



Design, scale up and safe piloting of thymol hydrogenation and menthol racemisation

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A B S T R A C T

The hydrogenation of thymol and the racemisation of a menthol mixture were investigated as part of the development of novel continuous process for the production of *l*-menthol. The key innovation in this *l*-menthol process is enzymatic enantioselective resolution of *l*-menthol from 8 menthol isomers mixture. This continuous biocatalytic step has significant impact on process economy. The productivity of the enzyme (mass of *l*-menthylacetate produced/mass enzyme) is a key performance measurement of this process. The demonstration of the required enzyme productivity was therefore a key objective of the process piloting. The effect of possible side products and impurities on the process also needed to be tested and therefore five cycles of piloting were performed using approximately 500 kg of feed into resolution in each cycle. The required quantities of the racemic menthol mixture were obtained by thymol hydrogenation in pilot plant trickle-bed reactor.

Both hydrogenation and racemisation were developed as batch processes at laboratory scale and tested at bench scale in a continuous trickle-bed reactor system and scaled up to a pilot scale trickle-bed reactor. A bench scale trickle-bed reactor was designed, constructed and extensively used in the optimisation of the hydrogenation of thymol to racemic menthol. The process was successfully operated for more than 660 h in a bench scale reactor and subsequently scaled up to a pilot scale trickle-bed reactor. The pilot scale experiments were used to verify process scale-up and generate material for menthol resolution and downstream processing. Both the bench and pilot scale reactors were operated as adiabatic systems and the operation was found to be safe and reliable. Safety problems leading to formation of undesirable hot spots were experienced as consequence of insufficient catalyst wetting, high thymol concentration in the feed (above 40 wt.%) and because of possible equipment, operation and power failure.

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1. Introduction

Menthol is one of the most important terpenoids. After vanillin, it is the most widely used aroma chemical worldwide. It finds use in the cosmetic, flavour and fragrance, pharmaceutical, tobacco and oral hygiene industries, and it is the chief constituent of the essential oil of peppermint.

A commercial synthetic menthol process (Fig. 1) starts with thymol hydrogenation. The *d/l*-menthol is resolved enzymatically and *l*-menthol depleted menthol mixture after distillation from *l*-menthylacetate is equilibrated in a racemisation step.

Hydrogenation of the aromatic ring in alkylated phenols results in stereoisomers of alkylated cyclohexanol. The hydrogenation represents a system of parallel–consecutive reactions for which selectivity strongly depends on catalyst used, reaction conditions (especially pH and solvent) and the reactant structure. In the case of thymol hydrogenation the intermediate is the corresponding alkylated cyclohexanone. Reaction mechanism, catalysts and their effect on stereoselectivity and products distribution, reaction kinetics and thermodynamics of hydrogenation of alkylated phenols are described in open literature for example (Allakhverdiev et al., 1994, 1993, 1995, 1996; Konuspaev et al., 1994; Besson et al.,

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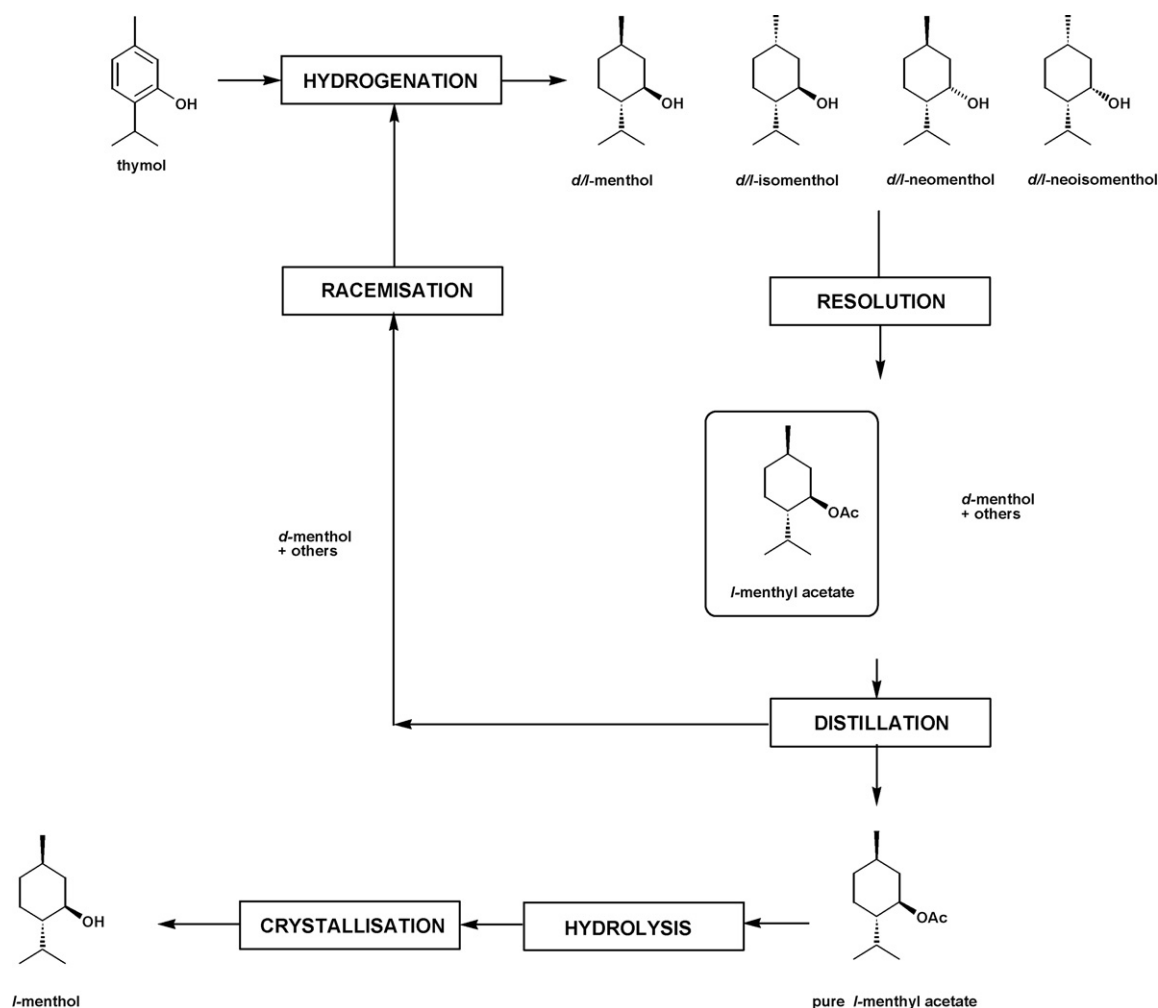


Fig. 1 – Scheme of l-menthol preparation.

1993; Kukula and Cervený, 2000a,b; Tobicik and Cervený, 2003; Pawelec et al., 2007).

Several alumina supported nickel catalyst were tested in-house in laboratory conditions. The powder catalyst (28% of Ni/Al₂O₃) identified as most suitable for this reaction ensured complete thymol conversion and concentration of d/l-menthol more than 55% in product after 3 h at temperatures above 150 °C and pressures above 0.9 MPa.

l-Menthol can be selectively resolved from the racemic menthol mixture as l-menthylacetate and separated by means of a relatively easy distillation. The unreacted menthol mixture after resolution and distillation is recycled to the thymol hydrogenation reactor via a racemisation step to equilibrate the d/l-menthol content.

Thymol hydrogenation and menthol racemisation can be executed in the presence of the same catalyst in the same type of reactor at similar temperatures. While hydrogenation of the aromatic ring requires elevated pressure, the racemisation (re-arrangement) requires significantly lower hydrogen pressure.

The reaction kinetics of the thymol (98 wt.%) hydrogenation (hydrogen 99.99%) was studied using a high-pressure autoclave at 150–180 °C and 0.85–1.6 MPa using 5 kg of thymol and 165 g of powdered (10 μm) Nickel catalyst (28% Ni/Al₂O₃). The reaction was found to be first order with respect to hydrogen and zero order with regard to thymol. From experiments at different temperatures, the activation energy of thymol hydrogenation was estimated as 18.3 kJ/mol (Dudas et al., 2005).

Unlike the exothermic thymol hydrogenation, the racemisation reaction is thermodynamically neutral and proceeds at lower pressures. The probability of more exothermic side reactions, including methanation, increases during the racemisation process (Cheng et al., 2001).

2. Trickle-bed reactor system

A trickle-bed reactor system for hydrogenation and racemisation was developed and scaled up using extensive literature information (Larachi et al., 1999; Tukač et al., 2007; Satterfield, 1975; Shah, 1979; Gianetto and Silveston, 1986; Hanika et al., 1986, 1990; Hanika and Staněk, 1986; Tukač and Hanika, 1992; Dietz et al., 2003; Hickman et al., 2004; Hanika and Lange, 1996; Hanika, 1999; Silveston and Hanika, 2002, 2004; Lange et al., 2004), personal experience and experimental data (Dudas et al., 2005). The novelty of the continuous process consists in trickle-bed reactor application which operates with minor axial dispersion of reaction mixture in catalyst bed resulting in better selectivity in comparison to bubble column slurry reactor. Moreover, trickle-bed reactor arrangement does not require catalyst separation from reaction mixture.

The reactor (Fig. 2) was designed in-house. The parameters of bench scale and pilot scale reactors are presented in Table 1. The pre-heater and bottom sections were equipped with independent heating elements and control systems. The catalytic bed has three independent heating elements with

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