

Design, Scale up and Safe Piloting of Thymol Hydrogenation and Menthol Racemisation

Jozef Dudas¹, Jiří Hanika²

BioSciences CSIR, Private Bag X2, Modderfontein 1645, Republic of South Africa,

Fax: + 27 11 6083200, Tel: +27 11 6052382, E-mail: jdudas@csir.co.za,

² *Institute of Chemical Process Fundamentals CAS, 16502 Prague 6, Czech Republic,*

Fax: +420 220 920 661, Tel: +420 220 390 286, E-mail: hanika@icpf.cas.cz

Abstract

The hydrogenation of thymol and the racemisation of a menthol mixture were investigated as part of the development of novel process for the production of *l*-menthol. The key innovation in this *l*-menthol process is the enzymatic resolution of *l*-menthol from 8 menthol isomers mixture. 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 menthol mixture were obtained in pilot plant trickle bed reactor.

¹Corresponding author. Tel: +27 11 605 2382, Fax: +27 11 608 3200
E-mal address: jdudas@csir.co.za

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 hours in a bench scale reactor and subsequently scaled-up to a pilot scale trickle-bed reactor. The pilot scale experiments were used to verify scale-up and generate material for 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 equipment, operation and power failure.

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

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 (Figure 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.

Figure 1

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. The process is known and described in open literature for example¹⁻⁹.

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 hours at temperatures above 150°C and pressures above 0.9MPa.

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 – 1.6MPa using 5kg of thymol and 165 g of powdered (10 micrometers) 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/mol¹⁰.

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 process¹¹.

Trickle-bed reactor system

A trickle-bed reactor system for hydrogenation and racemisation was developed and scaled up using extensive literature information¹²⁻²⁷, personal experience and experimental data¹⁰.

The reactor (Figure 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 independent reactor wall temperature control. The reactor was equipped with thermowell with 8 thermocouples positioned in the reactor axis to allow the measurement of the temperature profile in the catalyst bed. The gas-liquid outlet mixture was cooled in a coil heat exchanger and the gas was separated from liquid phase in a high-pressure gas-liquid separator and vented. The process conditions are presented in Table 2.

Figure 2

Table 1

Table 2

Thymol hydrogenation

The hydrogenation of thymol to a racemic menthol mixture requires complete thymol conversion and *d/l*-menthol content in the product mixture of more than 55% wt. Thymol hydrogenation is performed at elevated pressures (1.5MPa) and temperatures of 150 to 200°C. Thymol/racemic menthol mixture was used as a feed into the trickle bed reactor.

The process in an adiabatic trickle-bed reactor is affected mainly by gas/liquid flow rate, inlet thymol concentration in feed and pre-heater temperature. The axial temperature profile in adiabatic trickle bed reactor is determined by catalyst activity, thymol conversion (exothermic process) and also product distribution. The temperature profile was affected mostly by inlet temperature, liquid flow rate and thymol concentration. In terms of catalyst activity a uniform axial temperature profile is ideal for the process. The effect of the liquid flow rate on the axial temperature profile in the bench scale trickle-bed reactor is presented in Figure 3. Temperature profiles indicated that the bench scale trickle-bed reactor could be effectively operated at liquid flow rates up to 1.8 kg/h (Liquid Hour Space Velocity (LHSV) ~ 2.4 kg/(kg.h)). Reactor temperatures at flow rates above 2.5 kg/h are too low, leading to low catalyst activity in the upper section of the reactor. The effect of thymol concentration on the temperature profile was similar. The inlet temperature to catalyst bed at thymol concentrations above 25% wt. was maintained below 100°C to maintain hot spot temperature below 200°C¹⁰. Experimental investigation of the effect of thymol concentration has proven that

reasonable temperature profiles were achieved at thymol concentrations in racemic menthol up to 20% wt.

Figure 3

Based on both experimental results from bench scale reactor and calculation of hydrodynamic characteristics¹² the pilot plant reactor was designed in-house and constructed (Figure 2). The estimated safe thymol concentration in the feed was 10% wt. Piloting started with 10% wt. of thymol in the feed and relatively low inlet temperature (120°C). The feed concentration was increased to 13% wt. of thymol and no significant difference in axial temperature profiles was observed at steady state conditions.

Bench scale experimental results indicated that *d/l*-menthol content in product is strongly affected by temperature in the lower section of catalyst bed¹⁰. This was confirmed in the pilot scale reactor (Figure 4). Since the reactor is operated as adiabatic, different temperature profiles were obtained at different thymol concentrations at the same inlet temperature and flow rates. Trends in temperatures in the bottom section of catalyst bed (T1 (1800 mm) and T2 (1450 mm)) and *d/l*-menthol concentration in the product clearly demonstrated that the lower the temperature in the bottom section of the reactor the higher the *d/l*-menthol concentration. One can conclude, that the commercial reactor should be divided into two sections for better temperature control: the first one for exothermic hydrogenation mainly should operate as adiabatic in temperature interval from 160 to 180°C; and the second one with thermostating jacket for menthols isomerisation should operate at approximately 150°C.

Figure 4

The axial temperature profiles vs. dimensionless catalyst bed length observed in the bench and pilot scale reactor are presented in Figure 5. The comparison of experimental results of thymol hydrogenation in the pilot scale reactor indicated that the process could be safely scaled up.

Figure 5

Menthol racemisation

L-Menthol (EE=96%) was used for the racemisation study in a 300 mL slurry reactor at 200°C and 0.6 MPa. It was found that after 3 hours *l*-menthol was racemised to ~50:50 of *l*-menthol to *d*-menthol mixture over the same nickel catalyst (1% wt.) used in the hydrogenation of thymol. The process was reproducible and less than 1% wt. of menthone was formed.

The synthetic mixture of liquid menthol prepared by thymol hydrogenation enriched with 10% wt. *l*-menthol was racemised in a trickle-bed reactor. Preliminary experiments in the slurry system showed that a high temperature and low pressure is required to achieve optimum racemic mixture composition (*l*-menthol to *d*-menthol ratio ideally equal to 1).

The results of racemisation obtained in the bench scale trickle-bed reactor using the synthetic liquid menthol mixture indicated that the process was feasible. The 8 menthol isomers mixture (from thymol hydrogenation) enriched by *l*-menthol to 73.6 % wt. of *d/l*-menthol was successfully racemised. The content of *d/l* –menthols in the post – racemisation mixture reached the steady state

after ~2 hours and was constant and above 55 % wt., at pressures below 0.5MPa and an average temperature of ~160°C and liquid flow rate 1 kg/h, for the rest of the test (Figure 6).

Figure 6

The effect of total pressure on *d/l* -menthol ratio during racemisation in the bench scale trickle-bed reactor (liquid flow rate 1 kg/h and average temperature 160°C) is presented in Figure 7. These results show that at an average reactor temperature ~160°C lower pressure had a positive effect on racemisation. Data also indicated that the *d/l*-menthol ratio in the feed could be changed, in this case from 43.2: 56.8 to 47.9:52.1 at total pressure 0.5 MPa or to 48.2:51.8 at total pressure 0.35 MPa. This indicated that the equilibrium composition depended on the total pressure. The lower the total pressure the better the *d/l* -menthol ratio. However, at low pressure the process was more sensitive to temperature, particularly in the bench scale trickle-bed reactor where liquid maldistribution, the local ratio of catalyst to reactant was high and also internal diffusion effect on process selectivity could play a significant role.

Figure 7

The racemisation process was scaled up to a pilot scale reactor. The distillate from menthylacetate distillation (Figure 1) - the “real” feed was used in the pilot scale racemisation. The feed contained 53.2 % wt. of *d/l* menthol and *l*-menthol to *d*-menthol ratio was less than 1 due to depletion of *l*-menthol in resolution step. The main feed and product stream characteristics are presented in Table 3. Experimental data indicated that the product composition remained constant with time on stream and that the required ratio of *l*-menthol and *d*- menthol (cca 1) can be achieved. The data also

indicated that a significant proportion of menthones and side products were formed during the process as a result of partial dehydrogenation of menthol and skeletal re-arrangement of the molecules. The level of menthones and side products is determined mainly by pressure - the lower the pressure the higher the content of side products. Since the side products did not convert to menthol during hydrogenation they represent a loss of menthols in the racemisation step. This fact was also proven experimentally during racemisation of menthol in presence of heptane as solvent (~30% wt.). Vapour pressure of heptane at the same total pressure decreased the hydrogen partial pressure at the temperature used and more side products were found in the product stream (up to 8% wt.).

Table 3

Experimental results have proven that the racemisation in a trickle-bed reactor is feasible, however more sensitive to experimental conditions than in a slurry system where the ratio reactant/catalyst is significantly higher and possible effect of internal diffusion is limited due to small catalyst particle size.

Peculiarity-of the trickle-bed system and its safe operation

Safe operation of trickle-bed reactors generally depends on various parameters like system thermodynamics (heat capacity, heat of reaction), reaction rate and order, hydrodynamic conditions (catalyst wetting, superficial velocity), control of inlet parameters (liquid/gas flow rate and feed concentration), mass and heat transfer, etc., see e.g. ^{17, 23-27}. The optimization of the reactor control parameters brings the possibilities to improve both the throughput and the safety of the reactor

performance mainly for exothermic reactions. Parametric sensitivity is different for hydrogenation (exothermic reaction) and racemisation (isothermal reaction) in a trickle-bed reactor. The effect of several parameters was investigated with regard to safe operation of the reactor.

Thymol Hydrogenation

The preliminary mass balance of the entire *l* – menthol process has shown that thymol hydrogenation will proceed with thymol-menthols mixture containing up to approximately 27% wt. of thymol. Thymol hydrogenation, as mentioned above, is highly exothermic and a distinctive exotherm was expected in the reactor during the process. The reactor productivity and hot spot on temperature profile depend on liquid flow rate, thymol concentration and process control.

Liquid flow rate

A low liquid flow rate (0.59kg/h) was employed during commissioning of the bench scale system. The development of temperature profile in the catalyst bed during the start-up using 13 % wt. thymol feed is presented in Figure 8. Experimental results indicated a moving ‘hot zone’ in the reactor during the first 15 hours. This may be an indication that at low liquid flow rate, the catalyst bed is probably insufficiently wetted and liquid maldistribution and/or ‘liquid channelling’ (rivulets) appears in the bed. A distinctive exotherm observed after 7 hours disappeared after 12 hours. Maximum temperature (almost 350°C) was found at a position 400 mm from top of catalyst bed. Later, the maximum shifted towards the reactor bottom and the maximum temperature dropped down to approximately 220°C. Temperatures above 200°C resulted in partial decomposition of

menthols and side products (including water) appeared in the reactor outlet. After 13 hrs a steady state temperature profile was reached. The maximum temperature at liquid flow rate 0.59 kg/h was observed at the top of the bed and gradually dropped along the reactor bed. **One can conclude that the trickle bed reactor for thymol hydrogenation should not be operated at LHSV below 1.**

Figure 8

Thymol concentration

Investigation of the effect of thymol concentration on axial temperature profile inside bench scale trickle bed reactor has shown that a steady state temperature profile can be achieved at thymol concentration up to 35 % wt. The feed inlet temperature at 35 % wt. was low (less than 100°C to maintain the hot spot temperature below 200°C) resulting in low reaction rate in the upper part of the catalyst bed but the temperature profile was stable. However, at higher thymol concentrations (40% wt.) temperature oscillations were observed (Figure 9) and maximum temperature exceeded 220°C. The potential for side reactions increases dramatically at temperatures above 200°C. Increased extend of side reactions results in greater loss of menthol and the exothermic nature of the side reactions also requires more complex safety measures.

Figure 9

Operation and equipment failure

During bench scale hydrogenation at standard conditions (20% wt. thymol and ~1 kg/h of feed, pressure 1.5MPa), due to an operational error, the temperature in the top section of the reactor increased above the required value ($>200^{\circ}\text{C}$). A temperature runaway was observed as a consequence of overheating of the preheating section. The temperature runaway occurred at the top of catalyst bed (the first 100mm). Both the liquid feed and hydrogen were stopped and hydrogen was replaced by nitrogen. These measures limited the temperature runaway to the first portion of the catalyst bed. The maximum temperature in that zone reached 420°C for approximately 5 minutes. The system was cooled down to temperatures well below 200°C , nitrogen was replaced by hydrogen and the feed pump was restarted. The process was stabilised and the reactor bed temperature profile was measured and compared with the original one obtained at the same experimental conditions. Comparison of experimental temperature profiles indicated that the catalytic activity of the catalyst had dropped in the first 100mm of catalyst bed during the temperature runaway by approximately 20%¹⁰.

Menthol Racemisation

The racemisation of menthol mixture is a reaction without any net thermal effects and it could easily proceed at isothermal conditions ($\sim 160^{\circ}\text{C}$) and low hydrogen pressure. However, the probability of exothermic side reactions increases with higher temperature and lower hydrogen pressure.

During the racemisation piloting the power failed, causing reactor heating and the feed pump to stop. Due to the high heat capacity of inert solid material in the pre-heater and catalyst and without liquid flow to remove heat, the reactor content (liquid holdup) overheated and the temperature of

the liquid in the reactor increased. The liquid in contact with the catalyst (in catalyst pores and bed voidage) at relatively low pressure of hydrogen (0.3MPa) was locally overheated (above 200°C) and exothermic decomposition of the menthol could start. Partial formation of low boiling components like methane, ethane, etc. and water (products of methanation) increased total pressure in the reactor and the hydrogen flow stopped. Increased local temperature resulted in a further increase of menthol partial pressure and menthol decomposition was extended. The menthol mixture held in the catalytic bed (pores of the catalyst were full of the liquid menthol in intimate contact with the catalyst surface) was gradually involved in the side reactions and a moving hot spot was observed. The maximum observed temperature was above 450°C and it lasted only for approximately 5 minutes. As soon as the hot spot in the first portion of the catalyst occurred, nitrogen was introduced in the reactor and it took approximately 40 minutes to cool down the catalyst in the reactor below 200°C.

Subsequent thymol hydrogenation test at standard hydrogenation conditions indicated significant deactivation of the catalyst had occurred (Figure 10). The maximum on temperature profile was observed in the lower part of the catalyst bed what has indicated significant catalyst deactivation in the upper section of the reactor. The activity of the catalyst was not recovered after repeated regeneration under hydrogen flow, indicating that the deactivation was irreversible and the physical properties of the catalyst were changed due to the high temperature shock.

Figure 10

Analysis of the temperature runaway indicated that although the racemisation itself was not hazardous, possible highly exothermic side reactions could lead to potentially dangerous situation

particularly at the low hydrogen pressure used in the system. Since equipment failure is possible it is necessary to avoid conditions in the system when hazardous situations could occur. In the case of racemisation it means that the temperatures in any section of the system should not exceed 190°C and the total pressures should be maintained above 0.3MPa in the system. This information is critical for process control.

Conclusion

The experimental investigation of thymol hydrogenation using a bench scale trickle-bed reactor showed that complete thymol conversion and required menthols isomerisation (55 % wt. *d/l* - menthol) could be achieved at the following conditions: thymol concentration below 15 % wt. in the feed, temperature interval from 150 to 190°C, total pressure of 1.5MPa and liquid flow rate of up to 1.5 kg/h (Liquid Hour Space Velocity (LHSV)~ 2 kg/(kg.h)). Experimentally it was also proven that the hydrogen flow rate (10 – 30 g/h in bench scale reactor) had a minor effect on the process performance and that the process was controlled by the reaction thermodynamics. Low levels of reaction side products (methane 800 - 1100 ppm, ethane 4 – 11 ppm, propane 9 –11 ppm) in the outlet gas indicated a limited extent of side reactions at the experimental conditions. The results of thymol hydrogenation piloting have proven that pilot scale trickle bed reactor can operate as adiabatic. However, a commercial reactor consisting of two separate sections with heat removal for better temperature control is recommended.

Safe and successful hydrogenation (required conversion and selectivity) is affected by the following process parameters: Too low liquid flow rate caused liquid channelling (insufficient utilisation of catalyst); too high liquid flow rate results in a non-uniform temperature profile with low reaction

conversion at low temperatures. Thymol feed concentration is limited by maximum safe hot spot temperature (undesirable temperature oscillation occurred at concentrations above 35% wt.).

Results of the racemisation in a trickle-bed reactor showed that the process was feasible using the same nickel catalyst as that used for thymol hydrogenation. However, experimental conditions differed from those used in a slurry reactor. Recommended average temperature at 1 hour residence time is 160°C. The maximum temperature should not exceed 190°C (in any section of the system) and the minimum total pressure in the system should be above 0.3MPa. The racemisation is a thermodynamically neutral reaction (no net thermal effect). However, side reactions (decomposition) are highly exothermic and initiated at temperatures above 200°C. This fact must be taken into account in the process scale up.

The trickle-bed reactor is more sensitive to process parameters than the slurry reactor because of a different reactant/catalyst ratio. The system is more sensitive at lower pressures and higher temperatures, conditions favourable for the side reactions, especially to methanization reaction. Hot spots and even temperature runaway can occur due to fluctuation of inlet parameters and/or failure of equipment (dosing pump or control system). Increased temperature results in not only a loss of product but it can irreversibly deactivate the catalyst.

From the authors' point of view, both the thymol hydrogenation and menthol racemisation represent feasible technology steps for industrial application. The scale-up of trickle bed reactor has been confirmed in bench and pilot scales. The important finding of the study is that undesirable hot spot formation in the catalyst bed during hydrogenation and/or racemisation accompanied by serious temperature excursions and followed by partial catalyst deactivation requires strict definition of

operating conditions. A good strategy for the loss prevention and/or of hot zone formation in the catalyst bed consists both in the stability of inlet conditions (inlet stream temperature, higher operation pressure) and in control of the adiabatic temperature rise by thymol concentration. Moreover, minimisation of liquid maldistribution in catalyst bed and improving its wetting efficiency by e.g. dense catalyst packing or by liquid feed rate optimisation and/or periodic modulation^{13,25-27} are important challenges for safe operation improvement and better process control.

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Figure 2 Pilot scale trickle bed reactor and sketch of the system

Ti-temperature in reactor axis, TWi – wall temperature

R – reactor, FC – frequency controller, HE – heat exchanger, PRV1,2 – pressure relief valves,

PR1 – pressure regulator

Figure 3 Effect of liquid flow rate on axial temperature profile in bench scale trickle bed reactor (13% wt. of thymol, P= 1.5MPa, inlet temperature from 100 to 155°C)

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Tables:

Table 1 Parameters of trickle bed reactors

	Bench scale	Pilot scale
Internal diameter [mm]	40	108
Maximum design pressure [MPa]	3.5	3.5
Maximum design temperature [°C]	450	450
Maximum flow rate [kg/h]	5	35
Preheating section length [mm]	300	750
Catalyst bed length [mm]	620	1800
Bottom section [mm]	50	200
Axial thermocouples positions	7	8

Table 2 Process conditions in bench and pilot scale trickle bed reactors

	Bench scale	Pilot scale
Liquid flow rate [kg/h]	1-4	10 – 28
Liquid linear velocity [mm/s]	0.3-1	0.35-0.62
Gas flow rate [g/h]	10 – 30	80-250
Gas linear velocity [mm/s]	2.5	2.5
Temperature [°C]	100-200	100-200
Pressure [MPa]	0.3 – 1.5	0.3 – 1.5
Ni Catalyst (trilobe, 1.2x4.8mm) [kg]	0.78	13.7

Table 3 Typical feed and products characteristics for racemisation in pilot scale trickle bed reactor at 0.5 MPa, temperature 160°C and liquid flow rate 13 kg/h

	Feed	Product
Menthol (% wt.)	53.20	43.0
<i>l</i> menthol/ <i>d</i> -menthol ratio	0.71	0.97
Menthone (% wt.)	0.43	9.27
Iso-menthone (% wt.)	0.20	5.28
Side products (% wt.)	0.4	4.97
Thymol (% wt.)	0.00	0.48

Figures

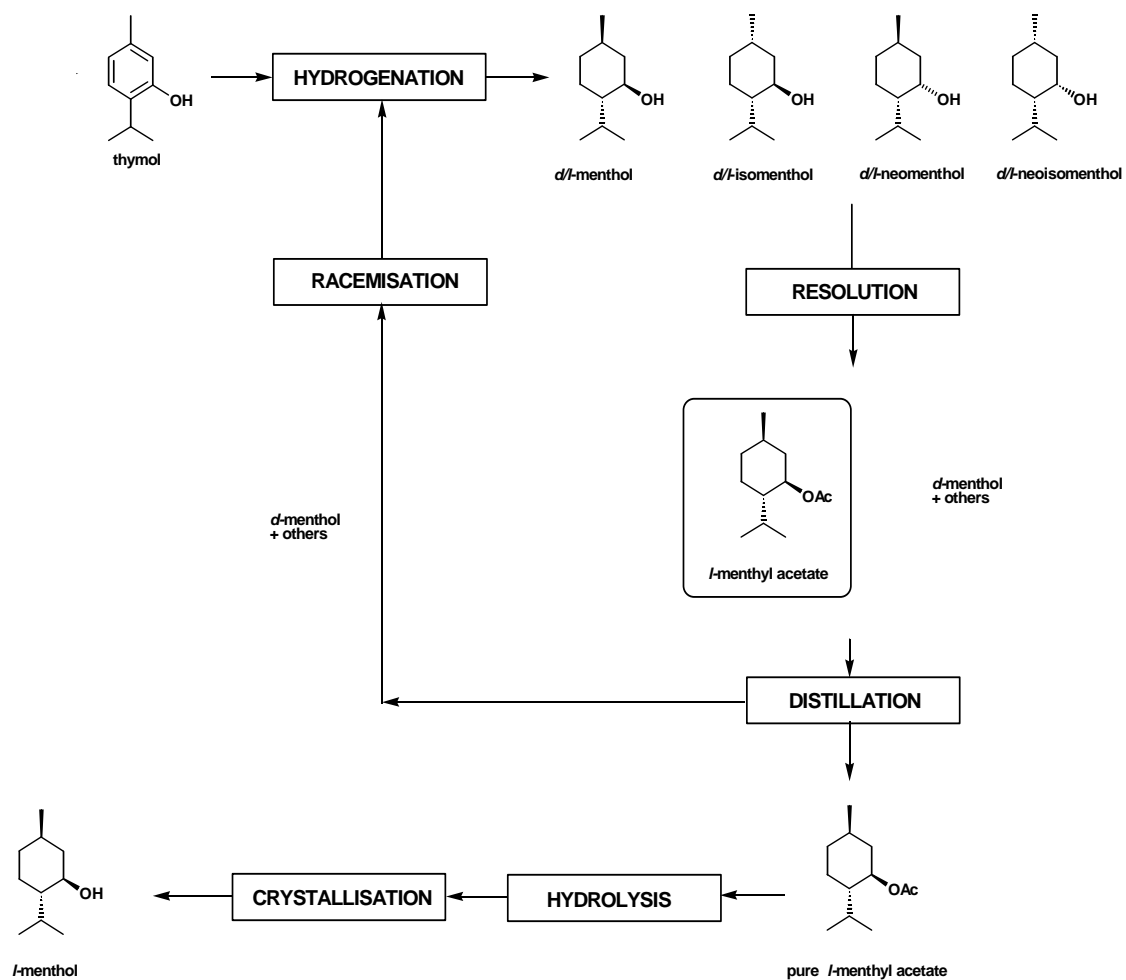


Figure 1 Scheme of *l*-menthol preparation

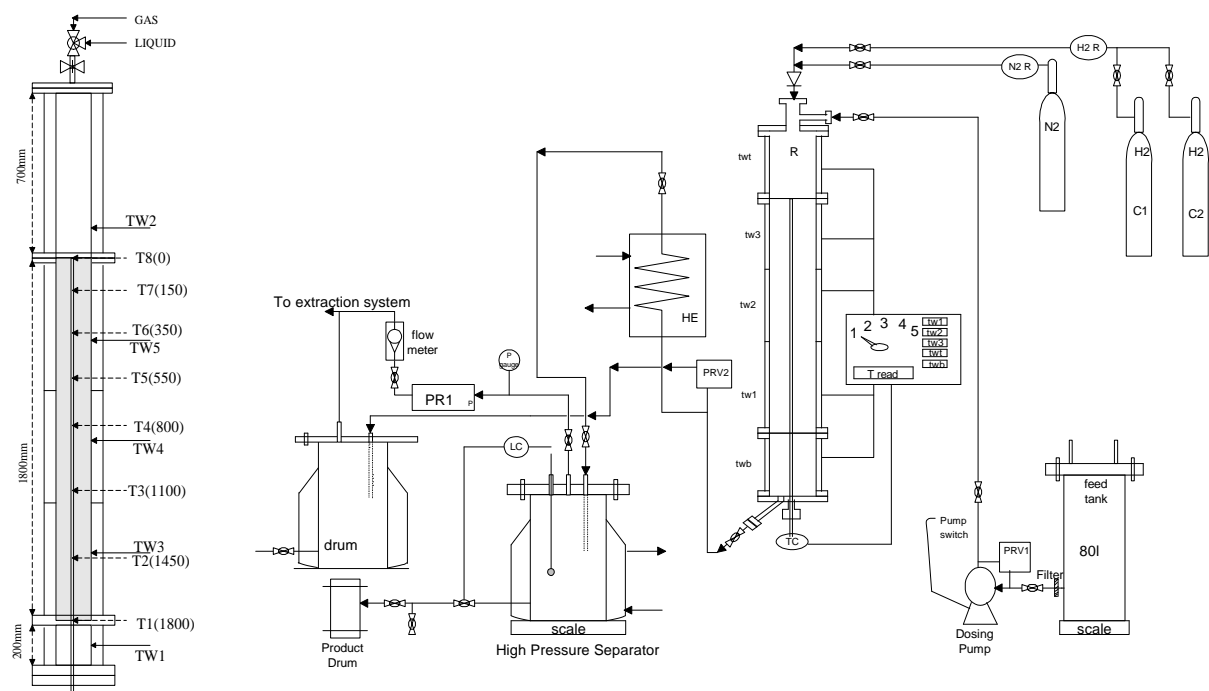


Figure 2 Pilot scale trickle bed reactor and sketch of the system

T_i – temperature in reactor axis, *T_{wi}* – wall temperature
R – reactor, *FC* – frequency controller, *HE* – heat exchanger,
PRV1,2 – pressure relief valves, *PR1* – pressure regulator

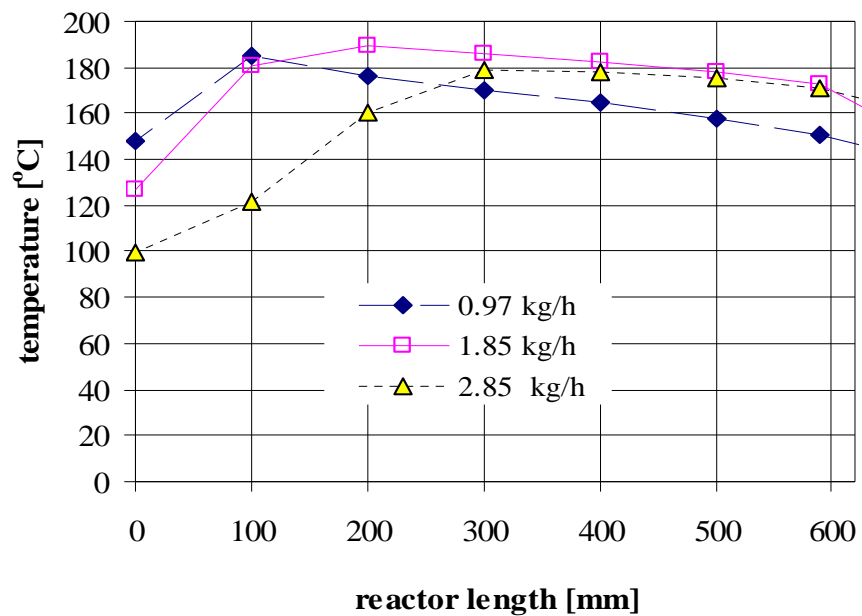
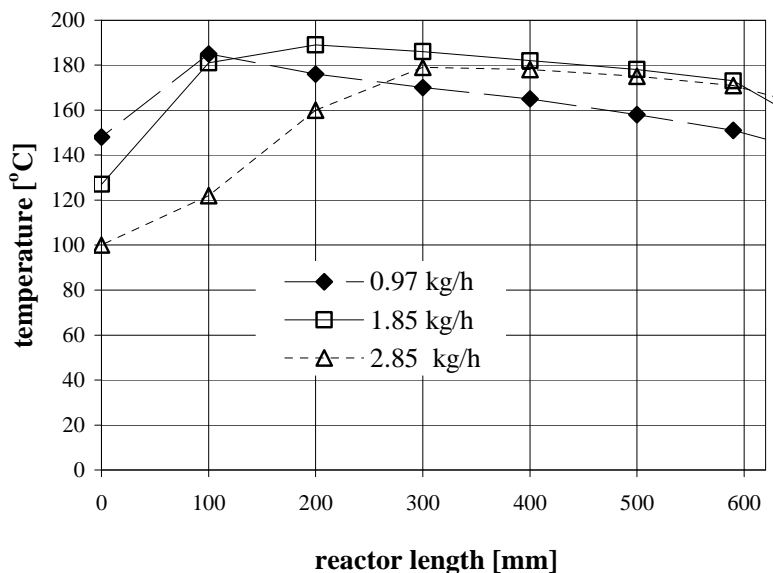


Figure 3 Effect of liquid flow rate on axial temperature profile in bench scale trickle bed reactor (13% wt. of thymol, P= 1.5MPa, inlet temperature from 100 to 155°C)



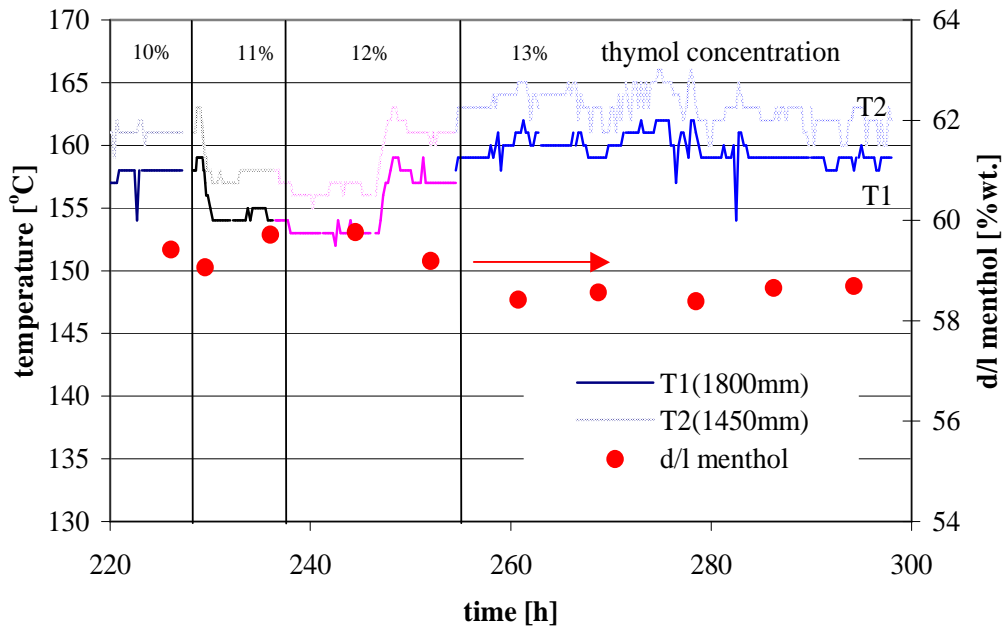
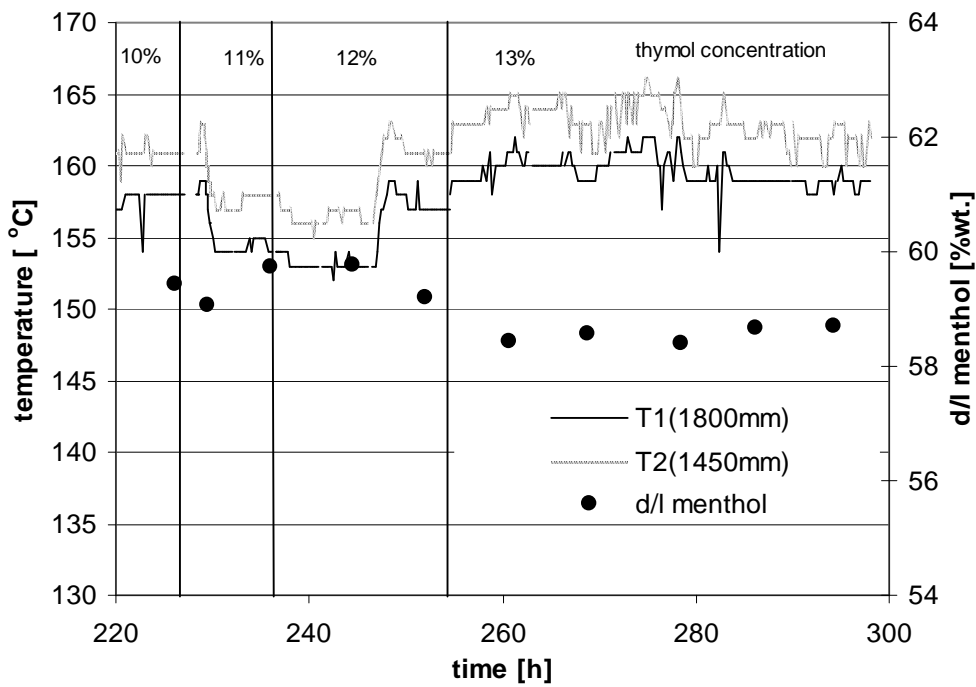


Figure 4 Effect of temperature in bottom section of catalytic bed on *d/l* menthol concentration in the product ($P=1.5$ MPa, inlet temperature 120°C , liquid flow rate 12kg/h)



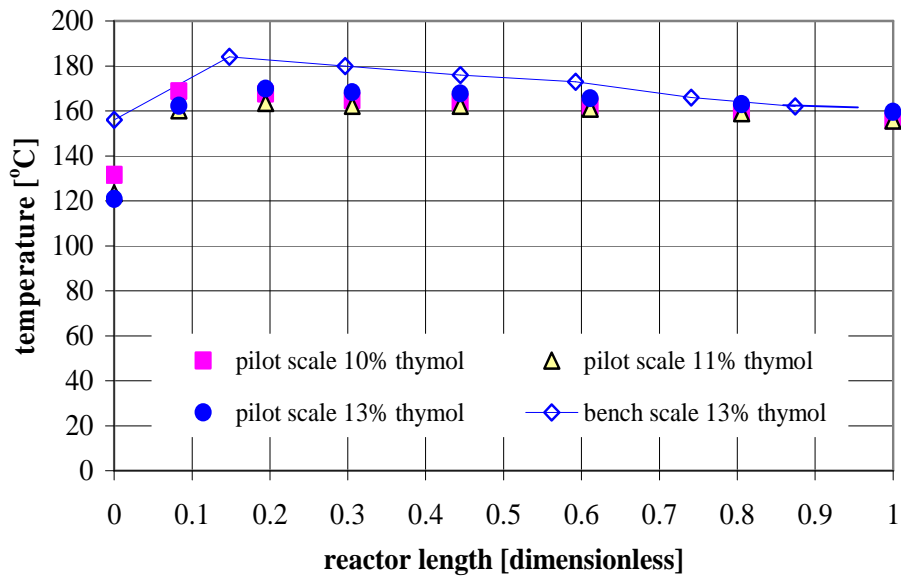
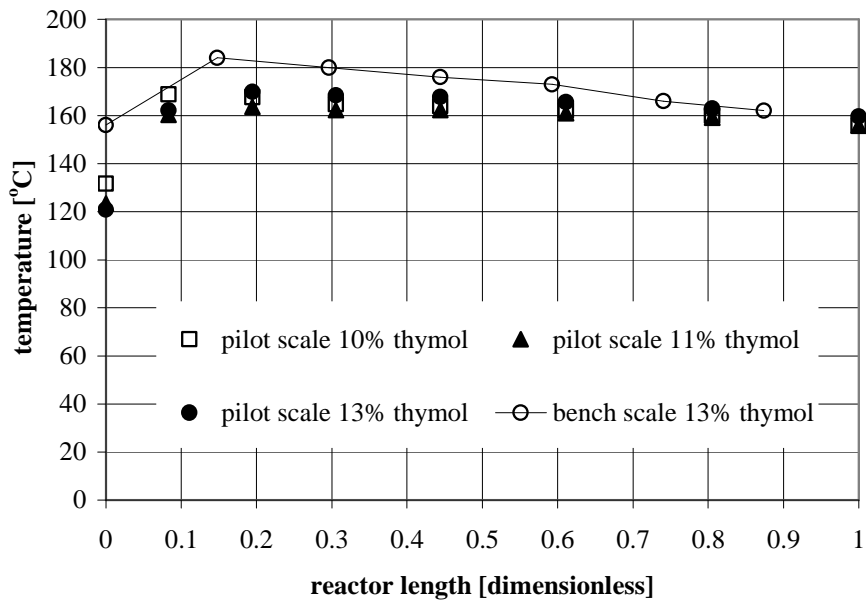


Figure 5 Comparison of temperature profiles in bench (liquid flow rate 1.2 kg/h) and pilot scale reactor (liquid flow rate 10 kg/h) at 1.5MPa



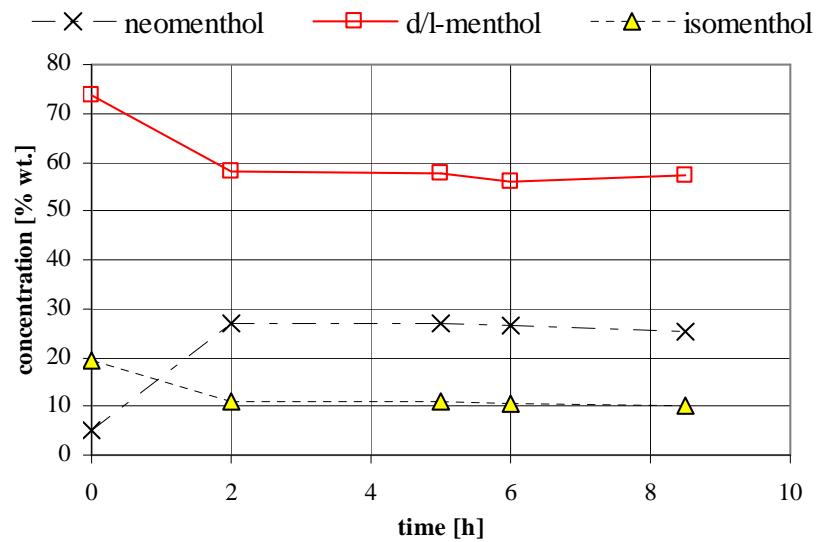
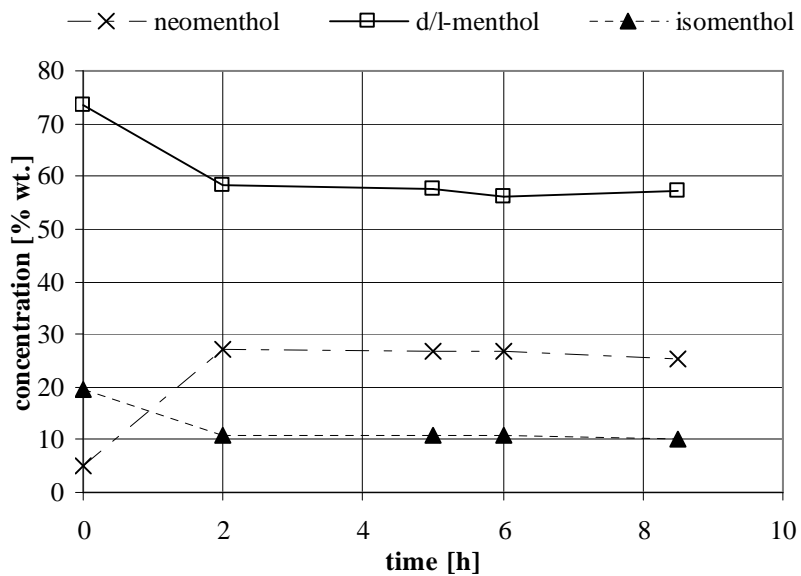


Figure 6 Concentration of selected components vs. time on stream for racemisation in the bench scale trickle-bed reactor (liquid flow rate 1kg/h, 160°C, 0.5 MPa)



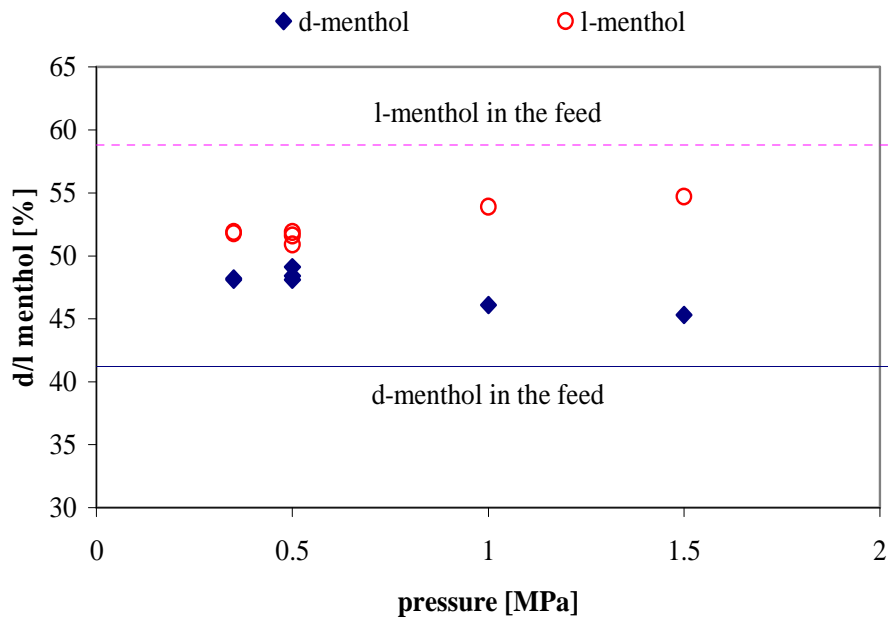
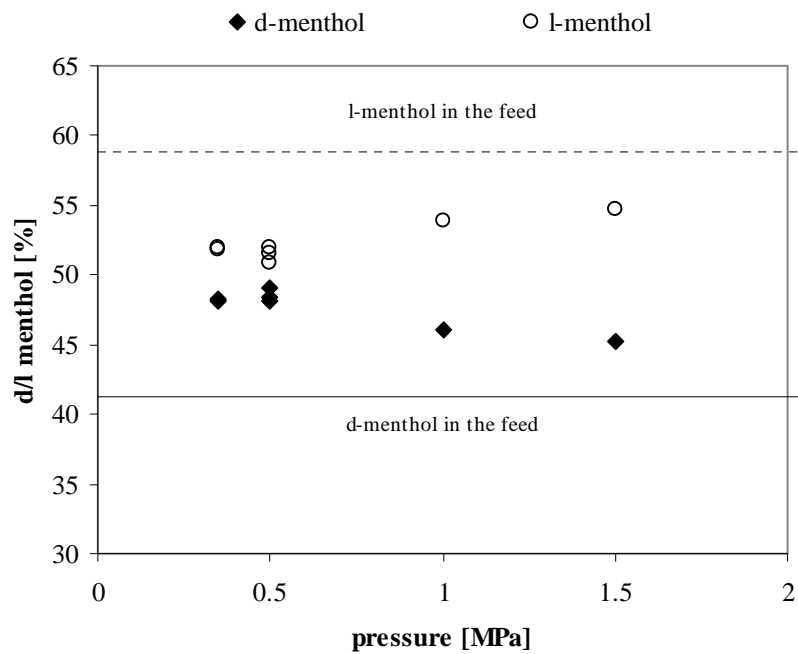


Figure 7 Effect of pressure on *d/l* menthols ratio during racemisation of a *l*-menthol (10% wt.) enriched menthol mixture in bench scale trickle bed reactor



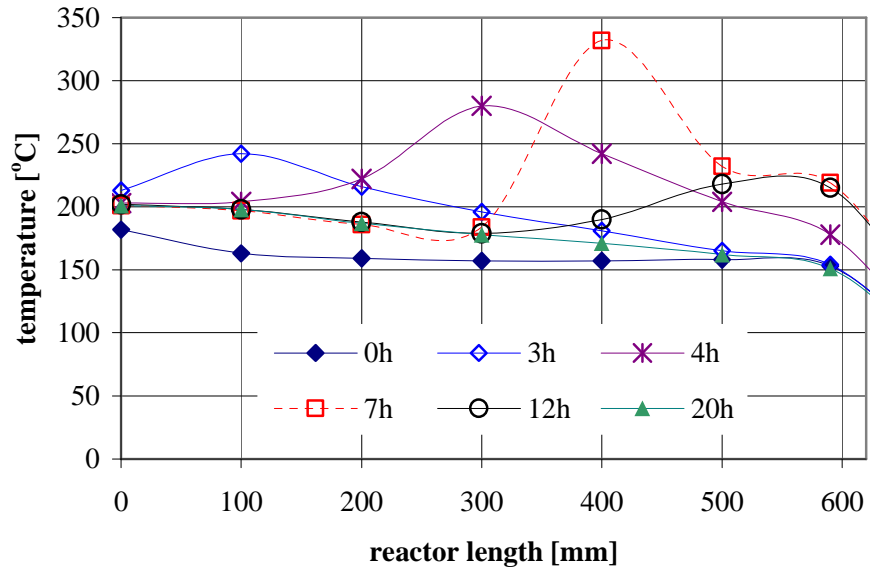
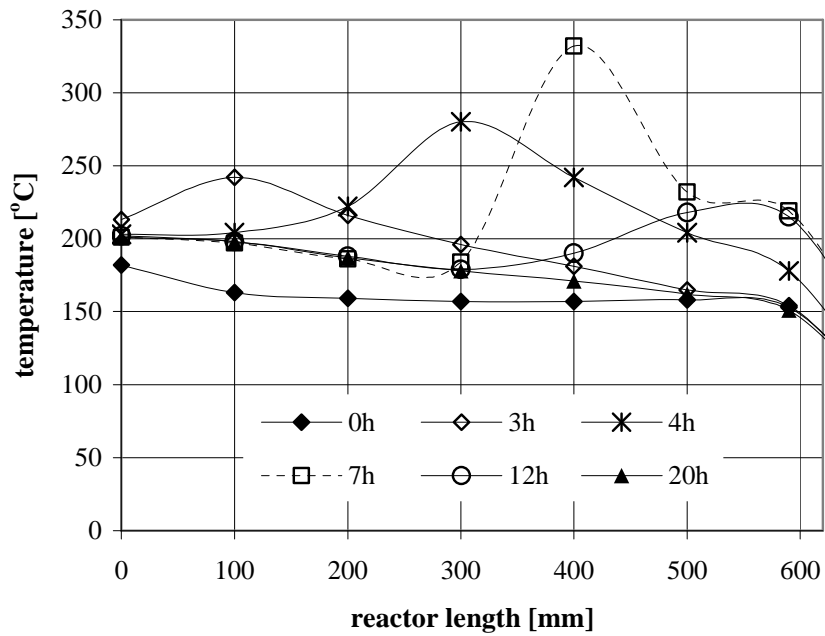


Figure 8 Temperature profile in bench scale reactor during initial stage of hydrogenation

13% wt. thymol at liquid flow rate 0.59kg/h



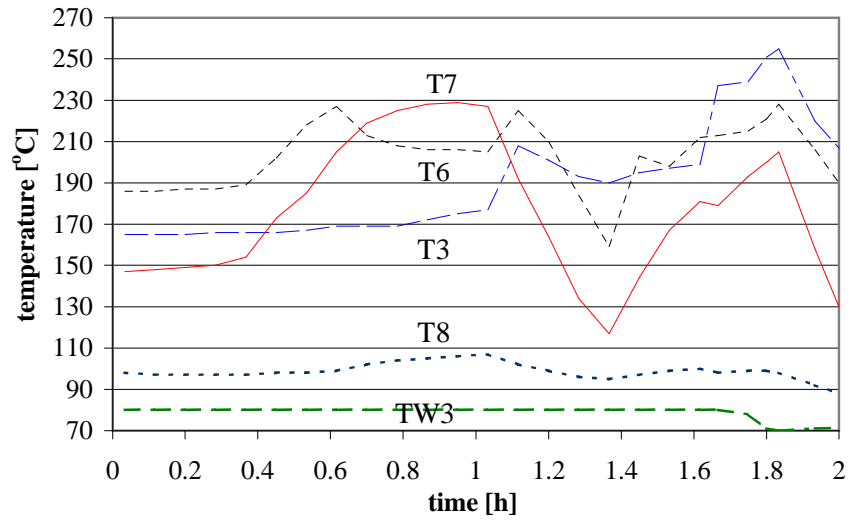
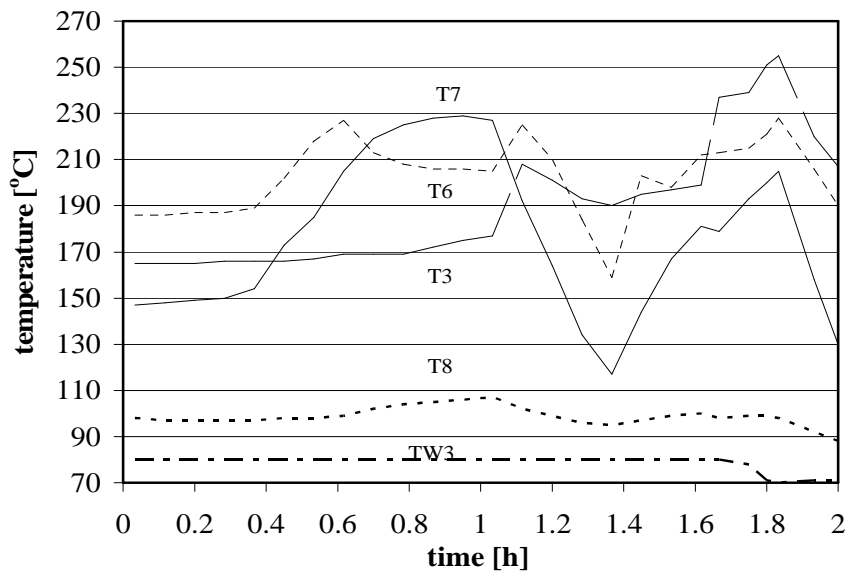


Figure 9 Temperature profile development in bench scale trickle bed reactor at 40 % wt. of thymol in the feed (liquid flow rate 1kg/h)



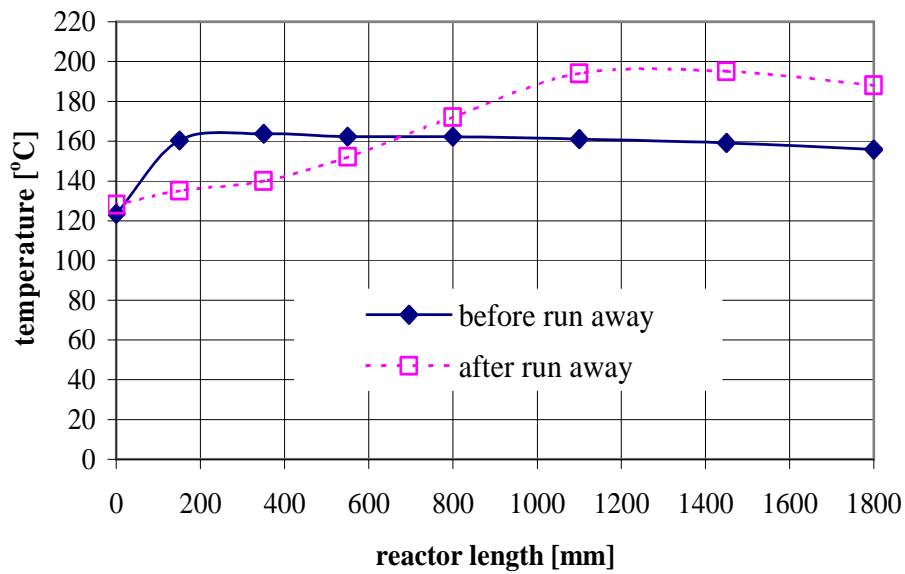


Figure 10 Experimental temperature profiles in pilot scale trickle bed reactor during thymol hydrogenation before and after temperature run away (11% wt. thymol, 1.5 MPa, liquid flow rate 10 kg/h)

