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# Methoxylation of dihydromyrcene in an intensified fixed bed reactor



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## ABSTRACT

In this work we systematically investigated scale-up of methoxylation of dihydromyrcene (DHM) to produce dihydromyrcenyl methyl ether (DME) using cation exchange resin catalysts. Optimization of the reaction conditions for the methoxylation of DHM was initially carried out in a 500 mL stirred tank reactor (STR). A subsequent scale-up to carry out the reaction in a 5 L STR under the same reaction conditions failed to reproduce the high yield of DME due to possible limitation in mass and heat transfer. Successful scale-up was achieved by using an intensified fixed bed reactor (IFBR) where mass transfer limitation was essentially eliminated. The thermodynamic and kinetic parameters of the methoxylation of DHM were determined in the IFBR. The equilibrium constants of the methoxylation of DHM decreased with increasing reaction temperature, indicating an exothermic reaction. The kinetic data suggested that the methoxylation of DHM follows the Eley–Rideal mechanism.

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## 1. Introduction

Terpenic alcohols, ethers and esters obtained through acid-catalyzed hydration, alkoxylation and acetoxylation of monoterpenes have been widely used as flavors, fragrances and medical additives in perfumery and pharmaceutical industry (Kozhevnikov et al., 1997; da Silva et al., 2003). Dihydromyrcene (DHM) is manufactured from pyrolysis of pinane that is obtained through hydrogenation of  $\alpha$ -pinene or  $\beta$ -pinene in turpentine. DHM is one of the most common monoterpenes used for the industrial synthesis of various fragrance ingredients (Gusevskaya, 2014). For instance, methoxylation of DHM produces dihydromyrcenyl methyl ether (DME) that has high economic value and is mainly used as intermediate in the synthesis of methoxy elgenol (Wang et al., 2011). Thus, it is of great industrial significance to study the reactions with DHM.

The hydration, alkoxylation, acetoxylation, and oxidation of DHM have been extensively studied. Using triflic acid as catalyst, Davey et al. (2010) performed the direct hydration of DHM, obtaining high

selectivity of dihydromyrcenol under a series of reaction conditions. H-beta zeolite has been tested by Botella et al. (2000) for the hydration of DHM to produce dihydromyrcenol, and 59% yield and 98% selectivity of dihydromyrcenol were reached when Si/Al ratio (molar) in zeolite was 27. In a modified Soxhlet extractor, Lin et al. (1998) studied the hydrated DHM with the catalysis of cation exchange resins R-H that was modified with metal ions (Sn, Al, Zn). It was explored that the catalytic activity of cation exchange resins was greatly enhanced through the modification. Employing a Keggin-type heteropoly acid  $H_3PW_{12}O_{40}$  (HPA) as catalyst, Kozhevnikov et al. (1997) made the liquid-phase hydration and acetoxylation of DHM, and obtained 90% selectivity of dihydromyrcenol and dihydromyrcenyl acetate at 21% DHM conversion. Noticeably, the catalyst could be easily recycled without loss of activity. The regioselective epoxidation of DHM was studied by Schofield et al. (2002) with titanium-containing silicates TS-1 or  $TiAl\beta$  as catalyst, and aqueous hydrogen peroxide, *tert*-butyl hydroperoxide and urea-hydrogen peroxide as oxidants, respectively. Using sulfuric acid as catalyst, Wang et al. (2011) methoxylated DHM to produce DME for the eventual synthesis

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### Nomenclature

$a$	Activity
$a_s$	External surface of particles in unit mass of catalysts ( $\text{m}^2 \text{g}^{-1}$ )
$D_A$	Molecular diffusion coefficient at infinite dilution ( $\text{cm}^2 \text{s}^{-1}$ )
$D_e$	Effective diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )
$E_a$	Activation energy ( $\text{kJ mol}^{-1}$ )
$f_s$	Volume of particles in unit volume of reactor
$K_e$	Equilibrium constant
$K_M$	Equilibrium adsorption constant of methanol
$k_0$	Pre-exponential factor ( $\text{mol g}^{-1} \text{h}^{-1}$ )
$k_f$	Forward reaction rate constant ( $\text{mol g}^{-1} \text{h}^{-1}$ )
$k_p$	Reaction rate constant ( $\text{s}^{-1}$ )
$k_r$	Reverse reaction rate constant ( $\text{mol g}^{-1} \text{h}^{-1}$ )
$k_s$	Film coefficient of catalyst particle ( $\text{m s}^{-1}$ )
$M_B$	Molecular weight of solvent B ( $\text{g mol}^{-1}$ )
$M_{cat}$	Catalyst weight per unit volume of the reactants ( $\text{gL}^{-1}$ )
$R$	Gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$Re$	Reynolds number
$R_p$	Average radius of catalyst particle (mm)
$Sc$	Schmidt number
$T$	Temperature (K)
$t$	Time (h)
$V_A$	Molar volume of component A at its normal boiling temperature ( $\text{L mol}^{-1}$ )
$w/w$	Weight of catalyst/weight of total reactants
$x$	Mole fraction
$X_{cal}$	Calculated conversion
$X_{exp}$	Experimental conversion
<b>Greek letters</b>	
$\gamma$	Activity coefficient
$\Delta_r G^0$	Gibbs free energy ( $\text{kJ mol}^{-1}$ )
$\Delta_r H^0$	Reaction enthalpy ( $\text{kJ mol}^{-1}$ )
$\Delta_r S^0$	Entropy ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )
$\varepsilon_p$	Particle porosity
$\eta$	Effectiveness factor
$\mu$	Viscosity of solvent (mPa s)
$\rho$	Density ( $\text{g cm}^{-3}$ )
$\tau_m$	Tortuosity factor
$\phi$	Thiele modulus
$\varphi$	Association factor of solvent
<b>Subscripts</b>	
DHM	Dihydromyrcene
DME	Dihydromyrcenyl methyl ether
MeOH	Methanol
<b>Abbreviations</b>	
DHM	Dihydromyrcene
DME	Dihydromyrcenyl methyl ether
IFBR	Intensified fixed bed reactor
MeOH	Methanol
STR	Stirred tank reactor

of methoxy elgenol. Xiao et al. (1988) studied H-mordenite-catalyzed methoxylation of various terpenes including myrcene, isocitronellene and DHM within a long reaction time. For the methoxylation process, inorganic acid catalysts like sulfuric acid strongly suffer from long production cycle, high energy consumption, serious corrosion, troubles

in post-processing and the like. Although solid acid catalysts are better than sulfuric acid, the unsatisfactory stability and reusability and considerable byproducts owing to the extremely high hydroscopicity of zeolites, greatly hinder the application of solid acid catalysts. Comparatively, cation exchange resins are preferred, due to high catalytic activity, superb reusability and convenience for separation.

Traditional stirred tank reactor (STR) is commonly used to accomplish various reactions of terpenes, including hydration, esterification, and oxidation (Robles-Dutenhefner et al., 2001; Castanheiro et al., 2003; Mochida et al., 2007). However, there are some obvious disadvantages such as high energy consumption, low yield, long residence of reactants, and inefficiency of heat exchange for the application of STR. In our lab, a jet reactor that had efficient energy utilization as well as significant heat- and mass-transfer, has been successfully used for hydration of terpenes (Liu et al., 2010, 2011; Yang et al., 2011, 2012). However, for the methoxylation of terpene in the jet reactor, solid catalysts tend to be broken by the strong liquid flow. This can be overcome by intensified fixed bed reactor (IFBR).

In this work, DME was first synthesized by methoxylating DHM in STR using Lewatit 2620 cation exchange resin as a catalyst to explore the influences of the reaction variables on the yield of DME. The reaction process is shown in Fig. 1. DHM is first converted to carbenium ion under the catalysis of acid, and then nucleophilically attacked by methanol to generate DME.

The experiments were subsequently carried out in both enlarged STR and specially designed IFBR. The experimental results in the three different reactors were compared and discussed.

## 2. Experimental

### 2.1. Materials

DHM (industrial grade, purity  $\geq 92\%$ ) was supplied by Xiamen Doingcom Chemical Co., Ltd. (China). Methanol (purity  $\geq 99\%$ ) was obtained from Nanjing Chemical Reagent Co., Ltd. (China). Amberlyst 15 and Amberlyst 35 resins were purchased from Rohm and Hass Co. Lewatit 2620 resin was bought from Lanxess Chemical Co. All the catalysts were washed several times with distilled water and dried at 353 K under vacuum (0.01 bar) before usage.

### 2.2. Apparatus and procedures

Lab-scale methoxylation reactions were conducted in a 500 mL glass STR (sphere, diameter: 9.8 cm; stirrer: 2-flat-blade paddle, at center near the bottom of reactor, paddle length: 3 cm) with temperature and agitation speed measured online. During the experiment, reactants were fed into the reactor at the scheduled mass ratio under fully agitating. As the pre-set temperature was reached, the catalysts were added and the reaction was started. During the experiments, samples were taken at regular intervals and were diluted with acetone for gas chromatography (GC).

Scale-up methoxylation experiments were carried out in both a 5 L STR (cylinder, diameter: 18 cm, height: 20 cm; stirrer: 2-flat-blade paddle, at center near the bottom of reactor, paddle length: 6 cm) and a stainless steel IFBR (cylinder, diameter: 8 cm, height: 22 cm) (Fig. 2). In IFBR, the catalysts were fixed in a cylindrical cage (diameter: 6 cm, height: 20 cm) with filter. DHM and methanol were added into the reactor. The reactants could be mixed sufficiently by a circulating pump and passed through the bed of catalyst at a high speed. When the circulating pump worked, the liquid phase flowed through the pipe and the reactor in a loop. When the scheduled temperature of the reactor reached, the timer was started. Samples were also taken out regularly for analysis.

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