ONE-POT SYNTESIS OF MENTHOL FROM CITRONELLAL : APPLICATION OF CITRONELLA OIL

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ABSTRACT

Synthesis of menthol ($C_{10}H_{20}O$) from citronellal ($C_{10}H_{18}O$) has been performed by a one-pot process. The process was conducted in a 250 mL capacity autoclave with acidified natural zeolite and Raney Nickel as catalysts at temperature 120°C, pressure 5 bar, and variation of time 1-8 hours. Natural zeolite and Raney Nickel were placed in the autoclave and it was found that the cyclisation and hydrogenation reaction to form menthol could undergo in the same reactor. FTIR Analysis showed peak formation at 3346.50 cm^{-1} indicating - OH group was formed. Result of ^{1}H-NMR and ^{13}C-NMR analysis reports chemical shifts at δ=71.53 ppm and δ=4.05 ppm. Gas chromatography analysis showed that the conversion was 80% with concentration of menthol about 68% (v/v).

Keywords : menthol, citronellal, one-pot reaction, citronella oil.

INTRODUCTION

Menthol ($C_{10}H_{20}O$) is widely used in cosmetics, pharmaceuticals, toothpastes, chewing gums, and also cigarettes. Currently, synthetic menthol is produced commercially in the world by two companies, Haarman & Reimer and Takasago Corp. In the Haarman & Reimer process racemic (±)-menthols are obtained by hydrogenation of thymol, where as Takasago Corp. developed an asymmetric synthesis technology for producing (-)-menthol from myrcene. Considerable effort have been devoted to the production of menthol by synthetic means from other more readily renewable raw materials and simplify the process into a one-pot process with the help of a selected catalyst.

Citronella oil is a potential renewable material for the development of fine chemicals. The oil is used extensively as a source of important perfumery chemicals like citronellal, citronellol and geraniol, which find extensive use in soap, perfumery, cosmetic and flavoring industries throughout the world (Guenther. E., 1998). Citronella oil is classified in trade into two types : Ceylon citronella oil, obtained from *Cymbopogon nardus Rendle*, is the inferior type, while Java type citronella oil obtained from *Cymbopogon winterianus Jowitt*, is considered superior (Hardjono, 2002)

The synthesis of menthol from citronellal is generally carried out through the selective isomerisation of citronellal to the cyclic alcohol, isopulegol, on acid catalysts. Classically, this cyclization is carried out in protonic media, such as formic acid, phosphoric acid, acetic anhydride, or solid catalysts. Ohloff (1965) has shown that thermal cyclization occurs acidic cleanly and in high yield. The resultant isopulegol isomers formed possess the necessary asymmetric center at C-1 of the p-menthane skeleton for (-)-menthol production.

The unsaturated alcohol is then separated from the reaction mixture and hydrogenated to the corresponding saturated alcohol, menthol (Misono and Noijri, 1990). Hydrogenation is performed in presence of a catalyst. Raney nickel is used in a large number of industrial processses and in organic synthesis because of its stability and high catalytic activity at room tempe-rature. It is typically used in the reduction of compounds that have multiple bonds, such as alkynes, alkenes, nitriles, dienes, aromatics, and carbonyls (http://en.wikipedia.org/wiki/Raney_nikel, 2007).

Milone *et al.* (1999) conducted isomerization of citronellal under mild condition on ZnX_2 (X= Cl, Br, NO3) supported on high surface area and yielded 85% menthol. The research continued on selective one step synthesis of (−)menthol from (C)citronellal on Ru supported on modified SiO_2. Menthol was also developed by enzymatic cleavage. With this method, menthol was produced from menthyl derivatives (Gatfield *et al.*, 2002). Schlemenat *et al.* (2002) reported preparation of menthol by catalytic isomerization of D-menthol at temperatures from 30 to 120°C and pressure of 50 mbar to 300 mbar. The process was in presence of a supported (Al_2O_3) rutherium catalyst.