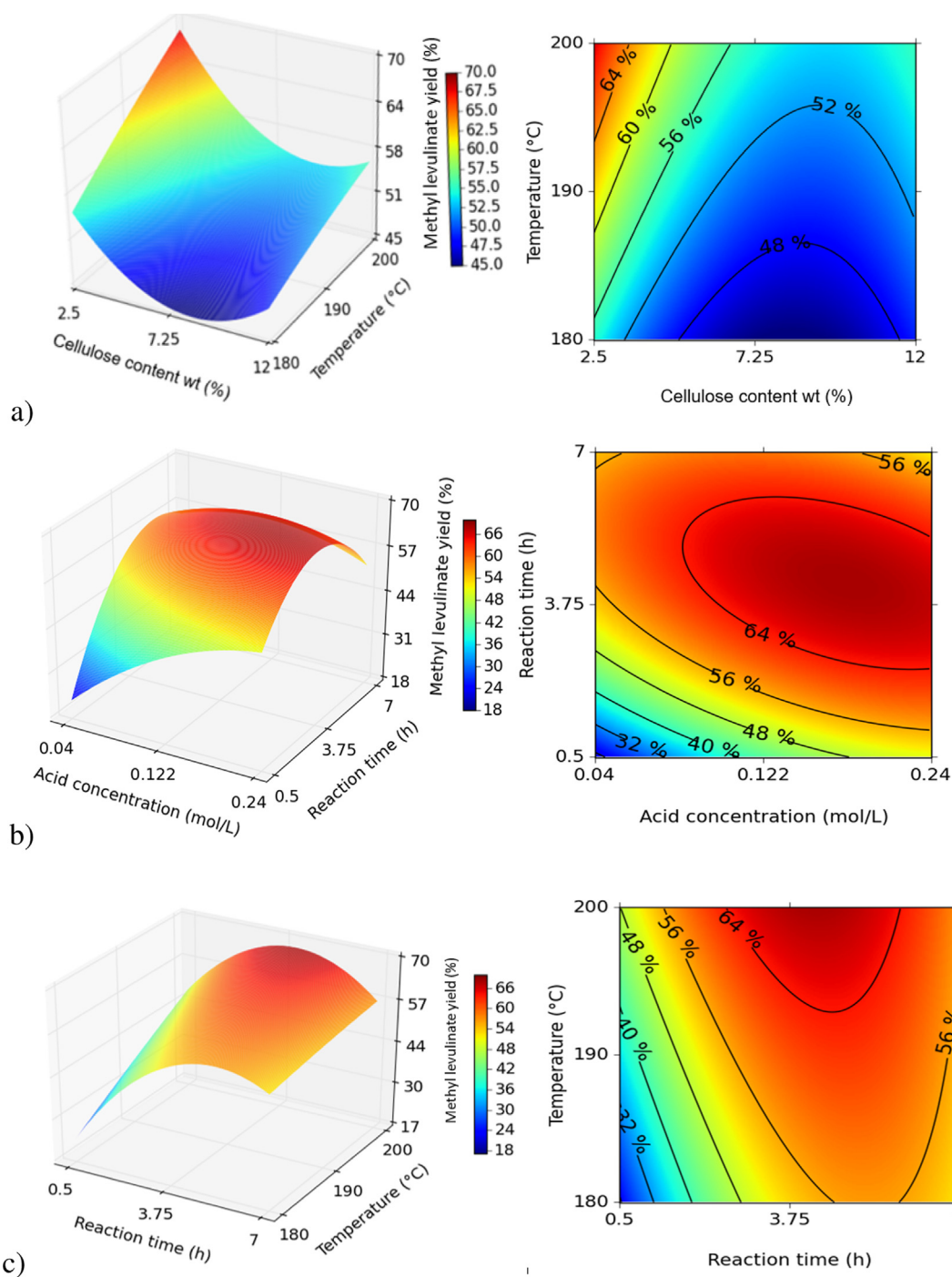
Fig. 1. 3D response surface plots and isoresponse curves of methyl levulinate yield versus cellulose content and temperature (a); acid concentration and reaction time (b); and reaction time and temperature (c) obtained from the acid catalyzed treatment of cellulose in methanol.

Afterwards, to reach maximum conditions of temperature and reaction time (200 °C at 4 h), methyl levulinate yields decreased due to potential degradation, increasing the percentage of residues and corrosion in the reactor.

The presence of levulinic acid is due to the severity in the alcoholysis of α-cellulose. It means that at high reaction conditions, water molecules are produced from the dehydration of cellulose leading to levulinic acid formation. Fig. 2a shows that increasing temperature and reaction time led to an increase of levulinic acid yields.

As shown in Fig. 2b, levulinic acid yields increased with higher acid concentration, a phenomenon that was also reported by [8].

The impact of acid concentration and reaction time on the production of residues is reported in Fig. 3a where results suggest that a low sulfuric acid concentration and short reaction time lead to an increase of residue content. In this case, most residues originated from cellulose. Low acid concentrations decreased the availability of acid sites for completion of the reaction and transformation of cellulose into the desired products. Fig. 3b shows the interaction effects of cellulose content and temperature on residue production. A high cellulose content and low temperature tend as well to increase the quantity of residues.
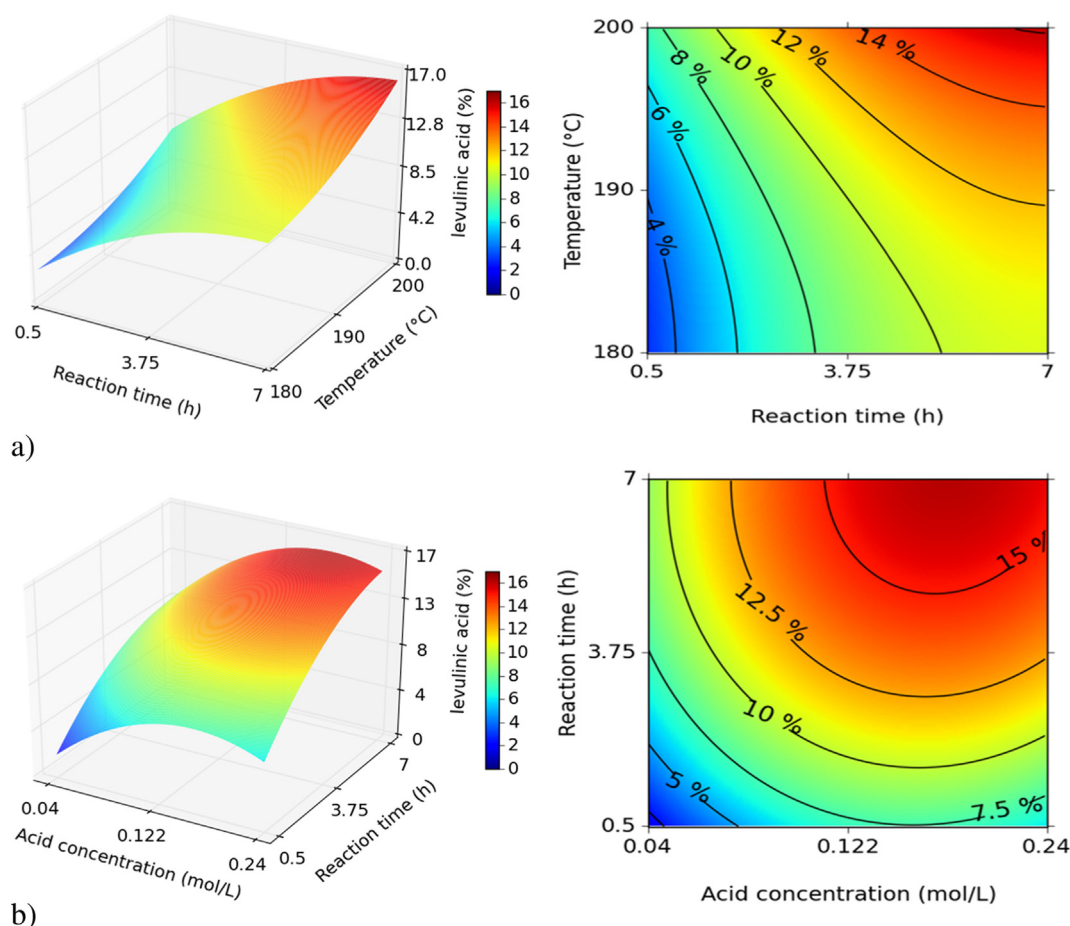
Fig. 2. 3D response surface plots and isoresponse of levulinic acid yield versus reaction time and temperature (a) and acid concentration and reaction time (b) obtained from alcoholysis of cellulose using H_2SO_4 as catalyst.

3.3. Optimization of methyl levulinate yields

Based on the study of central composite design and response surface methodology, optimum conditions for methyl levulinate yields could be predicted, according to variables in the range of experimental design using the desirability function. Predicted optimum conditions involved an acid concentration of 0.1796 mol/L, a 2.5 wt% of α-cellulose content and a reaction time of 4 h at 200 °C. Calculated values of methyl levulinate and levulinic acid, and amount of residues corresponded to 68.14 wt% ± 10.22 wt%, 14.30 wt% ± 3.27 wt%, and 9.32 wt% ± 2.33 wt% respectively. To verify predicted methyl levulinate yields, three validations were performed at optimum conditions. The mean values for methyl levulinate, levulinic acid, and residue yields were 62.0 wt% ± 0.3 wt%, 15.95 wt% ± 2.2 wt%, and 11.2 wt% ± 0.5 wt% respectively. As a result, the models developed were accurate and reliable for the prediction of methyl levulinate and levulinic acid production from cellulose using sulfuric acid as a catalyst system. According to additional tests at 210 °C, it was observed that an increase of temperature above 200 °C decreased the production of levulinates due to their degradation, and increased the production of dimethyl ether, generated from the combination of two methanol molecules (not covered in this work).

From related literature, Wu et al. 2012 [7] obtained a 55 wt% yield of methyl levulinate using 20 g/L of cellulose with a cellulose/catalyst ratio between 7 and 20 in 10 mL of methanol under almost critical conditions, 190 °C for 5 h. Peng et al. 2012 [6] investigated the synthesis of methyl levulinate from glucose catalyzed by extremely low sulfuric acid (≤0.01 mol/L). The experiments were carried out at temperatures between 160 °C and 200 °C and maximum methyl

levulinate yield was 50 wt%.

In addition, Peng et al. 2013 [21] synthetized methyl levulinate from the degradation of paper sludge at moderate temperatures (< 230 °C) using low concentrations of sulfuric acid (< 0.05 mol/L). The researchers optimized methyl levulinate yields using four factors (H_2SO_4 concentration, temperature, stirring rate, and time) and two responses (methyl levulinate yield and dimethyl ether formation). Results showed that H_2SO_4 concentration and temperature were the most important factors, with optimum conditions at 0.031 mol/L of H_2SO_4 concentration, 222 °C, and 420 rpm during 215 min. Actual methyl levulinate yield was 54.8 wt%.

3.4. Comparison between different biomasses

In order to validate the model, three different types of residual biomass were used (residual poplar wood, sorghum bagasse, and softwood bark). The comparison was done under conditions calculated in the experimental design. According to a "wet analysis", the cellulose content for each biomass was of 29 wt%, 30 wt%, and 32 wt% for poplar, sorghum, and bark respectively. The results for predicted and real values of levulinate yields produced with the different biomasses are shown in Table 5.

Total levulinate values were of 78 wt%, 72.5 wt%, 83 wt%, and 73 wt% using α-cellulose, poplar, sorghum, and bark, respectively. Maximum methyl levulinate yield obtained was of 68 wt% (from sorghum), together with a levulinic acid yield of 14.85 wt%. Residue production for each biomass was 11.2 wt%, 30.8 wt%, 31.0 wt%, and 42.1 wt% for α-cellulose, poplar, sorghum, and bark, respectively. Levulinate yields depended closely on the composition of the cellulosic
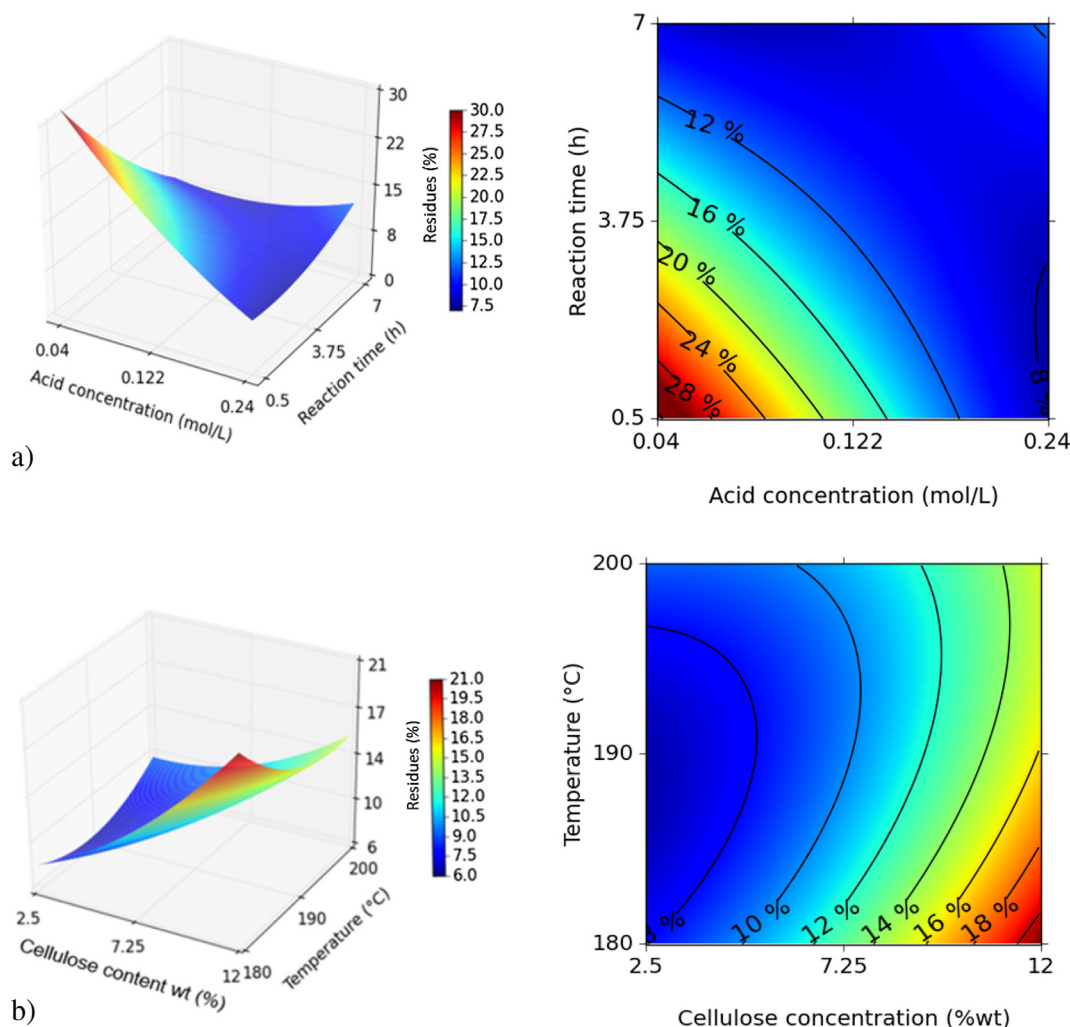
Fig. 3. 3D response surface plots and isoresponse curves of residue production versus acid concentration and reaction time (a); and cellulose content and temperature (b) obtained from results of cellulose conversion using an acid catalyst in methanol.

Table 5
Levulinate results obtained from different biomasses using optimal conditions: acid concentration of 0.1796 mol/L; cellulose content of 2.5 wt%; reaction time of 4 h at 200 °C (product yield (%) based on cellulose content).

	Methyl levulinate yield	Levulinic acid yield
α- Cellulose	62.0% ± 0.3%	16.6% ± 2.2%
Residual Poplar wood	53.2% ± 2.7%	19.3% ± 1.4%
Sorgho bagasse	68.1% ± 1.5%	15.2% ± 3.3%
Softwood Bark	55.7% ± 3.1%	18% ± 2.6%

raw material [18,22]. Residue production is mainly related to the quantity of lignin and tannins for each biomass (except alpha-cellulose).

Results from this work showed that the alcoholysis of cellulose and raw material using sulfuric acid as catalyst in methanol allows the production of methyl levulinate and levulinic acid in an easy one-pot procedure.

The maximum yield of methyl levulinate that was obtained in this work was 62.0 wt%, which is slightly higher than the values previously reported in literature [6,7,21,22]. Moreover, total levulinate compounds yield reached 77.95 wt% using alpha-cellulose, whereas when using different biomasses, maximum value obtained for levulinates compounds was 83 wt% (based on cellulosic glucose content) using sorghum. The effects of lignin and hemicellulose were not evaluated in this work but according to literature, lignin can reduce levulinate

production and increase residues production in comparison with pure cellulose. On the other hand, hemicellulose can promote the formation of levulinates and hence, depending on the concentration of C6 in this macromolecule, could boost levulinate yields when calculated on a cellulose basis such as was done in this work [23]. The highest yields obtained with sorghum can be explained by residual free sugars found after removing sugar juice from the stems.

In accordance with results obtained with regression coefficient analysis, reaction time and temperature were the most significant factors to influence methyl levulinate and levulinic acid yields.

4. Conclusion

Experimental results showed that all the experimental parameters considered in this work (acid concentration, temperature, reaction time, and cellulose content) had an influence on methyl levulinate yields obtained from cellulose as well as residual lignocellulosic biomass. Predicted yield values of methyl levulinate, levulinic acid, and residues using cellulose as feedstock corresponded to 68.14 wt% ± 10.22 wt%, 14.30 wt% ± 3.27 wt%, and 9.32 wt% ± 2.33 wt% respectively, whereas the real values were 62.0 wt% ± 0.3 wt%, 15.95 wt% ± 2.2 wt%, and 11.2 wt% ± 0.5 wt% for products in the same order. Using residual poplar wood, sorghum bagasse, and softwood bark, maximum levulinate yields were 72.5 wt%, 83 wt%, and 73 wt% (based on cellulosic glucose content) respectively. The use of

lignocellulosic biomass for levulinate production through a catalytic solvolysis such as what was performed here using sulfuric acid and methanol could lead to a more technically and economically feasible approach to produce levulinates and alkyl levulinates out of waste biomass. Hence, this work could represent the basis for a very effective approach to produce low-cost alkyl levulinates that could be used as chemicals or even fuel. As a matter of fact, adding alkyl levulinate as an additive to biodiesel could be a significant game changer for this industry, allowing a fast transition to second generation. At the same time, this work was addressing growing concerns related to residual biomass in locations where it is abundantly found (such as in Canada).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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