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HYDROGENATION OF ISOBUTENE IN FIXED BED MICROREACTOR – LONG TERM EXPERIMENTS

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Introduction

Aliphatic hydrocarbons with 4–5 carbon chain are very valuable starting materials for the steam cracking process. In terms of volume, the C4 and C5 fractions are the most important by-product streams from the pyrolysis of naphtha and other liquid raw materials. Total hydrogenation of C4 and C5 fraction is a way how to produce a high-quality raw material for pyrolysis, which in comparison with a simple recycle olefin (non-hydrogenated) fractions provides higher yields of ethylene and propylene and does not shorten the operating period of the pyrolysis furnaces by excessive coking^{1,2}.

For better understanding of the C4 fraction hydrogenating process, reaction kinetic study was performed in laboratory conditions. The hydrogenation of 2-methylpropene (isobutene) on platinum catalyst was investigated experimentally as a model reaction. The effort was focused on development of the methodology of kinetic data collection under the kinetic regime. To have a representative kinetic data, results reproducibility and process stability within several days on-stream was investigated.

Experimental

Continuous hydrogenation of isobutene (2-methylpropene, 2-MP) in gas phase was carried out on the 0.025g of commercial catalyst Cherox 3902, (0.5 wt. % Platinum on γ -alumina, egg-shell type) under the temperatures up to 110°C and hydrogen pressure 20 barg. A packed-bed microreactor with integrated reactant mixer (MCTU-600, Ehrfeld Mikrotechnik BTS GmbH, Germany,

Figure 1) suitable for high temperature and high pressure processes was used to perform the reaction.

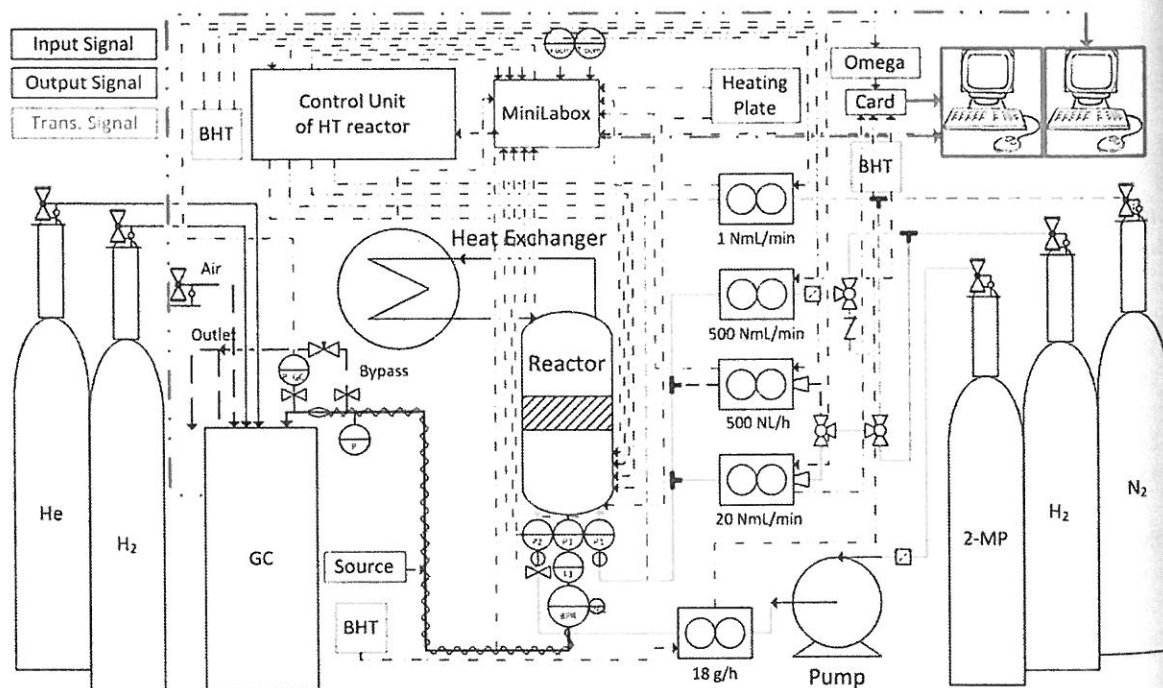


Figure 1. Schema of apparatus for continuous hydrogenation of 2-methylpropene (2-MP) in gas phase.

The reactor is designed to carry out gas-phase reactions in a packed catalyst bed at temperatures up to 600°C and pressures up to 100 bars (at <500°C) in a standard laboratory environment. The module is electrically

heated (840 W) and features two separate pre-heating lines with evaporation capability (up to 8 mL/min water in total), a gas mixing stage, the temperature-controlled packed bed and a liquid-cooled cooling unit, all within a compact, thermally insulated housing. The packed bed is implemented in a removable cartridge, which can easily be filled by the user with a powder or granular catalyst. Four integrated thermocouples allow a monitoring of the gas temperature at the inlet of the packed-bed cartridge, the product temperature at the outlet of catalyst bed, the product temperature at the outlet of the product cooler and the temperature of the heater jacket. The outlet stream composition was analyzed by an on-line GC-FID analyzer with a capillary column (GS-Gaspro 30 m x 0.32 mm x 0.1 μm). Gas chromatograph is connected by a six-way valve to the reactor outlet stream which allows continuous online analysis of products. Analytical method consists of the only one temperature ramp. One analysis takes about 11 minutes.

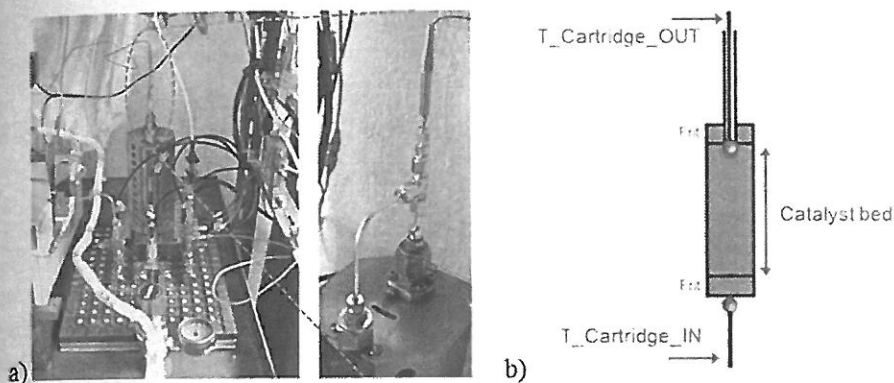


Figure 2. a) Reactor unit without cover with integrated reactant mixer, b) Schema of cartridge.

In this picture (Figure 2) there you can see the high temperature cartridge reactor unit without cover with integrated reactant mixer. The reactor is placed on the heated base plate with two inputs and one output. Inside the cylinder there is a cartridge. Originally we were able to measure only the temperature of the input stream entering the cartridge. Newly, the cartridge was modified for monitoring the temperature inside the catalyst bed. A thermocouple was added and placed on the top of the catalyst bed. Now we can measure temperature at the outlet of the cartridge as well.

Result and discussion

Stability of catalyst activity

Prior to hydrogenation experiments the catalyst was reduced in situ under the temperature up to 350°C and hydrogen pressure 20 barg.

Figure 3 presents the results of the long-term course of experiment for stability of catalyst activity, at temperature 68 – 88 °C, pressure 20 barg, and weight hourly space velocity (WHSV) of 51 – 102 grams of 2-methylpropene per gram of catalyst per hour. Gaseous reaction mixture contains 2-methylpropene, hydrogen and nitrogen as a diluting agent.

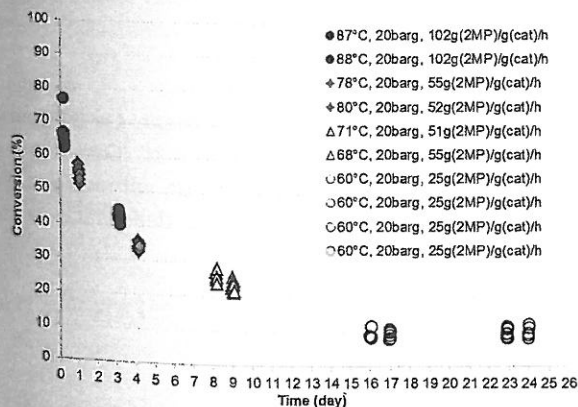


Figure 3. 2-MP conversion drop within first 16 days after the catalyst reduction in-situ

Within first 16 days of hydrogenation experiments after the catalyst reduction the conversion of 2-MP decreased substantially for the repeated trials with the same conditions (see

Figure 3). This catalyst deactivation stopped after approx. 16 days of discontinued experiments (interrupted overnight). Then the initial catalyst activity was stabilized and the experiments were more reproducible. Nevertheless, even with such a stabilized catalyst a relatively long time on stream to reach steady state performance (12 – 26 hours) was necessary to obtain steady state conversion after the interruption overnight. We assume that the performance stabilization of this catalytic system is a dynamic process. The hypothesis is that the slow stabilization of the thermal and absorption-desorption equilibrium on a catalyst surface might be responsible for such a slow behavior. Stabilization of the catalyst activity is also common in the industry when starting-up reactors with new catalyst. In contrast to laboratory reactors they operate 24 hours per day. To see if continuous reactor operation can help to reduce the time necessary to obtain steady state conversion for different trials, experiments without reactor operation interruption were conducted.

Stabilization of 2-methylpropene conversion – continuous operation 24 hours per day

Figure 4 presents the results of the long-term course of experiment for stabilization of 2-methylpropene conversion, at temperature 65 – 116 °C, pressure 18.7 – 20.1 barg, and weight hourly space velocity of 26 – 27 grams of 2-methylpropene per gram of catalyst per hour, with ratio of 2-methylpropene to hydrogen to nitrogen 1:3.1:12.5.

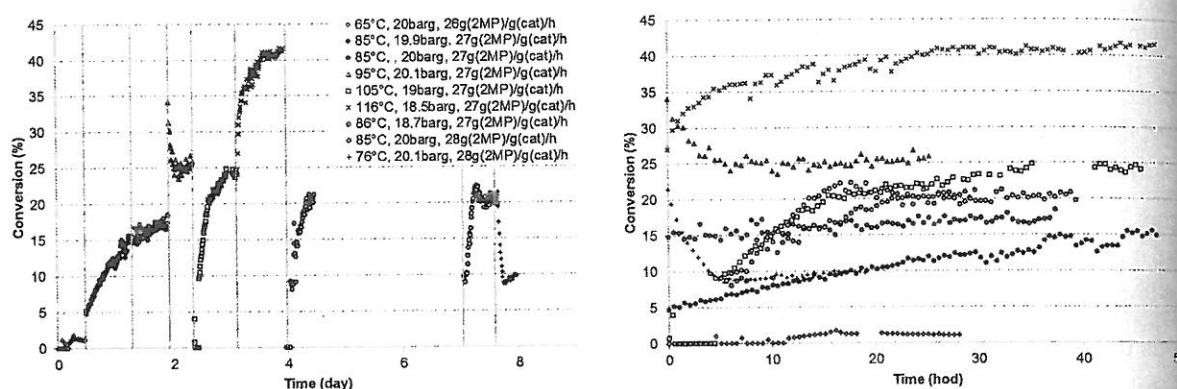


Figure 4. Stabilization of 2-methylpropene conversion a) in real time, b) in relative time (start of experiment = 0h).

During almost five days few different 24 – 48 hours long continuous experiments were conducted following each other (Figure 4a). The only difference of the experiments shown is the temperature which was increased stepwise by 10°C. Nevertheless, for some experiments still a long time was observed to reach steady state conversion (Figure 4b). The continuous operation 24h a day decreased the time necessary to reach the steady state between different experiments to 6 – 18 hours. The shortest time was about 3 hours in case of experiment at 95°C (triangular points). Experiments under the same conditions, blue color, show relatively good reproducibility. We concluded that a series of continuous experiments for few days 24 hours a day and smooth change of operating conditions change is beneficial to reach the steady state faster. However, after each change of experimental conditions the new sorption competition between H₂ vs. 2-MP, and slow stabilization of equilibrium on the catalyst surface occurs.

Sudden deactivation of the catalyst

As part of this work, we also carried out experiments without nitrogen as inert diluting agent. Experiments were focused on the identification of the temperature effect in the temperature range from 80 °C to 100 °C, pressure 20 barg, and WHSV of 76.7 grams of 2-methylpropene per gram of catalyst per hour, with ratio of 2-methylpropene to hydrogen 1:3.1. However, during this campaign sudden irreversible catalyst deactivation was observed.

Figure 5a shows the on-line recording of process parameters during the change of temperature settings in the reactor from 90 °C to 100 °C. During the change of temperature settings in the reactor, the non-optimal control of temperature caused the undesirable temperature overshoot of integrated heater (T_{Jacket}). This overshoot together with the pressure change due to liquid expansion in a 1.5 meter long capillary filled with liquid 2-MP reeled on the heating element causes an increase in the flow of the 2-MP to the catalyst bed. Since the hydrogen is in high excess, this increased the reaction rate which was observed as a high temperature peak. This uneven flow of 2-MP is reflected as oscillations of the flow meter signal (Flow_{iBE_ml_min}).

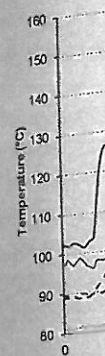


Figure 5. a) On-line recording of process parameters during the change of temperature settings in the reactor from 90 °C to 100 °C.

A higher temperature can prevent the ignition of the reaction. A sudden rise in temperature (dP) could place (Figure 5b) during the a temperature than 78°C experiment.

Tuning parameters. In order to reach the proper reactor temperature (Figure 6) but not temperature. Optimization get the

Table 1. Tuning

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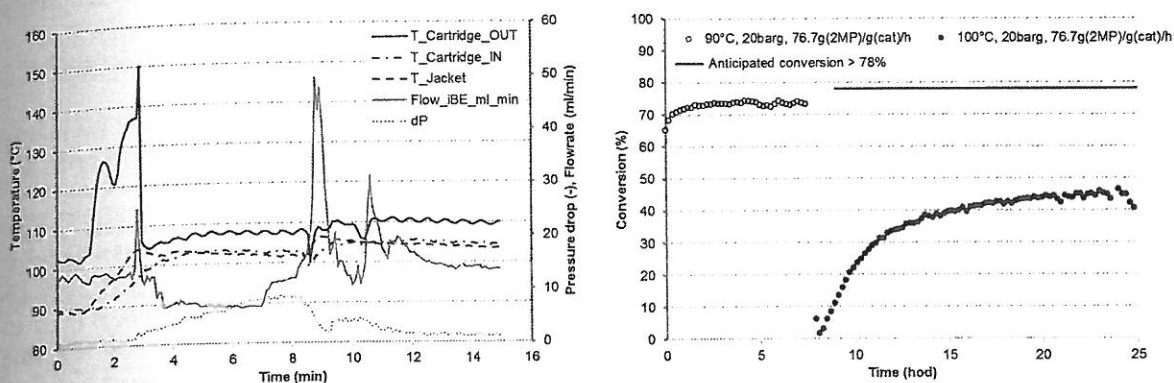


Figure 5. a) Recording of process parameters during the change of temperature settings in the reactor (from 90 °C to 100 °C), b) After the change, sudden deactivation of the catalyst.

A higher reaction rate will cause an increase of reaction temperature ($T_{\text{Cartridge_OUT}}$). During uneven flow, this can possibly lead to local overheating of the catalyst surface ($> 350\text{ }^{\circ}\text{C}$) and probably initialization of the ignition of the strongly exothermic hydrogenolysis of 2-methylpropene. Ignition and following extinction of the reaction occurs within a few seconds. After ignition reaction, hydrogenolysis progress is observable on the temperature at the outlet of the catalyst bed, which can even reach $150\text{ }^{\circ}\text{C}$ ($T_{\text{Cartridge_OUT}}$). The subsequent sudden rapid drop in temperature indicates the extinction of hydrogenolysis. Pressure increase in the reactor (dP) could be also attributed to hydrogenolysis, wherein 1 mole of 2-MP formed 4 moles of methane. Subsequently, the irreversible deactivation of the catalyst and conversion decrease by approximately half takes place (

Figure 5b). The subsequent decline in conversion of 2-MP describes a graph showing the conversion of 2-MP during the experiments with a temperature of $90\text{ }^{\circ}\text{C}$ (realized before the sudden deactivation, blue points) and a temperature of $100\text{ }^{\circ}\text{C}$ (realized after the sudden deactivation, red points). Where, in experiments with a temperature of $100\text{ }^{\circ}\text{C}$ conversion of 2-MP is anticipated in comparison with the experiments at $90\text{ }^{\circ}\text{C}$ higher than 78%, but only 47% was obtained after 24 hours of further operation. Has to be noted that within experiments with nitrogen dilution, similar sudden deactivation process was not observed.

Tuning procedure for the HT reactor controller

In order to prevent undesirable temperature overshoot during the temperature set point change in the reactor the proportional-integral-derivative (PID) parameters of the automatic controller was tuned. When heating the reactor with original PID values (Table 1), we saw an overshoot and then a couple of oscillations in the temperature of the cartridge ($> 6\text{ }^{\circ}\text{C}$,

Figure 6a). These values were optimal for maximal reactor performance ($600\text{ }^{\circ}\text{C}$, evaporation of 8 ml/min water) but not for our current operation window. We tuned the heating controller to suit better the lower temperature range. We usually operated the reactor between 50 and $150\text{ }^{\circ}\text{C}$.

Optimization of the PID temperature controller required tuning each parameter separately and in sequence to get the best possible control for a particular process.

Table 1

Tuning PID controller for operating the HT reactor in the temperature range $50 - 150\text{ }^{\circ}\text{C}$.

	P	I	D	Heating power
Original value	10	100	25	100% (840W)
Adjusted value	4	150	28	12% (101W)

We reduced the value of the proportional constant together with a slight increase of the integral constant and a slight increase of the differential part in order to reduce the overshooting and the subsequent oscillations (Figure 6 a, b). After the optimization, the system heats up well and settles optimally quickly at a setpoint with a minimal overshoot ($< 1\text{ }^{\circ}\text{C}$) and without excessive oscillations.

Figure 6b shows that even when heating the reactor with use of externally driven temperature ramp no significant temperature overshoot occurred. This is very important for the smooth stabilization of the thermal and absorption-desorption equilibrium on a catalyst surface during change of experimental temperature.

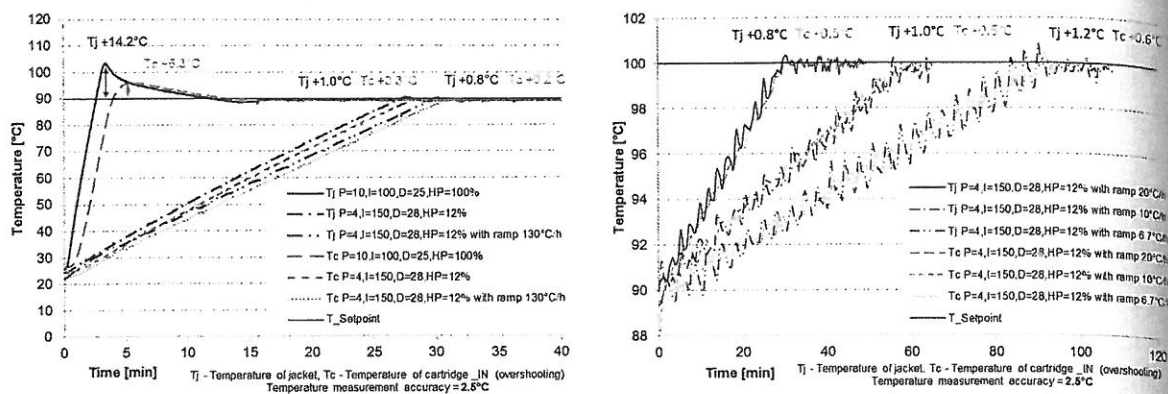


Figure 6. Transition curves with different PID control a) from 25 °C to 90 °C, b) from 90 °C to 100 °C.

Conclusion

The continuous long-term experiments of hydrogenation of isobutene in fixed bed microreactor without the overnight interruptions are necessary to reach the stable catalyst activity and the steady state process. Stable activity of the catalyst reduced in-situ was observed after 16 days of discontinued operation. We now organize the experiments at long term run to keep the catalyst activity independent on frequent start up and shut down conditions (Table II). The long term runs reflects more realistically the conditions of the real industrial continuous hydrogenation process. The continuous operation 24h a day decreased the time necessary to reach the steady state between different experiments to 6 – 18 hours. The experimental data and gained experiences will be used for the design of experiments under the reaction kinetic controlled regime without mass transfer limitation.

Table II

The main conclusions of the long-term experiments.

Observation	Cause	Action needed
Fast catalyst deactivation	Long period of extreme initial activity of the catalyst reduced in situ within first experiments	Conditioning the catalyst by long-term 24h experiment for 3-4 days to reach stable catalyst activity
Long time to steady state (10h)	Unstable values of conversion at constant conditions after interruption overnight.	Running of series of continuous experiments for few days 24h a day, smooth change of experimental conditions

We identified two actions to avoid the temperature overshoot and thus the undesired reactions leading to the catalyst deactivation. Firstly, it is necessary to work with diluting with nitrogen and secondly, the process temperature has to be carefully controlled with optimized PID temperature controller. The use of slow heating ramp during changes in temperature in the reactor is important for the gradual stabilization of the thermal and absorption-desorption equilibrium on a catalyst surface.

Keywords

Hydrogenation of isobutene, fixed bed microreactor, long-term experiments, stability of catalyst activity

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