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ABSTRACT

Levulinates could be used as oxygenated fuel additives or as blending components in biodiesel. In this work, a metallic salt was used for the direct conversion of biomass, ie. (softwood bark), to produce methyl levulinate (ML) and levulinic acid (LA). The experimental data were analyzed through using a response surface methodology (RSM) as well as a central composite design (CCD). Three dependent responses (ML yield, LA yield, and residue production) were studied to determine the optimum combination of the four factors. The total yield of levulinates was 62% at the optimum process parameters, including catalyst concentration (0.067 mol/L), reaction time (5.67 h), and softwood bark concentration (2.5 wt%) at 200 °C. Finally, the results showed that $Al_2(SO_4)_3$ allowed the production of levulinates probably in light of its good BrØnsted/Lewis acidity while also allowing t to decrease the corrosion inside the reactor (as compared to homogeneous acids such as H_2SO_4). This shows that the use of these metal salts for this specific application could positively affect the production costs of levulinates (either CAPEX or OPEX) at larger scale.

1. Introduction

The depletion of fossil carbon fuels and the large amount of greenhouse gas emissions (GHG) produced by the consumption of these resources have stimulated new paths towards alternative energies where lignocellulosic biomass could represent an environmentally beneficial raw material for the production of fuels, platform molecules, and other value-added products [1–4].

In Canada only, annual production of bark is estimated at 17 million m³ [5,6] and the price of this forest residue is often below 5 CAD per tonne (on site), which could be a cheap source of carbon for the production of green chemicals. Recent work have shown that bark could be used for the production of liquid and solid fuel [7–9], but another option for bark valorization could be the production of chemicals from carbohydrate dehydration such as levulinates (either their acidic or esterified form). Acid-catalyzed dehydration of C6 sugars in methanol of both hemicellulosic and cellulosic fractions of bark leads to the production of levulinates in concentrations that are often dictated by the severity of the process. Methyl levulinate is a short chain ester that could be compared to fatty acid methyl ester (FAME), with known

applications such as fuel additive, due to some of its properties (high lubricity, non-toxicity, and better flow properties under cold conditions) [10–12]. Levulinic acid (also known as 4-oxopentanoic acid) is a high-boiling point biomass-derived acid, soluble in many industrial solvents (such as alcohol, ether, and organic solvents). This platform molecule has two reactive functional groups (ketone and carboxylic acid) giving it functionality and reactivity to obtain a variety of products such as solvents, fuel additives or resins [13,14].

Over the years, several catalytic systems have been investigated for the conversion of C6 sugars (including but not limited to glucose, fructose, cellulose, and whole biomass) to produce methyl levulinate and levulinic acid [12,13]. Among the most commonly reported homogeneous acids used for this purpose in open literature, sulfuric acid (H_2SO_4) has always been the most efficient catalyst, producing ML and LA yields of 62.0% and 15.95% respectively when using different substrates ranging from α-cellulose to raw biomass as feedstock [15]. However, numerous issues have been associated with the use of H_2SO_4 in the reaction, such as the significant production of dimethyl ether (obtained from the dehydration of methanol), equipment corrosion, challenges for catalyst recovery, without putting aside potential

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environmental constraints [16].

Considering this situation, acid heterogeneous catalysts have been increasingly reported for the production of methyl levulinate and levulinic acid, hence addressing many issues related to their homogeneous catalyst counterparts [17–19]. Among the commercially available heterogeneous acidic catalysts reported for this purpose are zeolites, sulphated metal oxides, metal oxides, inorganic metal salts, and ion-exchange resins [20]. As for the latter, their long-term use has been reported to be limited by their low thermal stability [21].

In a previous report, Tominaga et al. [22] studied a catalytic system for the synthesis of methyl levulinate from microcrystalline cellulose, combining a Lewis acid and a BrØnsted acid in methanol. The most effective combination reported by this team was indium trifluoromethanesulfonate (III) combined with 2-naphthalenesulfonic acid (In $(OTf)_3$–2–NSA) leading to a 75% yield of methyl levulinate. However, the use of the mixed acid system (In$(OTf)_3$/2-NSA) involves an increase in production costs due to the higher price of In$(OTf)_3$ (25 CAD per gram).

Zhou et al., 2014 used $Al_2(SO_4)_3$ as catalyst for the conversion of different carbohydrates (fructose, glucose, mannose, sucrose, cellobiose, starch, and cellulose) to methyl levulinate in methanol. This catalyst benefits from the presence of Lewis and BrØnsted acid sites generated by the hydrolysis/methanolysis of Al^{3+}. The yield of methyl levulinate reported from using this catalyst on α-cellulose was 44% at 180 °C following a 300 min. reaction time. In contrast, the yield of methyl levulinate (this time using glucose as original feed) reached 64%, showing the ability of metallic ions to catalyze the isomerization of glucose to fructose followed by its dehydration [21].

According to open literature, aluminum sulfate $Al_2(SO_4)_3$ is a cheap, stable, and excellent BrØnsted/Lewis acid that could be used for the production of levulinates by direct conversion of lignocellulosic biomass [21,23]. However, to the best of our knowledge, there seems to be few reports studying the direct conversion of plant tissues (such as wood or straw) to methyl levulinate and levulinic acid, and even less using forest residues such as softwood bark and $Al_2(SO_4)_3$. Besides, detailed information about influences and interactions of reaction parameters could not be found in open litterature. In this work, the optimization of the experimental conditions leading to the production of levulinates (methyl levulinate and levulinic acid) was investigated using softwood bark and a metal salt ($Al_2(SO_4)_3$) catalyst through a central composite design (CCD) under the response surface methodology (RSM) approach. RSM is a mathematical and statistical method used to analyse the influence of various factors on processes [24]. Based on preliminary results, some operation variables were selected for the experimental design, including catalyst concentration, temperature, biomass concentration, and reaction time [15]. The response variables were methyl levulinate and levulinic acid yields and the mass of residues generated. Besides the different parameters that were investigated, corrosion reduction in the equipment and reusability of the catalyst were considered as well.

2. Experiments

2.1. Chemicals and materials

Softwood bark was collected in a local lumber mill in the Eastern Township region of Québec, Canada. Aluminum sulfate hydrate ($Al_2(SO_4)_3 \cdot 18H_2O$, ≥97%) was purchased from Sigma-Aldrich, USA. Methyl levulinate (≥98%) and levulinic acid (98%) were obtained from Sigma-Aldrich, Germany. Finally, Methanol Optima (≥98%) was purchased from Fisher Scientific, USA.

2.2. Experimental setups and procedures

Softwood bark was air dried, milled and sieved to select 40–60 mesh particle size fractions. The main composition of softwood bark was cellulose (34.2% ± 2.1%), hemicelluloses (20.2% ± 2.1%), lignin (28.01% ± 0.6%), and extractives (16.29% ± 1.9%) which were determined using classical ASTM, TAPPI and NREL standard methods at the Biomass Technology Laboratory.

The alcoholysis of softwood bark to produce methyl levulinate (ML) and levulinic acid (LA) was conducted in a 300 mL (total volume) cylindrical stainless steel (316 L) pressurized reactor from PARR instrument (USA). A 200 mL MONEL sleeve was used inside the reactor to prevent corrosion. Before the reaction, softwood bark was dried at 105 °C for 24 h. Predetermined quantities of softwood bark, $Al_2(SO_4)_3 \cdot 18H_2O$, and methanol were charged in the reactor. Air was removed by purging with nitrogen, then the system was pressurized to 20 bar with the same gas. The mixture was heated to the desired temperature by an adjustable mantle and the temperature inside the reactor was monitored using a G-type thermocouple. Time zero was taken when the autoclave reached set temperature. The reactions were carried out under isothermal conditions in the 180–200 °C temperature range, while $Al_2(SO_4)_3$ concentration ranged from 0.01 to 0.1 mol/L, reaction time from 0.5 to 7 h, and softwood bark concentration from 2.5 to 12 wt%, stirred at 800 rpm, and controlled with a variable-speed motor installed on the reactor. After heating, the system was cooled down to room temperature using cold water to quench the reactor. It was then opened and the mixture was filtered to separate the undesired insoluble black particles and the non-converted biomass (also known as residues). The latter were separated using a 1.5 μm Glass Microfiber filter (VWR International, UK) under vacuum. They were then dried at 105 °C for 24 h and then weighted allowing calculation of the residue yield using the following equation:

$$\text{Residues production} = \frac{\begin{array}{c}\text{Dry weight of solid residue produced (g)} \\ - \text{ weight of catalyst after recovery (g)}\end{array}}{\text{Dry weight of biomass before reaction (g)}} * 100\%$$

(1)

2.3. Catalyst recovery

To recover the catalyst, the methanol and other low boiling point products were evaporated at atmospheric conditions for 24 h. The crude residue was dissolved in 25 mL dichloromethane and washed three times (or until the dichloromethane solution became colourless). The catalyst was then separated from the dichloromethane solution using a Büchner funnel, then dried at 105 °C for 6 h prior to being calcined at 575 °C for 4 h to eliminate any biomass residues [25,26].

2.4. Products analysis

The yields of methyl levulinate, levulinic acid, and reaction products were analyzed using an Agilent 1100 Series HPLC system equipped with a Rezex ROA-Organic acid H^+ (8%) 300 × 7.8 mm column (Phenomenex). The system used an aqueous solution of sulfuric acid (2.5 mM) as a mobile phase at a 0.6 mL/min flow rate. The column temperature was maintained at 65 °C and, ultimately, 10 μL of the sample mixture was injected in the column while the detection was ensured by the refractive index detector (RID). A calibration curve was generated for each compound of interest produced in this reaction. The yields of methyl levulinate (ML) and levulinic acid (LA) were calculated (based on the cellulosic glucose content in biomass) using the following formulas:

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

(2)

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

(3)

Table 1

Factor values and their corresponding levels in the statistical model for the conversion of softwood barks to methyl levulinate and levulinic acid.

Factor	Symbol	Levels		
		−1	0	1
Catalyst concentration (mol/L)	x_1	0.01	0.055	0.1
Reaction time (h)	x_2	0.5	3.75	7
Biomass concentration (wt%)	x_3	2.50	7.25	12
Temperature (°C)	x_4	180	190	200

$$= \frac{\text{Theoretical amount of levulinate}}{\text{molecular weight of glucose}}$$

$$= \frac{\text{grammes of glucose in the feedstock} \; * \; \text{molecular weight of levulinate}}{\text{molecular weight of glucose}}$$

(4)

2.5. Response surface methodology

A four-factor central composite design (CCD) under the response surface methodology (RSM) was used to determine optimal conditions for maximizing the production of levulinates [27]. RSM allows the identification of a quadratic model that can describe the influence of the factors on the response [28]. The levels (-1,0 and + 1) of the x_1 (catalyst concentration), x_2 (reaction time), x_3 (biomass concentration), and x_4 (temperature) are reported in Table 1.

A software (JMP 11 (SW)) was used to analyze experimental results and to achieve maximal methyl levulinate yield, using a second-order polynomial model considered as follows:

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

(5)

where Y_i is the predicted response (ML yield, LA yield, and residues production); x_1, x_2, x_3 and x_4 are the factors; β_0 is the offset term, β_1, β_2, β_3, and β_4 are the linear regression coefficients of model; β_{11}, β_{22}, β_{33}, and β_{44} are quadratic coefficients; and β_{12}, β_{13}, β_{14}, β_{23}, β_{24}, and β_{34} are second order interaction coefficients.

The total number of required experiments to gather sufficient data was 30 while the standard experimental combinations of the test variables with the measured response values for the central composite design are shown in Table 2. At a 7.2% biomass loading, cooked at 200 °C for 3.75 h, and using 0.055 mol/L of catalyst, the highest levulinates production and residue production were 60.6% and 23.6% respectively. However, when operating at 190 °C, slightly lower results were obtained with a levulinate production of 57.4%. At the same conditions, increasing the reaction time to 7 h, reduced the levulinate yield to 54.6%.

3. Results and discussion

3.1. Reaction pathway

Biomass conversion into levulinates is a complex reaction involving the production of numerous intermediates at each step of the process. According to literature, Lewis acid accelerates the isomerization of glucose to fructose in water, and methyl glucoside to methyl fructoside in methanol, while Brønsted acid catalyzes the reaction of fructose and methyl fructoside to levulinates [21]. The catalyst ($Al_2(SO_4)_3$) offers both Brønsted and Lewis type acid sites, which are appropriate for biomass conversion into levulinates. The accepted mechanisms for the direct conversion of cellulose to levulinates are shown in Fig. 1 [29,30]. According to the figure, bark is first hydrolyzed to produce glucose units by Brønsted acids obtained from the hydrolysis/methanolysis of $Al_2(SO_4)_3$. In alcohol, the intermediates are different from those tha could be observed from a comparable reaction performed in water. For

example, in water, the mechanism follows a cellulose–glucose-fructose-hydroxymethylfurfural (HMF)-levulinic acid pathway, while in the presence of methanol, it shows a cellulose-methyl glucoside-methyl fructoside-methoxymethylfurfural (MMF)-methyl levulinate pathway.

3.2. Model analysis

A central composite design (CCD) under the response surface methodology (RSM) was used to study the response pattern and to determine the optimal conditions required to maximize methyl levulinate production. Methyl levulinate yield (Y_1), levulinic acid yield (Y_2), and residue production (Y_3) are correlated to tested factors: catalyst concentration (x_1), reaction time (x_2), biomass concentration (x_3), and temperature (x_4).

The significance of each coefficient of Eq. (5) was determined using the Student's *t*-test and *P*-value. A large magnitude of t-value and a small *P*-value show the high significance of the corresponding coefficient [31,32] (Table 3). Table 3 shows that the linear coefficients (x_1) and (x_2) were highly significant according to their *P*-value (< 0.005) when it comes to methyl levulinate and levulinic acid yields, as well as for the production of residues. The quadratic main effect (x_1^2) also was highly significant ($P = 0.0009$) for methyl levulinate yield. These results suggest that the catalyst concentration plays a crucial role in the production of methyl levulinate.

For the levulinic acid yield, the linear effect (x_4) and interaction coefficient for catalyst concentration and reaction time ($x_1 x_2$) were highly significant, showing small *P*-value (0.0009, < 0.0001). For the production of residues, the linear (x_3)coefficient was found to be highly significant at a *P*-value of 0.0009.

The analysis of variance (ANOVA) and the coefficient of determination (R^2) were used to verify the adequacy of the model (Table 4) for the estimation of the response value [33]. The ANOVA results of the quadratic regression model showed that the model for methyl levulinate, levulinic acid, and residue production was highly significant due to its low probability value (P < 0.0001). The R^2 of the quadratic model for the methyl levulinate, levulinic acid, and residue models were 0.93, 0.92, and 0.90 respectively, and tend to to show an agreement between the experimental and predicted values of levulinates yield.

3.3. Effects of reaction parameters

According to the blank test, no levulinates were detected in the absence of a catalyst. The effects of the factors on methyl levulinate as well as levulinic acid yield and residue production are shown in the response surface plots and the isoresponse curves of the RSM as a function of two variables (Figs. 2, 3 and 4), according to results presented in Table 3. In this case, the response surface methodology (RSM) was shown to be an efficient statistical technique that can be used to evaluate the effects of the factors of the reaction for a targeted response. It also provides the possibility to observe the effects of single variables and their combined interaction on the response [34–36]. According to the analysis of variance, both biomass concentration (x_3) and operating temperature (x_4) are significant parameters that can influence methyl levulinate yield in the current domain of investigation. As shown in Fig. 2a, at a low catalyst concentration, methyl levulinate yield remained low for all tests since 24 to 32% of methyl levulinate was produced. However, methyl levulinate yields increased with an increase of catalyst concentration (x_1), and reaction time (x_2), until a maximum value was reached (catalyst concentration of 0.067 mol/L after a 5.67 h reaction time). Increasing the catalyst concentration leads to an increase in Lewis acid sites, favoring the isomerization of methyl glucoside to methyl fructoside ultimately leading to the production of 5-methoxymethylfurfural (MMF) [37] and an increase in the reaction rate. Fig. 2b shows the interaction between temperature and reaction time on methyl levulinate yield. Lower temperature (< 190 °C) and low

Table 2

Experiment matrix and experimental results for methyl levulinate and levulinic acid production in methanol using aluminum sulfate $Al_2(SO_4)_3$ as catalyst.

Run	Variables				Responses		
	X_1 Catalyst concentration (mol/L)	X_2 Reaction time (h)	X_3 Biomass concentration (wt %)	X_4 Temperature (c)	Y_1 ML yield (%)	Y_2 AL yield (%)	Y_3 Residue production (%)
1	0.01	0.5	2.5	180	0.0	0.0	51.8
2	0.01	0.5	2.5	200	6.4	1.1	38.5
3	0.01	0.5	12.0	180	0.0	0.0	72.7
4	0.01	0.5	12.0	200	0.0	0.0	72.2
5	0.01	7	2.5	180	7.7	0.0	38.5
6	0.01	7	2.5	200	33.8	2.2	28.1
7	0.01	7	12.0	180	0.0	0.0	66.7
8	0.01	7	12.0	200	0.0	1.1	61.5
9	0.1	0.5	2.5	180	6.0	0.0	52.4
10	0.1	0.5	2.5	200	22.8	1.8	47.2
11	0.1	0.5	12.0	180	12.3	0.0	31.1
12	0.1	0.5	12.0	200	21.5	0.0	27.1
13	0.1	7	2.5	180	44.3	2.5	6.6
14	0.1	7	2.5	200	38.8	10.5	6.2
15	0.1	7	12.0	180	36.4	9.2	26.6
16	0.1	7	12.0	200	28.5	12.9	24.9
17	0.01	3.75	7.2	190	9.3	0.0	53.4
18	0.1	3.75	7.2	190	38.8	7.0	9.0
19	0.055	0.5	7.2	190	18.1	2.2	27.2
20	**0.055**	**7**	**7.2**	**190**	**47.2**	**7.4**	**23.5**
21	0.055	3.75	2.5	190	46.8	2.8	3.1
22	0.055	3.75	12.0	190	35.6	2.5	35.0
23	0.055	3.75	7.2	180	28.7	2.7	53.6
24	**0.055**	**3.75**	**7.2**	**200**	**51.8**	**8.8**	**23.6**
25	0.055	3.75	7.2	190	43.0	5.2	22.3
26	0.055	3.75	7.2	190	44.6	5.1	19.4
27	0.055	3.75	7.2	190	42.3	5.6	24.6
28	**0.055**	**3.75**	**7.2**	**190**	**50.5**	**6.9**	**21.5**
29	0.055	3.75	7.2	190	45.0	5.1	22.7
30	0.055	3.75	7.2	190	48.0	5.4	22.2
31	0	3.75	2.5	200	0	0	0.3

reaction time (< 3h) led to a low cellulose conversion, with a maximum 22% methyl levulinate yield. At higher temperature and a reaction time of 4 h, methyl levulinate yield improved up to 54%. These results suggest that, in order to depolymerize and decrystallize the biomass, it is necessary to increase the reaction time and temperature. Levulinates production was improved when the reaction temperature was elevated to 200 °C. At higher temperatures (> 200 °C) a decrease in levulinates yield was observed due to their degradation and conversion (probably in residues since their yield increased in such situation). After reaching the optimum catalyst concentration and reaction time, methyl levulinate concentration decreased due to the degradation of the products, hence increasing the production of residues. Similar results depicting the interaction between reaction time and catalyst concentration were reported in previous works, targeting methyl levulinate production using homogeneous catalyst [15].

The presence of levulinic acid in the methanolysis of biomass is related to the severity of the reaction. At high severity, water molecules are generated from the hydrolysis of biomass, leading to the production of levulinic acid. The high concentration of the catalyst could directly be related to the observed LA yields [38]. Figure 3a shows the interaction between catalyst concentration and reaction time. It was observed that an increase in catalyst concentration and reaction time is proportional to levulinic acid yields, observations that were also made by Chang et al. [39]. Figure 3b shows the interaction between temperature and reaction time. There, results show that an increase in catalyst concentration (> 0.05 mol/L) and reaction time (> 3h) seemed to increase the production of levulinic acid. In addition, the interaction between reaction time and catalyst concentration for residue production is shown in Figure 4. Results suggest that the reaction time plays a fundamental role in the depolymerization of biomass. High catalyst concentrations and longer reaction time could increase the conversion of cellulose into desired products and by-products,

decreasing residue production. Furthermore, lower residue were produced when using 0.24 mol/L for 7 h.

According to the central composite design and response surface methodology, when it comes to the production of levulinates using a metallic salt as catalyst. Optimal conditions as predicted by the software would thus involve a catalyst concentration of 0.067 mol/L, 2.5 wt% of biomass and a reaction time of 5.7 h at 200 °C.

According to the software, the estimated values for methyl levulinate, levulinic acid, and the amount of residues were 57.01 wt% ± 11.50 wt%, 7.62 wt% ± 3.00 wt%, and 10.07 wt% ± 6.12 wt% respectively. To verify the predicted performances of the variables, three validations were performed at optimal conditions. The average experimental yields for methyl levulinate, levulinic acid, and the amount of residues were 46.62 wt% ± 11.26 wt%, 15.21 wt% ± 1.28 wt%, and 15.43 wt% ± 1.47 wt%. The predicted and real value of levulinates yield were 68.51% and 61.83% respectively, both based on cellulosic glucose content.

As a result, it is possible to consider that the models developed for this work were reliable to predict the production of methyl levulinate and levulinic acid from bark when aluminum sulfate was used as catalyst. These results can be compared to the different work found in literature. Zhou et al. reported a methyl levulinate yield of 64% from glucose using 0.1 g of metal salt ($Al_2(SO_4)_3$) at 160 °C for 5 h [21]. In another work, Tan et al. [40] reported on ethyl levulinate production also using aluminum sulfate as catalyst. In this case, a yield of ethyl levulinate and levulinic acid of 36.4 wt% and 6.35 wt%. were obtained respectively using 5% by weight of cassava as raw material (here in ethanol), at 200 °C for 6 h. Hence, in this case, the total amount of levulinates was 42.82 wt%.

Chang et al., 2018 converted wheat straw into methyl levulinate using copper sulfate ($CuSO_4$) as catalyst. The researchers obtained a 42.2 wt% yield of methyl levulinate (based on the cellulosic glucose
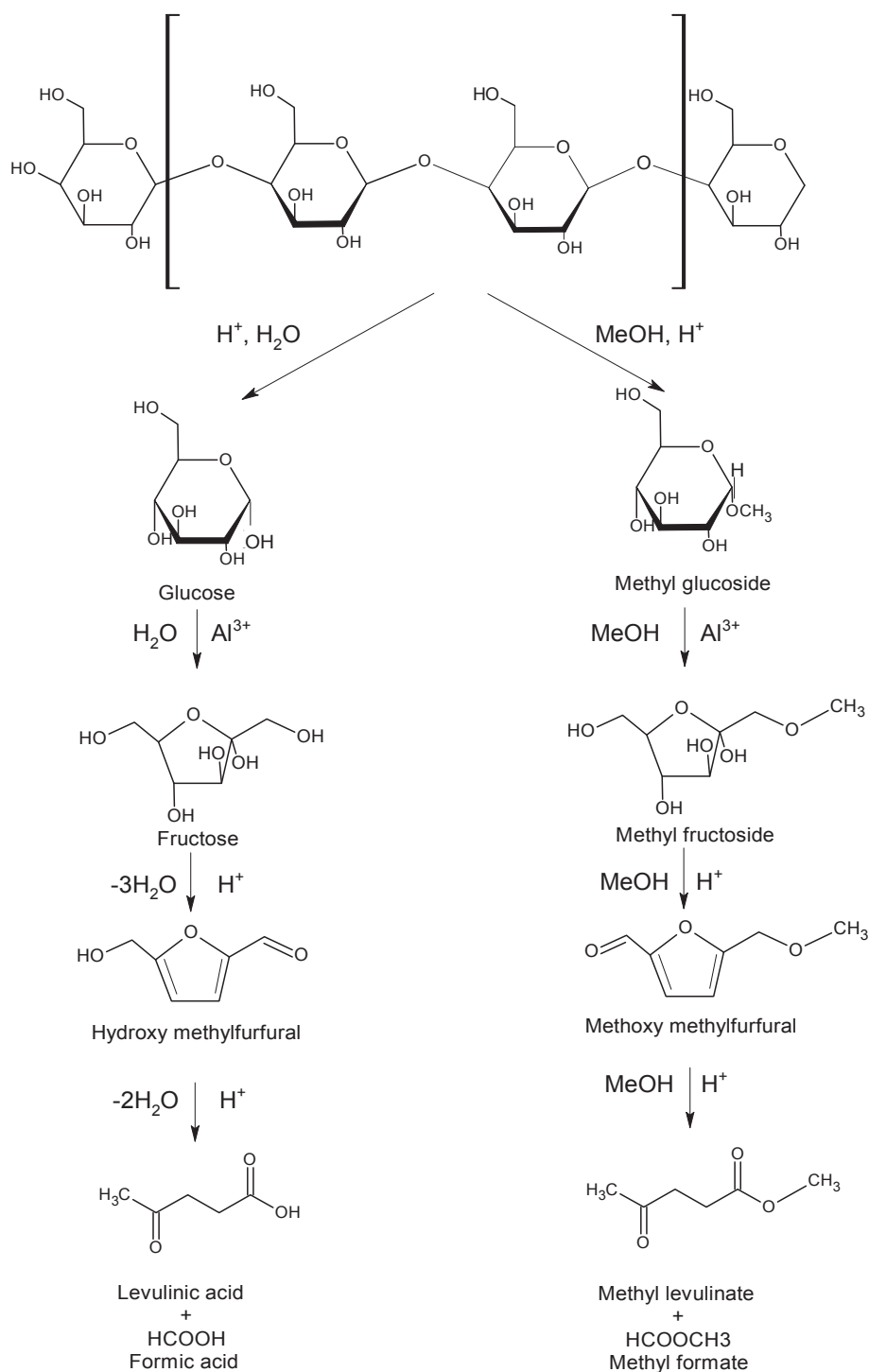
Fig. 1. $Al_2(SO_4)_3$ catalyzed cellulose conversion into levulinates.

content) using 0.64 g of catalyst at 182 °C for 3.3 h [17]. In this case, the full production of levulinate could not be estimated, since levulinic acid production was not reported.

In this work, the total amount of levulinates produced was of 61.83 wt% (based on the cellulosic glucose content), which was, to the best of our knowledge higher than those reported in literature. These results can be explained by the severe conditions used in the reaction (high temperature and increased reaction time).

In litterature, for cases where the raw material was biomass, low production of levulinates could be explained by different factors such as the high concentration of substrate or the low concentration of the catalyst. Since bark and metal salt are not soluble in methanol, mass transfer limitations could represent one of the factors explaining the low efficiency of solid catalyst as compared to mineral acids (e.g., H_2SO_4) [23]. According to literature, large particle sizes both of biomass and catalyst could affect mass transport properties, leading to a diffusion control of the reaction. At higher initial cellulose particle sizes, lower reaction rates and conversions of cellulose to levulinates were reported [41]. Large catalyst particle sizes could decrease the external active sites, also decreasing the reaction rate [42]. Additional studies will be carried out to investigate the influence of these parameters on this reaction.

Table 3

Significance of regression coefficients for methyl levulinate yield, levulinic acid yield and residue production for the conversion of softwood bark in methanol using $Al_2(SO_4)_3$ 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	43.51	2.10	20.71	< 0.0001	5.19	0.43	12.14	< 0.0001	23.11	2.58	8.95	< 0.0001
β_1	10.67	1.59	6.69	< 0.0001	2.19	0.32	6.75	< 0.0001	−14.02	1.96	−7.15	< 0.0001
β_2	8.30	1.59	5.21	0.0001	2.27	0.32	6.98	< 0.0001	−7.64	1.96	−3.90	0.0014
β_3	−4.01	1.59	−2.52	0.0236	0.27	0.32	0.83	0.4199	8.08	1.96	4.12	0.0009
β_4	3.79	1.59	2.38	0.0310	1.34	0.32	4.11	0.0009	−3.93	1.96	−2.00	0.0635
β_{12}	3.14	1.69	1.86	0.0831	1.95	0.34	5.65	< 0.0001	−3.32	2.08	−1.60	0.1313
β_{13}	2.17	1.69	1.28	0.2188	0.60	0.34	1.73	0.1042	−7.43	2.08	−3.57	0.0028
β_{23}	−3.64	1.69	−2.15	0.0480	0.68	0.34	1.98	0.0665	5.44	2.08	2.62	0.0194
β_{14}	−1.24	1.69	−0.74	0.4730	0.57	0.34	1.65	0.1198	1.13	2.08	0.54	0.5943
β_{24}	−1.24	1.69	−0.73	0.4760	0.76	0.34	2.21	0.0429	0.33	2.08	0.16	0.8755
β_{34}	−2.66	1.69	−1.57	0.1366	−0.51	0.34	−1.48	0.1589	1.12	2.08	0.54	0.5984
β_{11}	−17.36	4.20	−4.13	0.0009	−1.33	0.86	−1.55	0.1411	7.09	5.17	1.37	0.1900
β_{22}	−8.82	4.20	−2.10	0.0530	−0.05	0.86	−0.05	0.9578	1.24	5.17	0.24	0.8133
β_{33}	−0.26	4.20	−0.06	0.9520	−2.19	0.86	−2.56	0.0218	−5.06	5.17	−0.98	0.3431
β_{44}	−1.18	4.20	−0.28	0.7833	0.91	0.86	1.06	0.3068	14.49	5.17	2.81	0.0133

Table 4

Analysis of variance (ANOVA) for methyl levulinate and levulinic acid production from softwood bark in methanol using a metal salt ($Al_2(SO_4)_3$).

Mode	SS	Df	MS	F-Value	P
Methyl levulinate model					
Regression	9172.18	14	655.15	14.32	< 0.0001*
Error	686.05	15	45.73		
Total	9858.23	29			
R^2	0.93				
Levulinic acid					
Regression	356.20	14	25.44	13.40	< 0.0001*
Error	28.46	15	1.89		
Total	384.67	29			
R^2	0.92				
% Residues					
Regression	9833.308	14	702.37	10.15	< 0.0001*
Error	1037.33	15	69.15		
Total	10870.63	29			
R^2	0.90				

SS, sum of squares; D*f*, degrees of freedom; MS, mean square.

In addition, literature put an emphasis on the formation of undesirable dimethyl ether due to intermolecular methanol dehydration, which is catalyzed by acids (such as sulfuric acid). In the current case, the acidity of the system was not as strong as when using strong homogeneous acids and it was observed that the amount of dimethyl ether was reduced to 20% in comparison to what was observed using homogeneous catalyst [15].

4. Corrosion tests

Previous work on the subject [15] showed that the high concentration of sulfuric acid combined with a longer reaction time could increase levulinic acid yield, although high concentrations of sulfuric acid in such a reactive system could lead to significant corrosion in the reactor. Corrosion tests were performed on MONEL at 200 °C for 5.7 h using the weight loss method to verify the impact of sulfuric acid and aluminum sulfate at 0.067 mol/L. The corrosion rate of metal was calculated using the following equation:

$$MPY = \frac{3449 * W}{DAt} \tag{6}$$
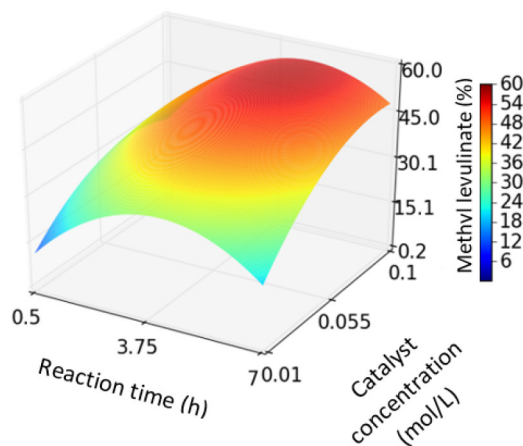
a)   b)
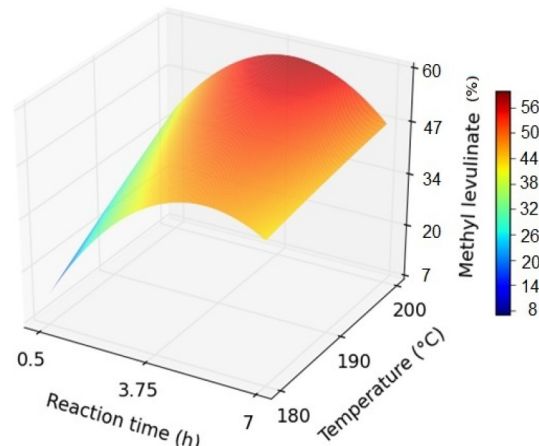
Fig 2. 3D response surface plots of methyl levulinate yield versus catalyst concentration and reaction time (a) as well as temperature and reaction time (b) obtained from the acid catalyzed treatment of softwood bark using a metal salt as catalyst in methanol.
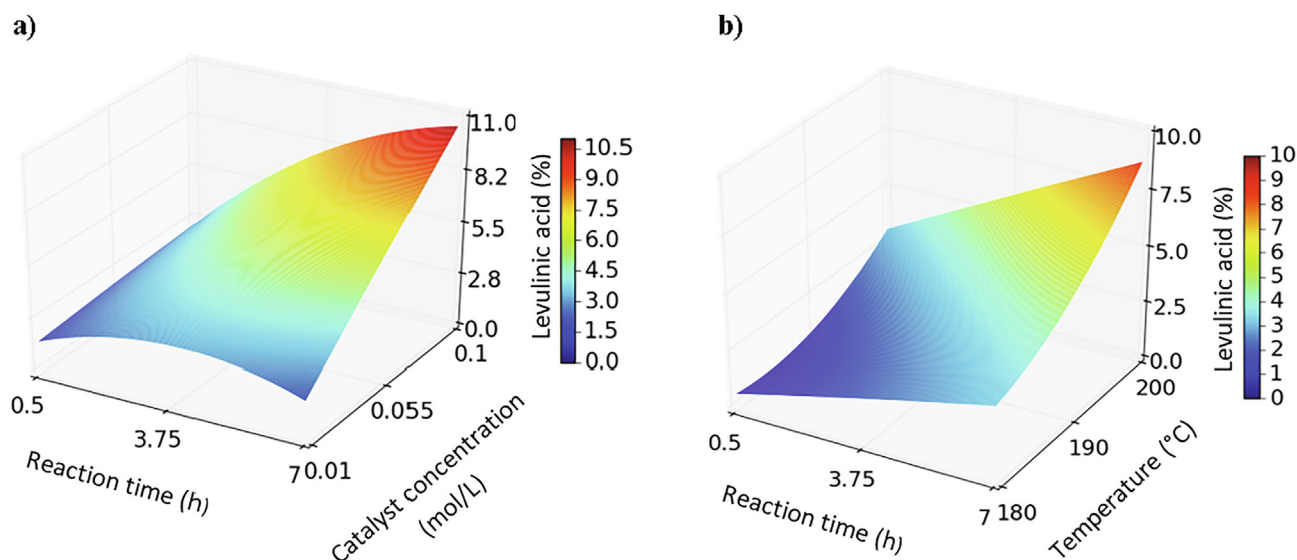
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Fig 3. 3D response surface plots of levulinic acid yield versus catalyst concentration and reaction time (a) as well as temperature and reaction time (b) obtained from the acid catalyzed alcoholysis of softwood bark using a metal salt ($Al_2(SO_4)_3$) as catalyst.
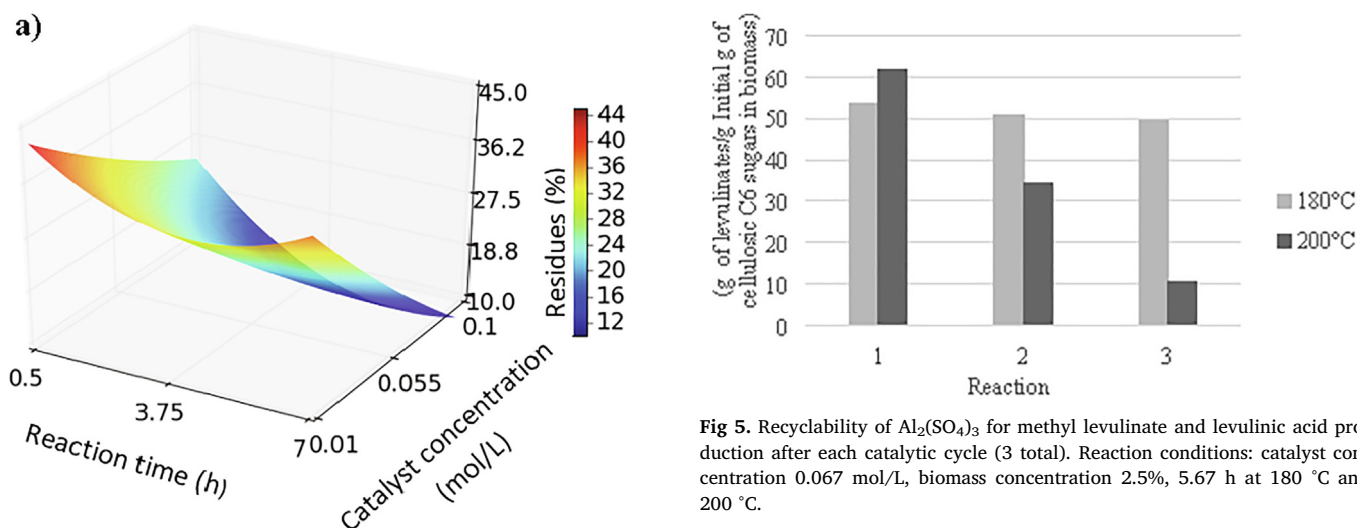

Fig 4. 3D response surface plots of residue production versus catalyst concentration and reaction time obtained from the acid catalyzed methanolysis of softwood bark using a metal salt as catalyst.

Fig 5. Recyclability of $Al_2(SO_4)_3$ for methyl levulinate and levulinic acid production after each catalytic cycle (3 total). Reaction conditions: catalyst concentration 0.067 mol/L, biomass concentration 2.5%, 5.67 h at 180 °C and 200 °C.

where: W is the weight loss (mg), D is the metal density (g/cm^3), A is the area of the sample (cm^2) and t is the time of exposure of the metal sample (h). Results showed that H_2SO_4 solution (0.067 mol/L) corroded Monel material at 49.38 mpy. In the present work, the use of aluminum sulfate (as catalyst) not only allowed the production of levulinate, but also allowed a decrease in corrosion inside the reactor of 67% (16.55 mpy) as compared to the value that was obtained with sulfuric acid. The use of metal salts to produce levulinates from biomass could hence reduce the production costs on a larger scale maybe even allow using cheaper metals to build the operating reactor.

5. Catalyst recovery and catalyst efficiency

To evaluate the catalyst recovery, three reactions were performed which were carried out at the optimal reaction conditions generated from the experimental design (catalyst concentration 0.067 mol/L, biomass concentration 2.5 wt%, 5.67 h at 200 °C) (Fig. 5).

Results showed that the yields of levulinates were reduced by 55% for the second reaction and by 30% (as compared to the second reaction) for the third one. One hypothesis to explain such observations would be that the degree of aggregation of Al^{3+} could be affected by the increase in temperature, hence resulting in a decrease in both Lewis and BrØnsted acids availability in the mixture [40]. To improve the recyclability of the catalyst, additional experiments were performed at low temperature (180 °C) to improve the recyclability of the metal salt. After recycling twice, the yield of levulinates decreased from 53% to 49.15%. Despite this situation, metal salt catalyst may be more economical for lignocellulosic biomass conversion in methanol although additional data would be required to support this affirmation.

6. Conclusion

Results from this work showed that the use of lignocellulosic biomass (softwood bark) for the production of levulinates through catalytic alcoholysis in methanol using aluminum sulfate as catalyst could potentially be beneficial for the technical and economical feasibility to produce levulinates. From the optimization approach developed in this work, levulinates were generated at 61.83% (based on cellulosic glucose content) when using $Al_2(SO_4)_3$ at 200 °C and for 6 h. These yields, which are among the highest reported in literature, could, if combined with the use of softwood bark (very cheap biomass), represent a potentially suitable approach for the large-scale production of levulinates

with potential applications as fuel additive and chemicals. The use of aluminum sulfate decreased corrosion into the reactor, which could decrease production costs at larger scale. In addition, this research could be a key step for a kinetic model and can contribute to the development of an industrial technology.

CRediT authorship contribution statement

Maricelly Martínez: Investigation. **Xavier Duret:** Validation, Formal analysis. **Thierry Ghislain:** Resources, Formal analysis. **Doan P. Minh:** Supervision. **Ange Nzihou:** Supervision. **Jean-Michel Lavoie:** Conceptualization, Funding acquisition, Supervision.

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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