



## Eco-friendly synthesis of maleate ester: A comparison between solid acid and enzyme-catalyzed esterification



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### ABSTRACT

In this study, two different eco-friendly methods were investigated for the synthesis of a dicarboxylic acid ester, dimethyl maleate (DMM). One method involves application of molybdate sulfuric acid (MSA) as a solid acid catalyst in the esterification of maleic acid with methanol. The effects of three parameters namely, temperature, time, and catalyst amount on the product synthesis were determined. By using response surface methodology (RSM) based on central composite rotatable design (CCRD), maximum conversion of the maleic acid (87.6%) was obtained at reaction conditions of 120 °C, 0.27 g MSA, and 103 min. In the other method, DMM was synthesized by enzymatic esterification using immobilized *Candida antarctica* lipase B as the catalyst. Maximum conversion was 72.3%, at the optimal conditions of 62.5 °C, 0.27 g enzyme, and 249 min. The reusability study showed that MSA lost its catalytic activity after five cycles. However, the immobilized enzyme maintained its activity and stability. The results indicated that both employed methods were efficient for the synthesis of DMM. A higher conversion could be obtained using MSA as the catalyst, which could be compensated by better reusability of the enzyme. The enzyme-catalyzed reaction was more energy efficient but it took a longer time to obtain maximum reaction yield.

### 1. Introduction

Organic esters as an important class of chemicals are commonly used in the production of pharmaceuticals, plasticizers, fine chemicals, fuels, solvents, perfumes, and skincare products (Liu et al., 2008). Synthesis of esters is usually catalyzed by mineral acid catalysts such as hydrofluoric acid, sulfuric acid or Lewis acid catalysts (D'Oca et al., 2012; Sirsam et al., 2016). Application of these homogeneous catalysts in esterification have several drawbacks in terms of handling, corrosiveness, difficult separation from the reaction medium, toxicity and environmental concern (Zatta et al., 2011). Recently, solid acids have been used as cost effective and environmentally benign catalysts in the esterification reactions (Ahmad and Dhar, 2017; Gupta and Paul, 2014). Compared to their homogenous counterparts, solid acid catalysts have lower toxicity, higher reactivity, lack of corrosion and environmental friendliness (Wang et al., 2015). Molybdate sulfuric acid (MSA) is a Brønsted solid acid which has been used in organic transformations (Shinde and Jeong, 2015; Tamaddon et al., 2013). MSA is an efficient proton source which can be applied as an inexpensive and reusable alternative to sulfuric acid (Tamaddon et al., 2012).

On the other hand, enzymatic esterification as a “green” alternative to chemical synthesis of esters offers several advantages such as mild

reaction conditions, low energy requirement, and high selectivity and specify (Lisboa et al., 2014; Rahman et al., 2011). High selectivity for esterification under mild conditions leads to fewer side reactions and thus less waste (Dong et al., 2017). This has a positive impact on process economy which can compensate for the cost of the enzyme (Adlercreutz, 2013).

Maleate esters are widely used as additives and intermediates in the production of thermoplast and thermoset plastics, pigments, pharmaceuticals, paints, adhesives, copolymers and agricultural products (Yadav and Thathagar, 2002). Synthesis of dimethyl maleate (DMM) in the presence of *p*-toluenesulphonic acid and ion-exchange resin has been reported previously (Harmer and Sun, 2001; Yadav and Thathagar, 2002). However, so far, there is no report on the synthesis of DMM using MSA or enzyme as the catalyst for the esterification reaction.

In order to optimize the yield of reaction, response surface methodology (RSM) with central composite rotatable design (CCRD) was applied. RSM is an efficient statistical technique useful for optimizing chemical and biotechnological processes (Myers et al., 2016). Statistical methods solve the problem of effective variables selection among various parameters and help to study the interaction between important factors (Dhiman et al., 2017; Othman et al., 2017).

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In this study, two environmental friendly methods, including solid acid and enzyme catalyzed esterification reactions, were applied for the synthesis of DMM. The objective of this work was to compare these two different synthesis processes in terms of reaction yield and operational parameters. The influence of important reaction parameters, i.e. temperature, reaction time and catalyst loading, on the esterification reactions catalyzed by MSA and immobilized *Candida antarctica* lipase B was investigated and optimized by RSM. The study also helps to understand relationships between the process parameters and the reaction yield and to determine the optimum conditions for the synthesis of DMM.

## 2. Material and methods

### 2.1. Materials

*Candida antarctica* lipase B produced by submerged fermentation of genetically modified *Aspergillus niger* and immobilized on macroporous acrylic resin ( $\geq 5000$  units/g) was obtained from Sigma-Aldrich. Maleic acid, methanol and n-hexane were purchased from Merck (Darmstadt, Germany). Anhydrous sodium molybdate and chlorosulfonic acid were purchased from Sigma-Aldrich. All other chemicals and solvents used in this study were of analytical grade.

### 2.2. Synthesis and characterization of the solid acid catalyst

For the synthesis of molybdate sulfuric acid (MSA), 4.118 g (20 mmol) of anhydrous sodium molybdate was added to 25 mL of dry n-hexane in a 100- mL round bottom flask at ice bath and stirred. Then, 0.266 mL (40 mmol) of chlorosulfonic acid was added dropwise to the flask and stirred for 2 h (Scheme 1). The mixture was gradually poured into 25 mL of chilled distilled water. The obtained bluish solid acid was separated by filtration, washed with cold distilled water and dried at 120 °C for 5 h (Tamaddon et al., 2012). The yield of the prepared MSA catalyst was 90%.

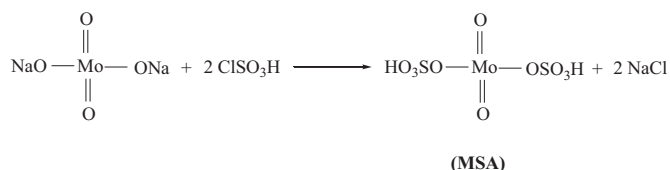
The prepared catalyst was characterized by X-ray diffraction (XRD) using a Philips X'Pert MPD diffractometer (Cu-K $\alpha$  X-radiation,  $\lambda = 1.54056$  Å). FT-IR spectra of the catalyst was recorded by an Alpha-Bruker FT-IR spectrophotometer.

### 2.3. Esterification procedure

Maleic acid (0.464 g) and methanol (0.256 g) with molar ratio of 1:2 were mixed in a 50 mL-flask. Five milliliter of hexane was added as solvent. Different amounts of catalyst (MSA or enzyme), according to the experimental design, were subsequently added. The mixture was stirred under reflux system at 150 rpm at different temperatures and for different time periods generated by RSM (Tables 1, 2). The reaction was terminated by the addition of 5 mL of ethanol/acetone mixture (50:50 v/v) and the catalyst was separated by simple filtration (Lee et al., 2010).

### 2.4. Analysis and characterization of the ester product

After each reaction, the remained free maleic acid was determined by titration with 0.1 M NaOH (Sirsam and Usmani, 2016b). The conversion of the acid was calculated from the values obtained for the



Scheme 1. Synthesis of MSA.

**Table 1**  
Composition of various experiments of the CCRD design for MSA-catalyzed synthesis of DMM.

Exp. no.	Variable			Conversion (%)
	Temperature (°C)	MSA amount (g)	Time (min)	
1	50.0	0.16	210.0	44.86
2	64.2	0.08	299.2	62.39
3	64.2	0.08	120.8	44.78
4	64.2	0.25	299.2	56.40
5	64.2	0.25	120.8	38.80
6	85.0	0.03	210.0	44.16
7	85.0	0.16	210.0	80.57
8	85.0	0.30	210.0	75.95
9	85.0	0.16	210.0	76.30
10	85.0	0.16	60.0	69.22
11	85.0	0.16	360.0	80.27
12	85.0	0.16	210.0	77.10
13	105.8	0.25	299.2	80.20
14	105.8	0.25	120.8	80.00
15	105.8	0.08	299.2	63.51
16	105.8	0.08	120.8	63.83
17	120.0	0.16	210.0	81.20

**Table 2**  
Composition of various experiments of the CCRD design for enzyme-catalyzed synthesis of DMM.

Exp. no.	Variable			Conversion (%)
	Temperature (°C)	Enzyme amount (g)	Time (min)	
1	25.0	0.16	210.0	32.14
2	33.1	0.08	299.2	21.53
3	33.1	0.25	299.2	41.72
4	33.1	0.08	120.8	27.02
5	33.1	0.25	120.8	36.88
6	45.0	0.16	210.0	40.87
7	45.0	0.16	60.0	23.11
8	45.0	0.16	210.0	43.20
9	45.0	0.03	210.0	24.85
10	45.0	0.30	210.0	50.13
11	45.0	0.16	360.0	36.64
12	45.0	0.16	210.0	41.50
13	56.9	0.25	120.8	60.17
14	56.9	0.08	120.8	40.99
15	56.9	0.25	299.2	62.66
16	56.9	0.08	299.2	38.50
17	65.0	0.16	210.0	60.35

control (without catalyst) and the test samples. The product was also identified by thin layer chromatography (TLC) using ethyl acetate/hexane (2:1 v/v) as the solvent, and also by an Alpha-Bruker FT-IR spectrophotometer. Further identification of the ester was performed using Gas Chromatograph/Mass Selective Detector (GC/MSD) on the Agilent (model GC 7890; model MSD 5977; Agilent Technologies, Inc., USA) instrument with HP-5 column (0.32 mm  $\times$  30 m, 0.25  $\mu$ m). The carrier gas was Helium and the total gas flow rate was 1.2 mL min<sup>-1</sup>. The inlet temperature was 280 °C with a split ratio of 1:30. The oven temperature was maintained at 60 °C for 2 min, elevated to 300 °C at a rate of 10 °C min<sup>-1</sup> and held for 10 min.

### 2.5. Experimental design and statistical analysis

For statistical analysis of the process, a three-variable, five-level response surface methodology (RSM) based on central composite rotatable design (CCRD) was used. Analysis was conducted using Design Expert Version 6.0.6 (Stat-Ease, Statistics Made Easy, Minneapolis, MN, USA) software. The optimum conditions were obtained using the

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