Thymol Hydrogenation in Bench Scale Trickle Bed Reactor

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Investigation of thymol hydrogenation was a part of novel *L*-menthol process development. The main objective of the investigation was to collect experimental data for the scale up of thymol hydrogenation in a trickle bed reactor.

Hydrogenation of thymol was performed in an adiabatic bench scale trickle bed reactor on alumina supported Nickel catalyst. The design parameters of the bench scale system were as follows: maximum pressure 3.5 MPa, maximum temperature 350 °C, liquid flow rates of 0.5 to 5 kg h^{-1}. The experiments were performed at different thymol mass fraction (10 to 40 % wt.) in liquid menthols mixture as solvent, liquid flow rates (LHSV of 0.8 to 3.6 h^{-1}), hydrogen flow rates ($Q_L = 23 - 46$ g h^{-1}) and with total pressures of between 0.9 and 1.5 MPa. Catalyst lifetime was measured for 660 hours with the total thymol/catalyst loading being 206.5 kg kg^{-1}. It was found that, trickle bed reactor at adiabatic conditions is feasible option for thymol hydrogenation, and for safe scale-up the maximum thymol mass fraction in the feed should be below 15 % wt.

Key words:
Thymol hydrogenation, trickle bed reactor, gas-liquid-solid reaction

Introduction

The hydrogenation of the aromatic ring in alkylated phenols results in stereoisomers of alkylated cyclohexanol. The hydrogenation reaction represents a system of parallel-consecutive reactions which selectivity strongly depends on catalyst used, reaction conditions, and on the reactant structure. In case of the hydrogenation of thymol the reaction proceeds *via* an alkylated cyclohexanone intermediate. Severe reaction conditions (temperature and pressure) over a nickel catalyst leads to hydrogenolytic cleavage.

The stereoselective hydrogenation of thymol in the liquid phase was studied using several nickel catalysts, some of which where modified by co-impregnation of inorganic compounds containing chlorine.[1] The modifiers influence the rate of keto-enol transformation, which is thought to be the key selectivity and stereoselectivity-governing step. The subsequent study[2] was devoted to the kinetics of thymol hydrogenation over commercial nickel-chromia catalyst with formation of 4 menthol diastereoisomers. However, the stereoselectivity obtained at a particular conversion was found to be independent of hydrogen pressure and reaction temperature.

The stereoselectivity of thymol hydrogenation to menthol using nickel-containing catalysts is governed by the rate of the side process of *cis-trans* isomerization. It was shown[3] that the direction of the hydrogenation and the isomerization and the rates of these processes depend on the nature of the catalyst. The stereoselectivity decreases in the order Ni/Cr$_2$O$_3$ > Ni/kieselguhr > Raney Ni.

Based on kinetic data measured, using Ni/Cr$_2$O$_3$ catalyst in the temperature range 140 – 170 °C and hydrogen pressure 2-10 MPa, the reaction mechanism of menthol stereoisomers formation and their *cis-trans* isomerization was suggested in another study.[4]

The catalytic properties of Pt, Rh and Ir catalysts in the thymol hydrogenation have been compared[5,6] with respect to their activities and stereoselectivities in the formation of menthones and menthols. Using iridium catalyst (Ir/C), strong formation of hydrocarbons was observed. Palladium catalysts are also usually recommended[7,8] for stereoselective thymol hydrogenation in the liquid phase. The properties of ruthenium catalysts for stereoselective thymol hydrogenation were described in papers.[9,10] Neoisomenthol was the major product with SiO$_2$, MgO or Al$_2$O$_3$ supports, while isomenthol predominated over Ru black. Neomenthol and neoisomenthol were formed in almost equal

amounts over Ru/C and no hydrogenation occurred over Ru/TiO$_2$. Using rhodium on supports leads to the intermediate ketones, menthone and isomenthone and their transformation into the stereoisomers of menthol.[11] Stereoselective thymol hydrogenation over Rh/alumina in the presence of various equivalents of beta-cyclodextrin[12] indicated very interesting thymol complexation by beta-cyclodextrin phenomena. There are also several studies devoted to stereoselective hydrogenation of menthone and isomenthone using nickel catalysts.[13,14]

Trickle bed reactors have found extensive application in the organic and petrochemical industries. Information about their performance, design and operation, mostly under steady state, may be found in reviews and monographs, see e.g.[17–21]

In a trickle bed reactor the conversion of reactants, the yield, and the selectivity toward desired products depend not only on the reaction kinetics, operating pressure, and temperature, but also on the hydrodynamics of the packed bed. The flow of the gas and liquid through the voids between the catalyst particles is very complex and difficult to describe at a microscale. Generally, the hydrodynamics is described by means of global parameters. The most important parameter for characterising flow behaviour is the flow regime in the packed bed. Other parameters that characterise the hydrodynamic situation are the liquid hold-up, the pressure drop over the bed, the dispersion of gaseous and liquid phases, catalyst wetting, and the mass and heat transfer coefficients. These parameters depend on the gas and liquid throughputs, the type of packing, and the physical properties of the three phases.

Hydrodynamic behaviour of trickle bed reactor can be simulated e.g. by software developed at Laval University,[15] its characteristic at high pressure operation can be simply monitored by pressure drop measurement.[16]

Chemicals and catalyst

The following commercial chemicals were used in all experiments: thymol (98 % wt), hydrogen purity grade (99.99 %) and Nickel catalyst (28 % Ni/Al$_2$O$_3$). Typical physical properties of the catalyst are presented in Table 1. The powder catalyst with main particle diameter 10 μm used for kinetic study was supplied in activated form. An application of such fine catalyst particles eliminated internal mass transfer effects on reaction during kinetic tests. The catalyst for the trickle bed reactor (trilobe shape; 1.2 × 4.8 mm) was passive and its activation proceeded at atmospheric pressure under hydrogen flow and elevated temperatures (up to 250 °C). Hydrogen flow rate was kept constant

T a b l e 1 – *Physical properties of the Nickel catalyst*

Physical quantity	Value	Units
Bulk density	810-910	kg m^{-3}
BET surface area	100-120	m^2 g^{-1}
Pore volume	0.38-0.46	cm^3 g^{-1}
Side crush strength	$\geq$12	N mm^{-1}

(6 Nm^3 h^{-1}) during the activation process. The catalyst bed heating rate was maintained at 5 °C min^{-1}. This level is acceptable to ensure water removal from the catalyst particles without any effect on catalyst morphology.

Apparatus and procedure

Thymol hydrogenation was preliminary studied in laboratory scale (300 mL) Parr reactor. The kinetic data was collected in Parr reactor with total volume of 8 L, equipped with gas entrainment impeller at n = 1000 min^{-1}, isothermally at temperatures from 160 to 180 °C, and pressure 0.85–1.6 MPa, using 5 kg of thymol and 165 g of powdered nickel catalyst. Preliminary experiments have proven no effect of agitation speed above n = 700 rpm on the process performance. Sampling during the thymol hydrogenation was performed *via* standard sampling probe. The samples were analysed by GC using flame ionisation detector (FID) with injection port temperature 250 °C and 30 m x 0.25 mm D_{in}. Stabilwax-DA 0.25 μm film thickness. The analysis started at oven temperature 50 °C ramp up at 10 °C min^{-1} to 145 °C and hold for 4 min, ramp up at 30 °C min^{-1} to 240 °C and hold for 4 min. Total run time was 21.7 min. The method is suitable for analysis of thymol and menthol isomers but it did not discriminate between optical isomers.

Hydrogenation tests in trickle bed reactor were conducted adiabatically, using the bench scale unit schematically, shown in Figure 1. Reactor configuration, thermocouple positions and heating control system is presented in Figure 2. The reactor internal diameter D_{in} was 40 mm and the axial thermowell external diameter d_{et} was 12 mm. The mean catalyst particle diameter 1.2 mm was determined as diameter of sphere of the same volume. The modified reactor diameter (D) to catalyst pellet diameter (d_p) ratio D/d_p for the system was thus 12. This implies that the wall effects on the reactor hydrodynamics cannot be ignored. According to a rule of thumb, the wall effect is nearly negligible for a D/d_p ratio higher than 15.
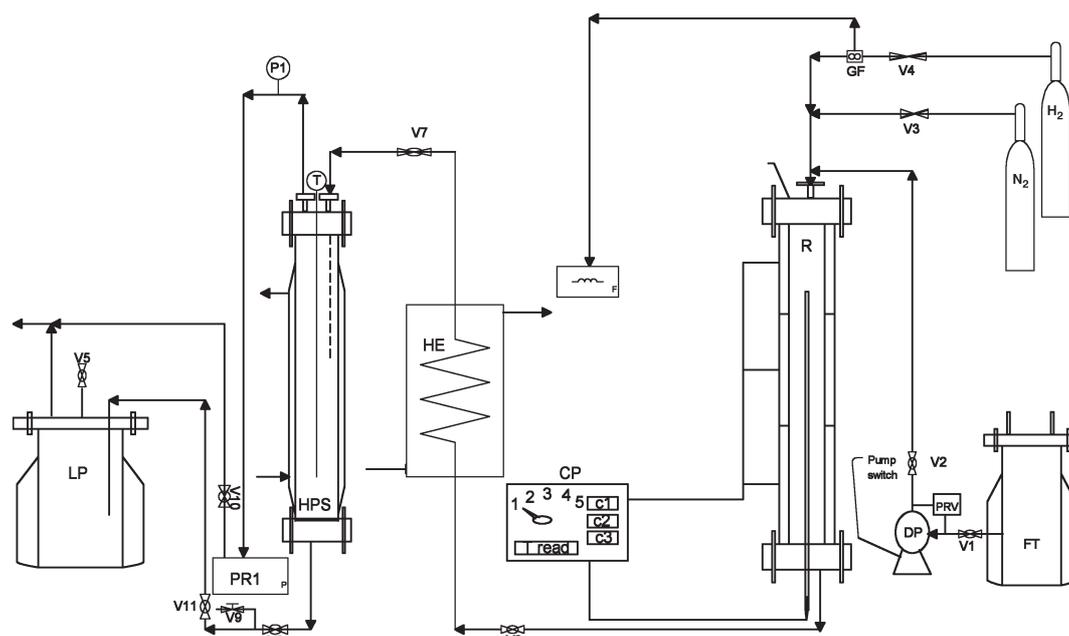
FT-feed tank, DP-dosing pump, PRV, – pressure relief valve, H$_2$,N$_2$-hydrogen, nitrogen cylinders, GF-gas flow meter, R-trickle bed reactor, HE-heat exchanger, CP-control panel, HPS-high pressure gas-liquid separator, PR1-pressure regulator, LP-liquid product

F i g . 1 – *Schema of trickle bed reactor system*
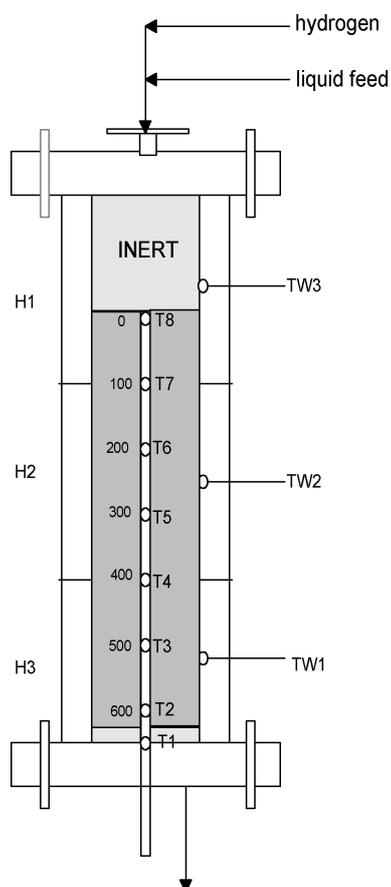
H1-3 – heating elements, TW1-3 – thermocouples on the reactor wall, T1-8 – thermocouples in the catalyst bed(positions in mm)

F i g . 2 – *Detail drawing of the bench scale trickle bed reactor*

Because gas and liquid reactants have to be preheated to enter the catalytic bed, a part of the reactor vessel volume (~30 %) is packed with inert material. Because of a heat loss from the system an inert material is usually used on the bottom of the reactor to avoid end effects on the system temperature profile. Glass beads with diameter 2 mm were used as an inert material for uniform reaction mixture distribution and preheating (300 mm) and to reduce the reactor end effect (50 mm) as it is presented in Figure 2. The nickel catalyst bed was 650 mm long. The deep catalyst bed was required to achieve full thymol conversion and sufficient residence time for menthol mixture equilibration. Since the catalyst was loaded from the reactor top, it was necessary to fill the reactor very slowly to avoid any non-uniformities (bridging because of size of the catalyst, non uniform bed voidage, empty spaces, etc.) in the catalyst bed structure. A mesh plate with 1 mm orifices for better gas and liquid distribution was used to cover the bed top.

The catalyst bed was pre-wetted with solvent (8 menthol mixture) before each hydrogenation experiment. The reactor was equipped with an electrical heating jacket and was operated under pseudo-isothermal conditions while reaching a steady state. After introduction of thymol/menthols mixture the reactor was operated as adiabatic (only pre-heater was heated). The low substrate mass fraction (13 % wt.) was chosen to enable temperature control of the bed during system commissioning. Both the

phases (liquid and hydrogen) were cooled and separated after passing through the reactor. Liquid samples drawn from the gas-liquid separator after steady state were collected and analyzed by GC.

Results and discussion

Kinetics of thymol hydrogenation using powdered nickel catalyst

Thymol as a reaction substrate is firstly transformed to several menthone isomers, which are hydrogenated to mixture of menthol, neomenthol, and isomenthol. The final ratio of the end products depends on selectivity of catalyst used. A typical example of reaction mixture composition *vs.* time is illustrated in Figure 3. The data were measured at 180 °C and 0.85 MPa. It is evident that desired product, menthol, represents the major component in the reaction mixture, its final mass fraction being nearly 60 % wt. (52 % of menthol was achieved after 6 h on Ni/Cr_2O_3 at 160 °C and 3.5 MPa[1]).
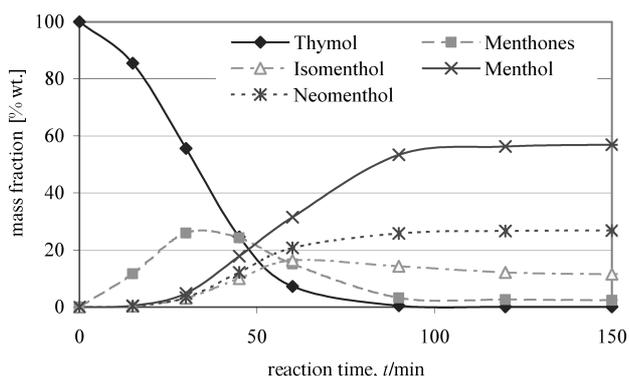
F i g . 3 – *Reaction mixture composition during thymol hydrogenation*

An example of time dependence of thymol concentration in the reaction mixture is given in Figure 4a. The experiment was performed at 160 °C and hydrogen partial pressure of 1.6 MPa. The linear decrease of thymol content in reaction mixture confirms the zero reaction order of hydrogenation with respect to the substrate. The mean reaction rate was determined from the slope of this linear function. Figure 4b represents the linear relationship between thymol hydrogenation rate and hydrogen partial pressure at 180 °C. The mean reaction rate was determined from the time dependence of thymol content in reaction mixture during the starting period of the reaction when its concentration as a mass ratio varied between 1.0 and 0.2. The first reaction order with respect to hydrogen is evident from these results. From experiments at different temperatures, the activation energy of thymol hydrogenation was estimated as 18.3 kJ mol^{−1}. Similar
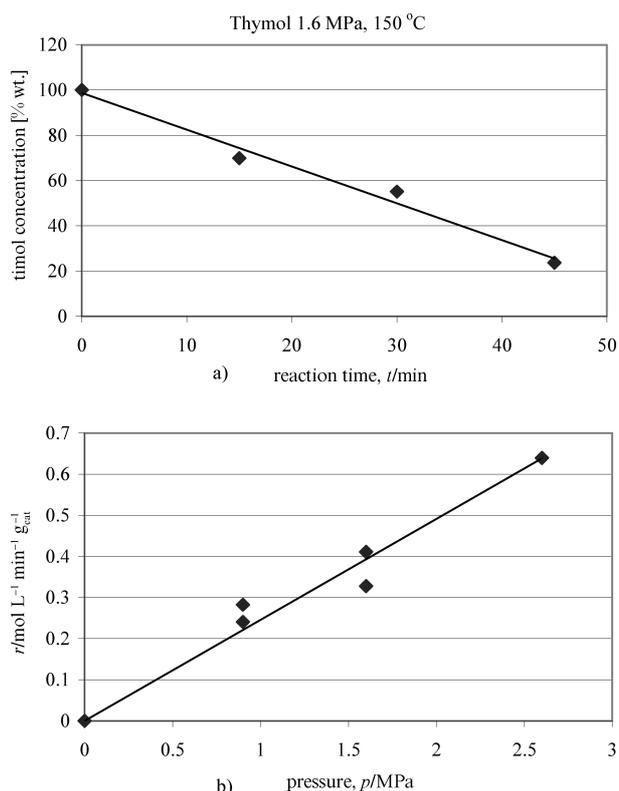
F i g . 4 – *a) Time dependence of thymol concentration; b) Effect of pressure on reaction rate*

activation energy was found for menthone hydrogenation[5] on platinum catalyst whilst thymol hydrogenation at the same catalyst was 63.5 kJ mol^{−1}.

Trickle bed reactor hydrogenation

Thymol hydrogenation is highly exothermic reaction and a distinctive exotherm was expected in the reactor during the process. A 13 % wt. of thymol-menthols mixture was therefore used as feed to the reactor for preliminary experiments. The axial temperature profile in the catalytic bed after introduction of the feed is presented in Figure 5.
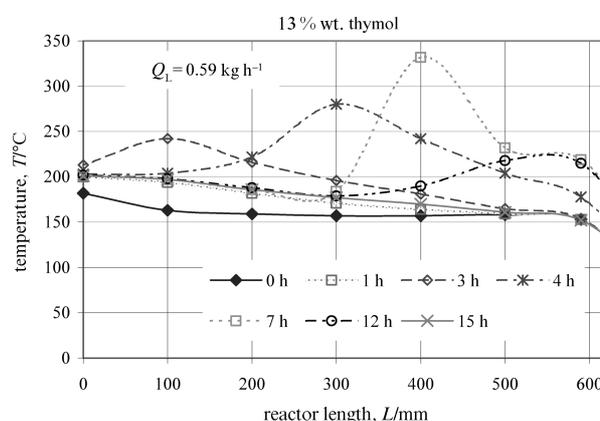
F i g . 5 – *Temperature profile in the reactor during initial stage of 13 % wt. thymol hydrogenation at different time on stream*

Experimental results indicate a moving 'hot zone' in the reactor with time on stream (TOS). This indicated that the heat of reaction is released at the reactor start up and at such a low liquid flow rate the catalytic bed is probably insufficiently wetted and so-called 'liquid channelling' (rivulets) appears in the bed, causing local temperature gradients. The distinctive exotherm after 7 h of introduction of thymol feed mixture disappeared after 13 h. The 'hot spot' moved along the bed and the highest temperature (almost 350 °C) was achieved at the distance of 400 mm from the top of catalyst bed. This maximum shifted towards the end of the reactor and the maximum temperature dropped to approximately 220 °C. Such a high temperature causes thermal decomposition and therefore undesired products (like alkylated phenol and cyclohexanol, methane) and water appeared at the reactor outlet. Steady state temperature profile was observed after 13 h. At a liquid flow rate of 0.59 kg h^{-1}, the maximum temperature was observed at the beginning of the bed and dropped along the reactor bed gradually. The temperature difference between hot spot and mean bed value was approximately 50 °C.

A flat axial temperature profile is optimal for a trickle bed reactor. The temperature profile in the reactor depends on the reactor-heating set-up, the heat of reaction, the feed concentration, and the gas and liquid flow rates. The key question is if the trickle bed reactor can be operated adiabatically (by heating only the pre-heating section). From a practical point of view (trickle bed reactor start up, process scale up and control), it is very important to know the process dynamics and its parametric sensitivity.

A trickle bed reactor was started using a menthol mixture to reach a steady state temperature profile without chemical reaction. The system dynamics was evaluated on the basis of temperature profile after the introduction of 13 % wt. of thymol feed into the reactor. The temperature in the catalyst bed was controlled by regulating the pre-heater temperature (TW3) only. Experimental temperature profiles in the upper part of catalyst bed are presented in Figure 6. A steady state temperature profile in the bench scale trickle bed reactor at thymol concentration of 13 % wt. and liquid flow rate 1.3 kg h^{-1} can be achieved in 3 h from a change of feed into the reactor. This was confirmed in several experiments.

The effect of liquid flow rate on temperature profile was experimentally investigated. Typical steady state temperature profiles in the catalytic bed, for different liquid flow rates and different pre-heating zone temperatures, are presented in Figure 7. The reactor temperature was controlled to main-
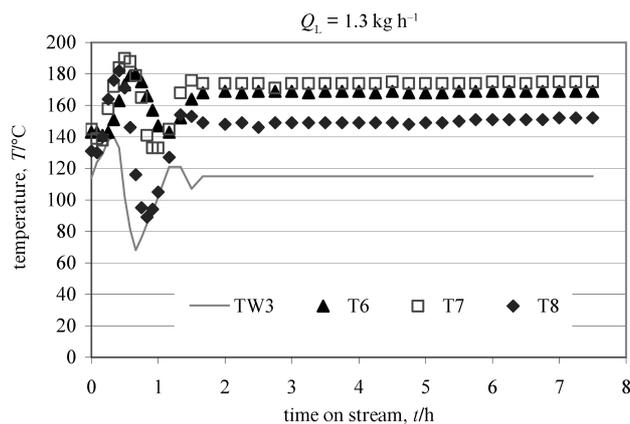
F i g . 6 – *Temperature profile development during reactor start, 13 % wt. thymol*
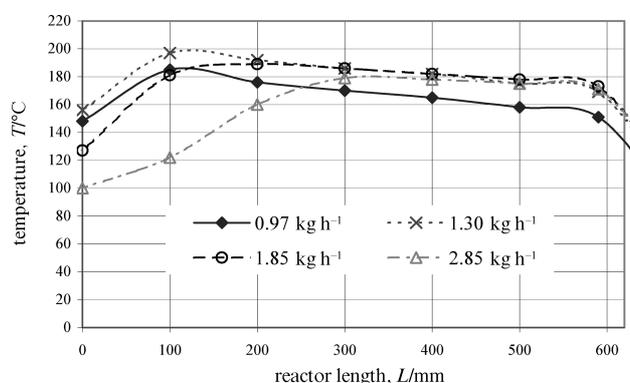
F i g . 7 – *Effect of liquid flow rate on temperature profile in the catalyst bed at 20 % wt. of thymol in the feed*

tain the maximum temperature in the bed below 200 °C. The results indicated that the reactor can be operated under adiabatic conditions and that the temperature profile can be controlled by means of only the pre-heater. However, at high liquid flow rates (2.85 kg h^{-1}, LHSV~3.7 h^{-1}) the pre-heater temperature needs to be very low (low catalyst activity at temperatures below 100 °C) and temperature profile is very non-uniform, potentially having a significant negative effect on the performance of the reactor.

The fraction of thymol in the feed has a small effect on the axial temperature profile in trickle bed reactor at thymol massfraction below 25 % wt. (see Figure 8). The adiabatic temperature rise at these concentrations is less than 50 °C. To maintain maximum temperature in the bed below 200 °C at thymol fraction above 25 % wt. requires a significant decrease in the inlet temperature (pre-heater temperature TW3). The temperature rise at 100 mm from the top of the catalyst bed at 27 % wt. of thymol is more than 60 °C. The observed temperature rise at 100 mm from the top of the of catalyst bed at 35 % wt. of thymol is low because of low catalyst activity at temperatures below 100 °C.
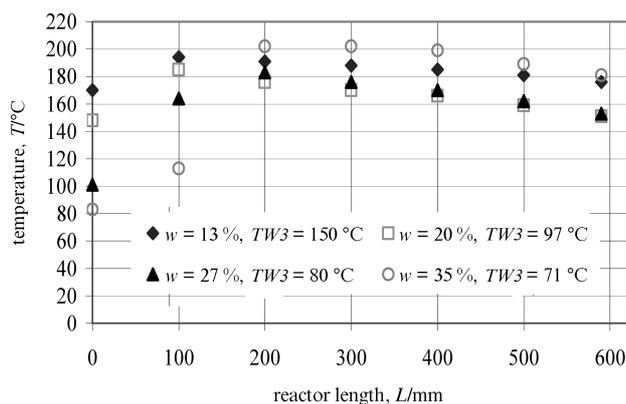
F i g . 8 – *Steady state temperature profile in the bed at different thymol mass fraction and feed rate 1.3 kg h⁻¹*

F i g . 9 – *D/L Menthol content in reaction product and mean temperature vs time on stream (TOS) at ~1.3 kg h⁻¹ and thymol mass fraction 13 and 20 % wt.*

However, the temperature rise at the next 100 mm is more than 85 °C and the maximum temperature is slightly above 200 °C, which is too high in terms of process selectivity. The utilisation of catalyst at such a high concentration is also low and the part of catalyst bed dedicated to hydrogenation (the first part of the reaction sequence) is longer, therefore the part of the catalyst used for equilibration of racemic mixture is shorter, which negatively affects selectivity of the process.

The most important process characteristics are complete thymol conversion and D/L menthol content in product above 55 % wt. Complete conversion of thymol and the chemical equilibrium of the outlet stream was achieved at experimental conditions used in the study. Thus, it is also evident that the reaction order with respect to thymol is close to zero.

Thymol hydrogenation is exothermic and a temperature profile in the catalyst bed was observed. A mean temperature was therefore used to express dependence of product composition on temperature in the process, since to use single temperature is irrelevant. The mean catalyst temperature was defined as the mean integral value calculated along the catalyst bed. Temperature dependence of D/L menthols content in reaction product is depicted in Figure 9.

Apparently, D/L menthol mass fraction depends mainly on the mean temperature in the bed (provided that complete conversion of thymol is achieved) and pressure (1.5 MPa versus 0.9 MPa), which indicate that the product stream composition is controlled by reaction thermodynamics and not kinetics.

Catalyst activity and deactivation

Thymol hydrogenation was performed in several cycles to investigate an effect of the recycle of the menthol mixture on the process performance. The catalyst was kept under hydrogen at ambient temperature during the idle period. It was found, that this preserved the catalyst with no degradation of performance being observed. The catalyst activity was tested periodically at standard process conditions (liquid flow rate Q_L = 1 kg h⁻¹, 20 % wt. thymol fraction at 1.5 MPa) and the same temperature profile was observed after more than 500 hours time on stream. It was however found that the reactor overheating (above 350 °C) had a detrimental effect on catalyst performance. Catalyst overheating can be caused by the exotherm from the side reaction (decomposition of menthol), low liquid flow rates or failure of the feed introduction into the system, too high temperature in preheating zone, too high thymol concentration in the feed at adiabatic conditions or low hydrogen partial pressure.
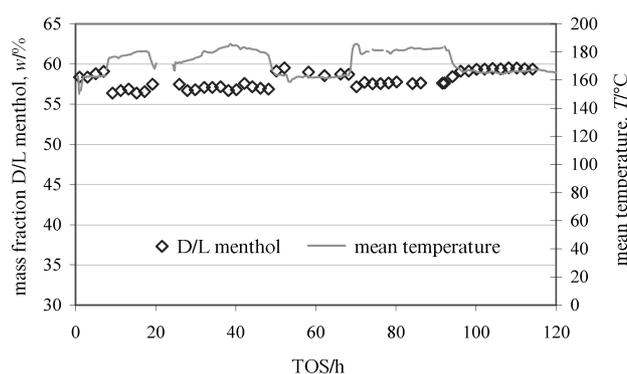
The catalyst bed temperature exceeded 200 °C during several of the experiments conducted without any effect on the catalyst activity. The 'hot spot' was situated mostly at a position 100 mm from the top of the catalyst bed and its position was influenced by the liquid flow rate, the feed concentration, and to a lesser extent by gas flow rate. The trickle bed reactor worked at almost adiabatic conditions and the temperature profile was determined and/or controlled by preheating zone temperature TW3.

During hydrogenation at standard conditions (20 % wt. thymol feed) due to the failure of control system, the temperature TW3 increased above the required value (> 200 °C). Temperature runaway was observed as a consequence of overheating of the preheating section. The temperature runaway occurred on the first 100 mm of the catalyst bed. Both, the liquid feed and hydrogen were stopped, and hydrogen was replaced by nitrogen. The maximum temperature in the zone was 420 °C for approximately 5 min. The system was cooled down to

temperatures well below 200 °C, nitrogen was replaced by hydrogen, and the feed pump (20 % wt. thymol feed) was restarted. The process was stabilised and the reactor bed temperature profile was measured (Figure 10). Comparison of experimental temperature profiles indicated lower catalytic activity in the first 100 mm of catalyst. Overall temperature rise was similar to previously observed values, however the 'hot spot' shifted along the reactor axis. This indicated that thymol hydrogenation was completed in the first 200 mm of catalyst bed. This shift of the 'hot spot' indicates that the original activity of the catalyst at the beginning of the bed was decreased by approximately 20 %.

achieved). This fact indicates that the process is controlled by reaction thermodynamics and no by its kinetics.

Both, the process dynamics and parametric sensitivity are important system characteristics and they are critical for the system operation and scale-up. Experimental investigation of the system dynamics indicated, that a steady state could be reached after approximately 3 h from a change in process parameters. Stability tests of the catalyst activity have shown, that practically the same temperature profiles were observed after more than 500 hours of operation. Activity of the catalyst was stable except for the catalyst overheating.

F i g . 1 0 – *Temperature profile for 20 % wt. thymol feed before and after temperature runaway*

Conclusion

Experimental hydrogenation of thymol was performed in bench scale slurry and trickle bed reactors.

Investigation of thymol hydrogenation on powdered catalyst in slurry system, with a gas entrainment impeller, has shown that the reaction is zero order with respect to thymol and the first order with respect to hydrogen. Based on experimental data the activation energy was estimated as 18.3 kJ mol^{-1}.

Experiments in a trickle bed reactor at low liquid flow rate indicated existence of insufficiently wetted catalytic bed and so called 'liquid channelling'. The results obtained in a bench scale trickle bed reactor indicated that the process is sensitive to feed temperature, liquid/gas flow rates, and liquid distribution in catalyst bed. Therefore, the process must be started carefully to avoid the occurrence of hot zones in the reactor. Experimental results and practical experience also showed the reactor system could be operated as an adiabatic system.

It was found, that D/L menthol mass fraction depends mainly on the average temperature in the bed and it does not depend on the residence time (provided that complete conversion of thymol was

List of symbols

d_p – particle diameter, mm

D_{in} – inside reactor diameter, mm

L – reactor length, mm

$LHSV$ – liquid hour space velocity, h^{-1}

n – stirrer speed, min^{-1}

p – pressure, MPa

Q_L – mass flow rate, kg h^{-1}

t – time, h

T – temperature, °C

w – mass concentration, %

V – volume, L

References

1. *Allakhverdiev, A. I., Kulkova, N. V., Murzin, D. Y.,* Catal. Letters **29** (1994) 57.

2. *Allakhverdiev, A. I., Kulkova, N. V., Murzin, D.Y.,* Ind. Eng. Chem. Res. **34** (1995) 1539 and **35** (1996) 989.

3. *Konuspaev, S. R., Zhanbekov, K. N., Bizhanov, Z. A., Imankulov, T. S., Nurbaeva, R. K.,* Kinet. Catal. **35** (1994) 824.

4. *Konuspaev, S. R.,* Izv. Nats. Akad. Nauk Resp. Kaz. Ser. Khim. **5** (1994) 32.

5. *Besson, M., Bullivant, L., Nicolaus-de Champ, N., Gallezot, P.,* Stud. Surf. Sci. Catal. **78** (1993) 115.

6. *Besson, M., Bullivant, L., Nicolaus-de Champ, N., Gallezot, P.,* J. Catal. **140** (1993) 30.

7. *Allakhverdiev, A. I., Kulkova, N. V., Murzin, D. Y.,* Kinet. Catal. **34** (1993) 934.

8. *Tungler, A., Mathe, T., Petro, J., Tarnai, T.,* Appl. Catal. **79** (1991) 161.

9. *Konuspaev, S. R.,* Izv. Nats. Akad. Nauk Resp. Kaz., Ser. Khim. **6** (1994) 36.

10. *Bizhanov, Zh. A.,* Izv. Minist. Nauki-Akad. Nauk Resp. Kaz. **4** (1998) 53.

11. *Konuspaev, S. R.,* Izv. Nats. Akad. Nauk Resp. Kaz. **5** (1994) 37.

12. *Ravi, P., Divakar, S.,* J. Incl. Phenom. and Macrocyclic Chem. **39** (2001) 27.

13. *Kukula, P., Cerveny, L.,* Appl. Catal. – General A, **193** (2000) 285.

14. *Kukula, P., Cerveny, L.,* Res. Chem. Intermediat. **26** (2000) 913.

15. *Larachi, F., Grandjean, B., Iliuta, I., Bensetiti, Z., André, A., Wild, G., Chen, M.,* Trickle bed simulator, Universite Laval Quebec, 1999.

16. *Larachi, F., Laurent, A., Midoux, N., Wild, G.,* Chem. Eng. Sci., **46** (1991) 1233.

17. *Satterfield, C. N.,* AIChE J. **21** (1975) 209.

18. *Shah, Y. T.,* Gas-Liquid-Solid Reactor Design, McGraw-Hill, New York (1979).

19. *Gianetto, A., P. L. Silveston,* Multiphase Chemical Reactors – Theory, Design and Scale Up, Hemisphere Publishing Co., Washington, DC, 1986.

20. *Hanika, J., V. Stanek,* Design and Operation of Trickle-bed Reactors, in Handbook of Heat and Mass Transfer, Vol. 2, Gulf Publ. Co., Houston, Texas, 1986, pp. 1029-1080.

21. *Kirillov, V. A.,* Gas-Liquid-Solid Catalytic Reactors, Rusian Academic Science Publishers, Novosibirsk, 1997 (in Russian).