



# Extremely low sulfuric acid catalyst system for synthesis of methyl levulinate from glucose

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## ARTICLE INFO

### Article history:

Received 22 December 2011

Received in revised form 2 March 2012

Accepted 6 March 2012

### Keywords:

Glucose

Methyl levulinate

Extremely low sulfuric acid

Kinetics

## ABSTRACT

A comprehensive experimental and kinetic investigation on the synthesis of methyl levulinate from glucose in methanol medium under mild conditions ( $\leq 473$  K) catalyzed by extremely low sulfuric acid ( $\leq 0.01$  mol L<sup>-1</sup>) was performed in this study. Glucose was rapidly and almost quantitatively converted into methyl glucosides as a key and stable intermediate product, and a high methyl levulinate yield of ca. 50 mol% can be achieved after the completion of reaction. Based on the detected compounds, a plausible reaction pathway for the acid-catalyzed conversion of glucose in methanol medium was proposed. The generation of methyl levulinate from glucose via methyl glucosides as a function of the process variables was modelled using a simplified first-order kinetic model, and a good fit between experimental data and the kinetic model was obtained. An advantage of this catalyst system is that negligible undesired dimethyl ether formed from the side reaction for the dehydration of methanol that was used as reaction medium, the equipment corrosion was slight, and less spent acid need to be addressed after the reaction. Overall, this catalytic strategy is efficient, economical and environmentally benign for the conversion of carbohydrates into high value-added chemicals and fuels.

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## 1. Introduction

A sustainable supply of fuel and chemicals in the future society requires feedstocks based on renewable rather than gradual depletion of fossil fuel resources. Glucose, an abundant and low cost six-carbon sugar molecule that is highly dependent on biomass, will be a potential feedstock toward this challenging goal (Zhao et al., 2007; Digman et al., 2009; Naik et al., 2010). However, inability to effectively and economically transform glucose is still a major obstacle today. Currently, chemical/catalytic process attracts more and more concerns for this purpose, and latest efforts have focused on direct converting carbohydrates derived from biomass to levulinate esters due to the synthetic technique is simple, wastewater is minimized and products are purified easily by distillation (Garves, 1988; Olson et al., 2001). Common levulinate esters, like methyl levulinate and ethyl levulinate, are a class of short chain fatty esters with numerous potential applications either in the flavoring and fragrance industry or as additives for diesel and biodiesel transportation fuels (Hayes, 2009; Lee et al., 2010; Joshi et al., 2011; Windom et al., 2011). Additionally, levulinate esters are preferred substrates for chemical conversion to many other useful chemicals

by various kinds of condensation and addition reactions at the ester and keto groups (Olson et al., 2001).

Up to now, there have been some reports on the direct acid-catalyzed conversion carbohydrates into levulinate esters. Initially, dilute H<sub>2</sub>SO<sub>4</sub> was widely used as catalyst in this study, since it is relatively cheap and also very active (Garves, 1988; Olson et al., 2001; Le Van Mao et al., 2011). However, during the reaction, massive alcohol as reaction medium dehydration into diether is one of the substantial obstacles for the development of this process (Mascal and Nikitin, 2010). Besides, dilute H<sub>2</sub>SO<sub>4</sub> also suffers from serious drawbacks, such as equipment corrosion and pollution. Recently, several novel catalyst systems were developed. For instance, Tominaga et al. (2011) presented an efficient catalyst system for the synthesis of methyl levulinate from cellulose and glucose by combining two different kinds of acid, a Lewis acid and a Brønsted acid, where the highest yield of methyl levulinate reached 75%. (Saravanamurugan et al., 2011; Saravanamurugan and Riisager, 2012) reported the catalytic transformation of fructose, glucose, and sucrose to ethyl levulinate with different sulfonic acid-functionalized ionic liquids (SO<sub>3</sub>H-ILS) and sulfonic acid-functionalized SBA-15 (SO<sub>3</sub>H-SBA-15) as catalyst. It was found that these catalysts showed a high catalytic activity for the conversion of fructose, but not well work for the transformation of glucose to ethyl levulinate. In our previous research, sulfated metal oxides was found to be effective for sugars conversion, leading to the synthesis

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## Nomenclature

$C_{GLC,0}$	initial concentration of glucose ( $\text{mol L}^{-1}$ )
$C_{MGO}$	concentration of methyl glucosides ( $\text{mol L}^{-1}$ )
$C_{MGO,0}$	initial concentration of methyl glucosides ( $\text{mol L}^{-1}$ )
$C_{MMF}$	concentration of 5-methoxymethylfurfural ( $\text{mol L}^{-1}$ )
$C_{MLA}$	concentration of methyl levulinate ( $\text{mol L}^{-1}$ )
$Y_{MGO}$	yield of methyl glucosides ( $\text{mol mol}^{-1}$ )
$Y_{MMF}$	yield of 5-methoxymethylfurfural ( $\text{mol mol}^{-1}$ )
$Y_{MLA}$	yield of methyl levulinate ( $\text{mol mol}^{-1}$ )
$C_{H_2SO_4}$	concentration of $H_2SO_4$ ( $\text{mol L}^{-1}$ )
$C_{H^+}$	concentration of $H^+$ ( $\text{mol L}^{-1}$ )
$k$	reaction rate constant of methyl glucosides decomposition ( $\text{min}^{-1}$ )
$k_1$	reaction rate constant of methyl glucosides for the main reaction to methyl levulinate ( $\text{min}^{-1}$ )
$k_2$	reaction rate constant of methyl glucosides for the side reaction to byproducts ( $\text{min}^{-1}$ )
$E_1$	activation energy of the main reaction to methyl levulinate ( $\text{kJ mol}^{-1}$ )
$E_2$	activation energy of the side reaction to byproducts ( $\text{kJ mol}^{-1}$ )
$\alpha$	reaction order of $H^+$ in the main reaction to methyl levulinate
$\beta$	reaction order of $H^+$ in the side reaction to byproducts
$R$	universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )
$A_1$	pre-exponential factor of the main reaction to methyl levulinate ( $\text{mol}^{-\alpha} \text{ L}^{\alpha} \text{ min}^{-1}$ )
$A_2$	pre-exponential factor of the side reaction to byproducts ( $\text{mol}^{-\beta} \text{ L}^{\beta} \text{ min}^{-1}$ )
$T$	reaction temperature (K)
$t$	reaction time (min)

of ethyl levulinate from glucose with a moderate yield up to 30% (Peng et al., 2011). Overall, it also found that the previous studies mainly focused on the optimization of levulinate esters production. A complete kinetic model on the synthesis of levulinate esters from the direct acid-catalyzed conversion of carbohydrates is lacking. Wu et al. (2010) investigated the kinetics of methyl levulinate production from glucose catalyzed by dilute sulfuric acid, however, where the model was obtained only by fitting of methyl levulinate data without the data of starting chemical and/or intermediate. The kinetic model did not have good persuasion and the degradation mechanism was not entirely explicit.

In the present study, we found that extremely low sulfuric acid catalyst system ( $\leq 0.01 \text{ mol L}^{-1}$ ) is highly promising strategy for the synthesis of methyl levulinate from glucose in methanol medium, which can offer enough acid site for the completion of reaction. An advantage of the catalyst system is that negligible undesired dimethyl ether formed from the side reaction for the dehydration of methanol, the equipment corrosion was mild and less spent acid need to be addressed after the reaction. In this paper, the effects of multiple process parameters (i.e. temperature, acid concentration, initial glucose concentration) on the reaction performance were conducted as a function of time to optimise the yield of methyl levulinate. Based on the experimental results, a plausible reaction pathway was proposed, and an available kinetic model describing methyl levulinate and byproduct formation from the acid-catalyzed methanolysis of glucose was developed by a key and stable intermediate of methyl glucosides.

## 2. Experimental

### 2.1. Chemicals and materials

Methyl levulinate (99% purity), methyl glucosides (98% purity) and 5-methoxymethylfurfural (97% purity) used for calibration were obtained from Alfa Aesar (Tianjin, China), Yangcun Chemical (Beijing, China) and Yingchuang Chemical (Suzhou, China), respectively. Other reagents and chemicals were all of analytical grade from Sinopharm Chemical Reagent (Shanghai, China) and used without further purification or treatment. The corrosion tests were performed on 20# carbon steel and 316L stainless steel with dimensions  $40 \text{ mm} \times 13 \text{ mm} \times 2 \text{ mm}$ . Table 1 presents the chemical compositions of the steels used. Prior to experiments, all specimens were wet around up to 1000 grit, cleaned with acetone and washed with distilled water, and finally dried in a compressed hot air.

### 2.2. Equipment and experimental procedures

The experiments were carried out in a cylindrical stainless steel pressurized reactor with 100 mL total volume made by PARR instrument company, USA. The reactor was heated in an adjustable electric stove. The temperature of the reactor contents was monitored by a thermocouple connected to the reactor.

#### 2.2.1. Methanolysis of glucose

For each experiment, a 50 mL portion of a solution of  $H_2SO_4$  in methanol and a given amount of glucose were introduced into the reactor, which was then brought to the desired temperature by external heating about 25 min to heat the system and shaken at 500 rpm for reaction. The experiments were conducted at 433, 453 and 473 K, respectively.  $H_2SO_4$  concentration was at 0.001, 0.005 and  $0.01 \text{ mol L}^{-1}$ , respectively. Initial glucose concentration was at 0.3, 0.6 and  $1.2 \text{ mol L}^{-1}$ , respectively. After certain reaction time, the reactor was taken from the stove and quenched in an ice cool water bath to terminate the reaction. Then, the sample take from the reactor was filtered and collected the liquid products for analysis.

#### 2.2.2. Methanol dehydration experiments

A 50 mL methanol solution of  $0.005 \text{ mol L}^{-1} H_2SO_4$  was poured into the reactor. The reactor contents were brought to reaction temperature of 473 K and endured a given period of time. For comparison, the pure methanol and methanol solution of  $0.1 \text{ mol L}^{-1} H_2SO_4$  were reacted under the same reaction conditions. After the completion of reaction, the reaction solution was collected. The formation amount of dimethyl ether from methanol was calculated according to weight loss of liquid phase before and after the reaction (Carr et al., 2011).

#### 2.2.3. Corrosion tests

Weight loss measurements were carried out in the reactor containing 50 mL methanol solutions of various concentrations  $H_2SO_4$ . The specimens were weighted before test by means of an analytical balance with a precision of 0.0001 g for the original weight. After immersion in the system at 473 K for 150 min, the specimens were withdrawn and carefully washed with distilled water and acetone,

**Table 1**  
Elemental compositions of specimens used in corrosion tests.

Alloy	Elemental compositions (wt%)								
	C	Si	Mn	P	S	Ni	Cr	Mo	Fe
20# carbon steel	0.18	0.29	0.43	0.03	0.03	0.22	0.21	ND	Bal
316L stainless steel	0.02	0.68	1.37	0.01	0.01	13.53	16.61	2.35	Bal

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