DEVELOPMENT OF CATALYTIC HYDROGENATION REACTORS FOR THE FINE CHEMICALS INDUSTRY

K.R. Westerterp, K.B. van Gelder, H.J. Janssen and M.H. Oyevaar

Chemical Reaction Engineering Laboratories
Chemical Engineering Department
Twente University
P.O. Box 217, 7500 AE Enschede
The Netherlands

Abstract

A survey is given of the problems to be solved before catalytic hydrogenation reactors can be applied in a multiproduct plant in which selectivity problems are experienced. Some results are reported on work done on the reaction kinetics of two multistep model reactions and on mathematical modelling and experimental verification of the models. Since hydrogenation reactions are often very exothermic, cooling by solvent evaporation has been applied where appropriate. Sufficient information has been collected and correlated to enable operation of multiproduct catalytic reactors of the slurry or packed bubble column type; interdependence of operating variables is so complex that a mathematical model is indispensable.

1. Introduction

In our laboratories cooperation with industry is intensive. It is our job to study the basic fundamentals for new operations or processes, which will be further elaborated by our partners and eventually developed on a larger scale into new processes and syntheses. This approach places us in a position to publish on our results. Since 1984 we are a.o. engaged in developing catalytic hydrogenation processes for the fine chemicals industry. In this undertaking we have a partner who has a production program which includes around twenty different hydrogenation reactions of a variety of raw materials. These hydrogenations are carried out according to the classical Béchamps process using Fe-powder and a HCL solution. As a consequence large amounts of iron hydroxides and neutralization salts have to be disposed of, a very costly affair. So it was obvious to look into possibilities for catalytic hydrogenation.

In catalytic hydrogenation a number of problems can be anticipated. It is too costly to build say 20 different small hydrogenation units if these reactions have to be carried out under different operating conditions. As a consequence one or two larger units have to be developed for multiproduct use. Hydrogenation reactions often are highly exothermic - in our case adiabatic temperature rises of 200-500 K are common - so methods have to be devised to cope with high heat production rates. In case of producing an intermediate product in a set of consecutive reactions or of combined reactions selectivity is a problem and operating conditions must be kept under accurate control. The number of catalysts to be used preferably should be small because of handling and recovery costs. It would be best to have one single, universal catalyst. Financial losses should be kept to a minimum. For raw materials this requires short and quick start-up and stop procedures, for hydrogen it requires low excess of hydrogen or recirculation of non converted material. For the catalyst it demands a good recovery system and in case of deactivation simple reactivation procedures. Therefore, a number of problems has to be solved before catalytic hydrogenations can be introduced on a large scale in a fine chemicals plant.

2. Development objectives

In order to solve the problems at hand we decided to opt for continuous operation of the reactor and to use an evaporating solvent to remove the reaction heat in the reactor. Miniplants have been built for catalytic hydrogenations in a slurry reactor, in a packed bubble column and in a cocurrent trickle flow column reactor. In addition, two separate miniplants have been built for the study of gas-liquid interfacial areas in several different reactor types, one for pressures in the range of 0.1-2 MPa and the other one for 0.1-10 MPa. To test the performance of the reactors experimentally two model hydrogenation reactions have been selected and the reaction rates of the individual reaction steps have been determined. Mathematical models have been developed to describe the different reactor types and their behaviour. The models have been tested experimentally. Interfacial areas are determined by a chemical method using systems of amines and CO₂-gas. In this communication we report briefly on some of the results we have obtained. Some fifteen papers are being prepared to report more extensively on our results.

3. Model reactions

Having considered many possible complex reactions we decided upon the catalytic hydrogenation of 2,4-dinitrotoluene (DNT) and of 2,4,6-trinitrotoluene (TNT) in methanol and as our model

reactions, and supported palladium as the catalyst. The heat of reaction of the reduction of a single nitrogroup is around 600 kJ/mole; at reasonable concentrations of TNT adiabatic temperature rises of 300 to 500 K occur. On theoretical grounds we can expect that the hydrogenation of DNT proceeds in two parallel paths, each of which consist of two consecutive reactions when amino-nitro compounds are formed as the sole intermediates. The hydrogenation of TNT involves an even more complicated scheme.

A large amount of literature has been published in recent years concerning the experimental investigation and the modelling of the catalytic hydrogenation of several nitrosubstituted aromatic compounds. Most of the literature refers to the hydrogenation of nitrobenzene. In general, aromatic nitrocompounds are converted to the amines quantitatively. Commonly Ni and supported Pd or Pt are used as catalysts. In general the reaction rates reported are zero order in the nitrocompound and between zero and first order in hydrogen. They can be described with Langmuir-Hinshelwood rate equations. Burge *et al.* (1980) reported that the hydrogenation of nitrobenzene, using Raney nickel as a catalyst, did involve the formation of azoxy- and of azobenzene as stable intermediates. The formation of azoxybenzene as an intermediate has also been reported by Yao and Emmet (1962). Burge concluded that the reaction mechanism followed a reaction pathway similar to that proposed by Haber (1898) for the electrochemical reduction of nitrobenzene. Collins *et al.* (1982) reported that the reaction pathway of the reduction of nitrobenzene also obeyed Haber's scheme when nickel boride was used as a catalyst. The maximum amounts of azoxy- and of azobenzene which build up during the reaction were found to be negligible. Bird and Thompson (1980) stated that the reduction of any nitrogroup on an aromatic ring, using supported palladium as a catalyst, will follow the same pathway as chemical reduction, but that it is very difficult to terminate the reaction at one of its intermediates. Yucelen (1984) studied the kinetics of the hydrogenation of 2,6-dinitrotoluene using Pt/C and Pt/Al₂O₃ as catalysts. The reaction proceeded according to a simple scheme of two consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, in which B represents the only intermediate 2-amino-6-nitrotoluene and where C is the end-product 2,6-diaminotoluene.

Although some studies have been published with respect to the catalytic hydrogenation of 2,4-DNT, practicable models of this reaction and of the hydrogenation of TNT have not yet been developed. Acres and Cooper (1972) and Bird and Thompson (1980) reported about the occurrence of two intermediates in half-hydrogenated samples of 2,4-DNT: 2-amino-4-nitrotoluene and 4-amino-2-nitrotoluene, respectively. Unfortunately they did not give any further information, neither on the change of the concentrations of the substrate and the products as a function of the course of the reaction, nor on the analytical technique used. Pawlowski and Kricsfalussy (1981) found a single step mechanism for the conversion of 2,4-DNT to 2,4-DAT. Acres and Cooper (1972) have found 2-amino-4-nitrotoluene (2-A-4-NT) and 4-amino-2-nitrotoluene (4-A-2-NT) as stable intermediates in half hydrogenated samples of DNT.

The kinetics of the hydrogenations of DNT and TNT have been investigated in a fully automated batch slurry reactor, which was operated isothermally and under constant pressure. As a catalyst 5% Pd on active carbon was used. The consumption of hydrogen during reaction was calculated from the drop in a hydrogen pressure. A set of preliminary experiments has been performed at several temperatures, agitation rates, catalyst and substrate concentrations to warrant the exclusion of any mass transfer effects that possibly mask the real reaction rates. For both DNT and TNT sets of hydrogenation experiments have been carried out at different hydrogen pressures to determine the effect of the temperature and hydrogen pressure on the overall conversion rates. Routine analysis were performed with a gaschromatograph which is equipped with a flame ionization detector and fitted with 6 ft., 1/8 inch column packed with Tenax-GC, 60-80 mesh. So far we have concentrated mainly on quantitative analyses of reaction mixtures of DNT. The concentrations of the relevant reaction compounds as a function of time have been determined at reactor temperatures of 308, 323 and 357 K and at a constant hydrogen pressure of 2 MPa. In the samples DNT, 2-A-4-NT, 4-A-2-NT and DAT have been identified by means of comparison with the retention times of the pure compounds. Two other products have been identified as 4-hydroxylamino-2-nitro-toluene (2-N-4-HAT) and 2-amino-4-hydroxylamino-toluene (2-A-4-HAT) by means of GC-MS analysis. Note that the hydroxylamines are formed at the para-position only and that an ortho-nitrogroup is converted directly to an aminogroup. The concentrations of 2-A-4-HAT were found to be so low that the pressure of this compound has been neglected.

A plot of the hydrogen conversion as a function of the reaction time during a typical hydrogenation of DNT at 308 K is presented in Fig. 1. In Fig. 2 the concentrations of the major compounds are plotted versus the hydrogen conversion. In Fig. 2 also the reaction pathway can be observed. At first DNT is converted in two parallel reactions into 2-A-4-NT and 2-N-4-HAT. The consecutive reactions do not start before almost all of the DNT has been consumed. This is known as molecular queueing and can be explained in terms of a competitive adsorption of the reacting species on the catalyst surface. Once all of the DNT has been consumed the 2-N-4-HAT is converted into the amine 4-A-2-NT which subsequently reacts to DAT, while in the parallel pathway simultaneously the 2-A-4-NT is converted to DAT. In Fig. 1 a sharp decrease is shown in the overall reaction rate to a conversion level of 0.4. As a consequence of the strong molecular queueing in the initial stage the reaction exhibits zero order behaviour with respect to DNT. The observed decrease of the overall reaction rate was caused by rapid deactivation of the catalyst in an induction period. The kinetic rate data of the hydrogenation of DNT and TNT have been modelled using Langmuir-Hinshelwood rate equations. The rate of conversion of species *i* into species *j* is given by $r_{ij} = c_{cat} k_{ij} \theta_i \theta_j$, where θ_H and θ_i are the relative concentrations on the catalyst surface of hydrogen and of species *i* respectively. The experimental results indicate separate active sites for hydrogen and for the aromatic molecules on the catalyst surface. Assuming dissociative adsorption of hydrogen on the catalyst θ_H and θ_i are given by:

$$\theta_H = \frac{\sqrt{(K_H P_{H_2}/RT)}}{1 + \sqrt{(K_H P_{H_2}/RT)}} \quad \text{and} \quad \theta_i = \frac{Q_i X_i}{(K_A C_{AO})^{-1} + \sum Q_j X_j},$$

where K_H is the product of the solubility constant of hydrogen in methanol and the true adsorption constant, Q_i is the relative adsorption strength of species i with respect to DNT or TNT, K_A is the adsorption constant, C_{AO} is the initial concentration of DNT or TNT and further $X_i = C_i/C_{AO}$. The model for the hydrogenation of DNT is based on the reaction pathway presented in Fig. 2. It was found that the overall hydrogen consumption rate of the hydrogenation of TNT could be described accurately over the whole temperature range of the experiments by a lumped model of three consecutive reactions TNT→DNHAT→DANT→TAT. Unfortunately we lacked sufficient quantitative data of the liquid phase concentrations of the reaction components to set up a realistic extended model for the hydrogenation of TNT.

Figure 1: Hydrogen conversion vs. reaction time for a typical hydrogenation of DNT in a mechanically agitated three-phase batch reactor.

Figure 2: Relative concentration C_i/C_0 vs. hydrogen consumption for a typical hydrogenation experiment of DNT (reaction conditions see figure 1). Symbols: ■ DNT, ○ 4HA-2NT, ◆ 4A-2NT, △ 2A-4NT, × DAT.

For the parameter estimation of both models we used the RKPES computer program developed by Klaus and Rippin (Klaus and Rippin, 1979) which applies the maximum likelihood approach. The parameters have been estimated for each experimental temperature separately. The temperature dependent relations for the parameters have been derived from the single temperature results. The relations are summarized in Table 1. The data for DNT comprised the data of the hydrogen conversion as a function of the reaction time of three different experiments (100 to 120 points) in addition to the data of the concentrations of the reaction components as a function of the reaction time (20 to 25 sets of 5 concentrations) for each temperature. For TNT only data of the hydrogen conversion as a function of the reaction time have been used. The t -values of the estimated rate parameters range up from around 10 to 60 whereas the t -values of the adsorption parameters are poor. This can be explained by the large difference in the relative adsorption strength of the reacting components on the catalyst: when a component i is strongly adsorbed and nearly covers the whole catalyst surface the relative surface concentration $\theta_i = 1$ and has thus become insensitive to the exact value of the adsorption constant.

Table 1: Parameter values in the rate equations for the hydrogenation of DNT and TNT.

substrate and reaction pathway	reaction constants		adsorption parameters	
	preexponential factor [mole/kg cat s]	activation temperature [K]	preexponential factor	activation temperature [K]
	k_{12}	$1.31 \cdot 10^{10}$	K_1	0.15 [m ³ /mole]
	k_{23}	$5.14 \cdot 10^{13}$	Q_2	130 [-]
	k_{34}	$2.60 \cdot 10^9$	Q_3	7.11 [-]
	k_{15}	$2.13 \cdot 10^{11}$	Q_4	0.011 [-]
	k_{54}	$7.17 \cdot 10^{13}$	Q_5	0.4 [-]
	k_{12}	$3.3 \cdot 10^{11}$	K_1	$3.8 \cdot 10^{-10}$ [m ³ /mole]
	k_{23}	$1.2 \cdot 10^{10}$	Q_2	1600 [-]
	k_{34}	$1.8 \cdot 10^{10}$	Q_3	$1.8 \cdot 10^5$ [-]
For both systems: $K_H = 9.14 \cdot 10^{-18} \exp(10360/T)$ [m ³ /mole]

Figure 3: Outline of a continuous stirred three-phase tank reactor with an evaporating solvent.

4. Mathematical modelling and experimental confirmation

4.1 Continuous stirred three-phase slurry reactor

A series of catalytic hydrogenation experiments has been carried out in a mini-installation with a three-phase slurry reactor using an evaporating solvent to control the temperature. In Fig. 3 the basic line-up of the installation is presented. A solution of the reactant, a concentrated slurry of the catalyst and hydrogen gas are fed to the reactor separately. We assume that the liquid and the gas phase in the reactor are well mixed and that the gas phase is saturated with solvent vapour. The reaction products and the catalyst leave the reactor in the product stream. The excess of non-converted hydrogen gas leaves the reactor via the vapour line to a condenser and carries away the evaporated solvent, thus withdrawing heat from the reactor. The solvent is condensed and returned to the reactor; the excess gas leaves the system via a back-pressure control valve. At constant reactor pressure and constant hydrogen excess the heat withdrawn from the reactor by solvent evaporation will rise strongly with increasing temperature because of the exponential

increase of the rate of evaporation. The maximum attainable reactor temperature, the boiling point of the reaction mixture, can never be reached, because the rate of evaporation would become infinitely large. The rate of heat production is also affected by the temperature because the partial pressure of hydrogen is lowered by the increase of the solvent vapour pressure. At a certain temperature the rate reducing influence of a lower partial pressure of hydrogen will become larger than the rate enhancing effect of a higher temperature. Consequently at increasing reactor temperatures the rate of reaction passes through a maximum and then decreases. At the boiling point the reaction stops completely because the hydrogen cannot dissolve anymore into the boiling liquid (Westertep and Crombeen (1983)).

A mathematical model of the slurry reactor has been developed which describes the hydrogen conversion, the rate of heat production (HPR), the total rate of heat withdrawal (HWR) and the liquid phase composition as a function of the reactor temperature. The material balances of the reaction components are solved simultaneously using the kinetic model of the reaction system. Thus the overall conversion rate of hydrogen gas and the HPR can be determined. Using the lumped reaction model, for the hydrogenations of TNT we write:

$$\Phi_{v,1}(c_{A0} - c_A) = V_{R,1}r_{AB} \quad , \quad \Phi_{v,1}c_B = V_{R,1}(r_{AB} - r_{BC}) \quad , \quad \Phi_{v,1}c_C = V_{R,1}(r_{BC} - r_{CD})$$

$$\text{and } c_D = c_{A0} - (c_A + c_B + c_C)$$

Where A, B, C and D represent TNT, DNHAT, DANT and TAT respectively $r_{ij} = c_{cat}k_{ij}\Phi_H\Phi_I$ is the rate of the reaction of i into j. The material balance for the hydrogen is given by:

$$\Phi_{H_2out} = \Phi_{H_2in} - \Phi_{v,1}V_{H_2}c_{A0}\zeta_{H_2}$$

$\Phi_{v,1}V_{H_2}c_{A0}$ represents the amount of moles of hydrogen required for complete conversion of the TNT in the feed to TAT, ζ_{H_2} is the hydrogen conversion. Φ_{H_2in} is related to the reactant feed by

$\Phi_{H_2in} = \Phi_{v,1}\alpha V_{H_2}c_{A0}$, in which α is defined as the amount of moles of H_2 fed to the reactor over the amount required for complete conversion. Now we can write:

$$\Phi_{H_2out} = \Phi_{v,1}V_{H_2}c_{A0}(\alpha - \zeta_{H_2})$$

The HPR is calculated on the assumption that the heat liberated by the reaction is directly proportional to the rate of hydrogen conversion in the reactor:

$$HPR = \Phi_{v,1}c_{A0}\zeta_{H_2}(-\Delta H_R)$$

For the HWR three contributions have been distinguished:

- 1) the heat absorbed by the cold feed streams of the reactant solution, the catalyst slurry and the hydrogen gas:

$$HWR_{ef} = \Phi_{v,feed}(\rho C_p)_1(T - T_{feed}) + \Phi_{v,cat}(\rho C_p)_1(T - T_{cat}) + \Phi_{v,1}\alpha V_{H_2}c_{A0}(MC_p)_{H_2}(T - T_{H_2})$$

- 2) the heat absorbed by evaporation of the solvent. We assume that the gas and the liquid in the reactor are at equilibrium. The vapour stream that leaves the reactor has the same composition as the gas-phase in the reactor and consists of hydrogen, methanol and reaction water. It is related to Φ_{H_2out} by:

$$HWR_{ev} = \Phi_{H_2out} \frac{p_S^0 x_S \Delta H_{vap,S} + p_W^0 x_W \Delta H_{vap,W}}{p - (p_S^0 x_S + p_W^0 x_W)}$$

The denominator of this equation represents the hydrogen pressure in the reactor.

- 3) the heat absorbed by the condensate returned to the reactor. We assume complete condensation of the vapour in the condenser, so we write:

$$HWR_{cond} = \Phi_{H_2out} \frac{p_S^0 x_S (MC_p)_S + p_W^0 x_W (MC_p)_W}{p - (p_S^0 x_S + p_W^0 x_W)} (T - T_{cond})$$

In Fig. 4 the results of model calculations of the hydrogenation of TNT are presented for a typical set of operating conditions. In Fig. 4a the HPR and HWR and in Fig. 4b the concentrations

Figure 4a: Results of calculations with the reactor model. Dimensionless heat production rate (HPR) and heat withdrawal rate (HWR) as a function of the reactor temperature at constant residence time of the liquid. Constant catalyst feed and gas feed temperature of 20°C. Feed temperature: a: 20°C, b: 30°C, c: 50°C, d: 70°C.

Figure 4b: Results of calculations with the reactor model. Dimensionless concentrations $Q/C_{TNT,0}$ in the reactor product as a function of the reactor temperature at the same operating conditions as in figure 4b case a. The dashed lines indicate the lower and upper stable operating point, respectively.

of the components in the reactor product are plotted versus the reactor temperature at constant residence time of the liquid in the reactor. The HPR and HWR have been normalized by dividing them by the maximum HPR at complete conversion of the TNT. The concentrations have been normalized by division by the feed concentration c_{A0} . Because the calculations have been based on the lumped kinetic model of TNT the concentrations plotted in Fig. 4b do not represent the true product distribution in the reactor but only give an impression of how the concentrations of the reaction components change as a function of the reactor temperature. Because the kinetic model does describe the hydrogen consumption rate very well the heat effects calculated with the reactor model are realistic. Curves a, b, c and d in fig. 4a represent the HWR at four different feed temperatures. The reactor works at a stationary operating point when the stability criteria $HWR = HPR$ and $\delta HWR / \delta T > \delta HPR / \delta T$ are fulfilled. In Fig. 4a multiplicity occurs at the feed temperatures of the a and b curves. In Fig. 4b the dashed lines indicate the lower and upper stable operating point of case b. The relative concentrations in the reactor outlet stream at the lower stationary point are 0.42 TNT, 0.55 DNHAT and around 0.03 DANT and in the upper stationary point are 0.04 TNT, 0.10 DNHAT, 0.51 DANT and 0.35 TAT. Multiplicity can be avoided by using a slightly higher feed then used for the calculations of case b. The most important parameters which control the behaviour of the reactor are the total pressure in the reactor, the residence time of the liquid phase in the reactor and the temperature of the reactant feed. In total of 22 hydrogenation of TNT experiments have been carried out in the mini-installation. By varying the operation conditions a temperature range of around 35 to 100°C has been covered. In Fig. 5 the experimental results are compared with the results of model calculations with respect to the hydrogen conversion and the temperature at the operating point. The agreement is satisfactory, especially when realising that small errors in the calculation of the HPR or HWR may result in a drastic change of the predicted steady state temperature.

Figure 5: A comparison of experimentally determined hydrogen conversions and reactor temperatures and those predicted by our model.

4.2 The three-phase-packed-bed-bubble-column-reactor

A model comprising plug flow and axial dispersion of mass and heat is used to describe the behaviour of the packed bed reactor. The derived model equations are based on the following assumptions: 1. the reactor is adiabatic and isobaric, 2. the gas phase is in equilibrium with the liquid phase when it enters the catalyst bed, 3. the gas and the liquid feed temperature are equal, 4. there are no mass transfer limitations, 5. the temperature in all three phases is uniform in a plane perpendicular to the direction of flow, 6. there are no concentration profiles in the radial direction, 7. the reactants are not volatile, 8. there is no heat conduction in the axial direction, 9. the gas phase is ideal, 10. the contribution of the reactants to the specific heat and the molar weight of the liquid phase can be neglected, 11. the available catalyst area is fully wetted and utilised, 12. a mass transfer rate equation is used to describe the evaporation of the solvent. The partial pressure of the solvent at the gas-liquid interphase is equal to the vapour pressure of the solvent.

The gas-liquid equilibrium at the entrance of the catalyst bed is achieved by assuming that the gas and the liquid feed flow through an adiabatic mixer in which this equilibrium is reached before entering the catalyst bed. Since some evaporation will occur in the mixer, the temperature at the entrance of the catalyst bed will be lower than the feed temperature.

The dimensionless equations based on the above assumptions are:

$$* \text{ for the reactants } \frac{1}{Pe_m} \frac{d^2 X_i}{dz^2} - \phi_L \frac{dX_i}{dz} - X_i \frac{d\phi_L}{dz} + Da \eta R_{prod, i} = 0$$

$$* \text{ for hydrogen in the gas phase } Y_H \frac{d\phi_G}{dz} + \phi_G \frac{dY_H}{dz} - \frac{Da \eta}{dY_{sol}} R_{prod, H} = 0$$

$$* \text{ for the solvent in the gas phase } Y_{sol} \frac{d\phi_G}{dz} + \phi_G \frac{dY_{sol}}{dz} - St' P \left(\frac{Y_{sol} - Y_{sol}^*}{1 + \psi_0} \right) = 0$$

$$* \text{ for the liquid phase } \frac{d\phi_L}{dz} + St' P \left(\frac{Y_{sol} - Y_{sol}^*}{1 + \psi_0} \right) \frac{1}{\psi} = 0$$

$$* \text{ enthalpy balance } \frac{\psi}{Pe_h} \frac{d^2 \theta}{dz^2} + (\phi_L + C_{PG} M_G \phi_G) \psi \frac{d\theta}{dz} - Da \eta \sum (R_j \Delta T_{ad, j}) - St' P \Delta T_{ev, sol} \left(\frac{Y_{sol} - Y_{sol}^*}{1 + \psi_0} \right) \frac{1}{\psi} = 0$$

$$* \text{ from the definition of mole fractions } X_{sol} = \frac{1}{x_{AO}} - \sum X_j \quad \text{and} \quad \sum Y_i = 1$$

The boundary conditions for these equations are:

$$* \text{ at } Z = 0 \quad (C_{PG} M_G \phi_G + \phi_L) \left(\theta_{Z=0^-} - \theta_{Z=0^+} \right) + \frac{1}{Pe_h} \frac{d\theta}{dz} \bigg|_{Z=0^-} = 0$$

$$\frac{dX_i}{dz} \Big|_{z=0^-} - Pe_m X_{i,z=0^+} = -Pe_m X_{i,z=0^-} \quad \text{and}$$

$$Y_{sol} = Y_{sol,z=0^-} \quad Y_H = 1 - Y_{sol} \quad \Phi_L = \Phi_{L,z=0^-} / \Phi_{L0} \quad \Phi_G = \Phi_{G,z=0^-} / \Phi_{G0}$$

$$* \text{ at } z=1 \quad \frac{d\theta}{dz} = \frac{dX_i}{dz} = 0$$

The conditions at $z=0^-$ follow from the balances around the mixer. The dimensionless groups and variables are defined in the notation. The dimensionless temperature θ is defined in accordance to the definition used by Westerterp and Crombeen (1983).

The hydrogenation of TNT to TAT was chosen as a model reaction in our cocurrent upflow packed bed reactor. The kinetic rate equations presented in section 3 were used in the model calculations. The catalyst used in the reactor is a shell catalyst of 0.08wt% Pd on 4.2*4.2 mm porous cylindrical pellets. It was assumed that the carrier does not influence the kinetic parameters. An allowance is made however, for a difference in the activity of the catalysts. The term C_{cat} is replaced by $\eta n_0 \rho_b$, in which ρ_b is the packing density, η a scaling factor and n the parameter describing the catalyst activity.

Two important operating parameters are the hydrogen supply ratio α and the reactor pressure. The hydrogen supply ratio α is defined as the ratio of the number of moles of H_2 fed to the reactor to the number of moles of reactant fed to the reactor. If n_i is defined as the number of moles of the H_2 needed for complete conversion of all reactant into the desired product i , we can define a supply ratio α_i as: $\alpha_i = \alpha/n_i$. With this definition a value of $\alpha_i = 1$ means that the exact amount of H_2 is fed to the reactor necessary to convert all reactant into product i . For industrial purposes it can be advantageous to keep α_i , if i is the desired product, close to 1 to avoid hydrogen losses or high recycle ratios for unconverted hydrogen. On the other hand, if the value of α_i is chosen close to 1 the hydrogen partial pressure will drop to very low values because practically all hydrogen is consumed. Consequently the concentration of hydrogen at the catalyst surface will decrease, resulting in lower reaction rates and the need for larger reactors. Furthermore, the value of α determines how much hydrogen is present and thus how much solvent evaporates. Therefore, α also has a strong influence on the amount of heat that is absorbed by evaporation and thus on the temperature level in the reactor.

The reactor pressure determines the boiling point of the solvent and thus the maximum temperature that can be reached in the reactor.

Typical results from a model run are given in Fig. 6a-d. Some important effects can be noted from these figures:

- because more than one mole of solvent evaporates for each mole of H_2 consumed, the gas flow rate increases.
- the mole fraction of H_2 drops to low values near the end of the catalyst bed due to the evaporation of the solvent.

The influence of α_{TAT} and the reactor pressure on the fraction of the reaction heat that is absorbed and removed by evaporation of the solvent is given in Fig. 7.

A comparison between the temperature and conversion profiles measured during an experimental run and calculated with the model are given in Fig. 8a and 8b. The parameters that were varied to obtain a best fit between the model and the experiment are Pe_m , Pe_h and η . From this figure we conclude that the model can well describe the experimentally determined temperature and conversion profiles. Since the kinetic data available at the present time do not allow calculation of the composition of the liquid phase, no conclusions can be drawn concerning the selectivity to the reaction intermediates.

Figure 6: Calculated profile for the packed bed reactor model.

Model parameters: $Pe_m = 10$, $Pe_h = 1.5$, $P = 500$ kPa, $\alpha_{TAT} = 2.4$, feed temperature = 50 °C, adiabatic temperature rise = 170 °C, $Da = 5$.

a. conversion, b. temperature, c. dimensionless flows, and d. mole fraction of H_2 in the gas phase

Figure 7: Percentage of the reaction heat (at 100% conversion) that is used for evaporation of the solvent. Model parameters are: $Pe_m = 10$, $Pe_h = 1.5$, feed temperature = 55 °C and $Da = 3.5$.

Figure 8: Comparison between experimental data and calculated profiles. Model parameters are:

$Da = 6.95$, $\alpha_{TAT} = 2.4$, $\gamma = 5.38$, $\eta = 0.365$, $Pe_m = 5.0$, $Pe_h = 0.9$ and $St' = 760$.

Experimental data: $\phi_L = 1.06 \cdot 10^{-2}$ m/hr, $\phi_G = 1.08$ Nm/hr, $T = 50$ °C, $X_{TNT,0} = 0.00873$
adiabatic temperature rise = 170°C, $P = 490$ kPa and reactor length = 1 m.

a. temperature profile, b. conversion profile.

5. Discussion and conclusions

In a bird's eye view we presented some results of our program for the development for catalytic hydrogenation reactors for multi-product plants. We focussed on the kinetics of our model reactions, the modelling of our reactors and on the experimental verification of our models. We showed - both theoretically and experimentally - that for every exothermic reactions heat removal can easily be achieved by evaporation of a solvent. It is now possible to install the cooling area outside of the reactor. Temperature control can be easily achieved by adjusting the reactor pressure.

A disadvantage of the evaporation of the solvent is the subsequent decrease of the partial pressure of hydrogen. This may result in a decrease of the rate of reaction. The decrease in the partial pressure of hydrogen can be compensated for by increasing the reactor pressure, by using a larger excess of hydrogen or by employing larger interfacial areas.

The interdependence of all the operating variables of the reactors is so complex, that a catalytic hydrogenation reactor in a multi-product plant can not be run without the use of a mathematical model that describes its behaviour. The good agreement observed between our models and the experimental data gives us the confidence that our models will be adequate for this purpose.

The most difficult aspect is the acquisition of sufficiently reliable kinetic data. For fine chemicals the tremendous effort required to obtain these data with present methods is prohibitive. New methods have to be developed to this end. This will be a subject of further study, especially for the hydrogenation of TNT.

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Notation

2A-4NT	2-Amino-4-Nitrotoluene	
2A-4HAT	2-Amino-4-Hydroxylaminotoluene	
2N-4HAT	2-Nitro-4-Hydroxylaminotoluene	
4A-2NT	4-Amino-2-Nitrotoluene	
a_g	specific gas/liquid interfacial area	[1/m]
Bo	Bodenstein number	
C	concentration, [mol m ⁻³]	
C_{cat}	concentration of catalyst, [kg _{cat} m ⁻³]	
C_p	specific heat	[kJ/kg K]
C_{pG}	dimensionless specific heat of the gas phase defined as $\sum y_i C_{pi} / C_{pH_2}$	
D_{ax}	axial dispersion coefficient	[m ² /s]

Da	Damköhler number defined as $\eta_o \rho_b k_{1,S} L / \phi_{LO} X_{A,0}$
DANT	diamino nitro toluene DAT 2,4-diaminotoluene
DNHAT	dinitro hydroxylamine toluene
DNT	2,4-dinitrotoluene
HPR	Heat Production Rate, [W]
HWR	Heat Withdrawal Rate, [W]
k	mass transfer coefficient, [m s ⁻¹]
k _i	reaction rate constant, [mole s ⁻¹ kg _{cat} ⁻¹]
K	adsorption constant, [m ³ mol ⁻¹]
L	reactor length [m]
M	molar mass [kg/kmol]
M _G	dimensionless molar mass of the gas phase defined as $\sum y_i M_i / M_{H_2}$
n _i	number of moles of hydrogen needed for complete conversion of 1 mole of reactant to component i
P	dimensionless pressure defined as P/P _s
P _i	vapour pressure of pure species i, [Pa]
P _R	total pressure [N/m ²]
P _s	Standard Pressure
Pe _M	Peclet number for heat dispersion
Pe _M	Peclet number for mass dispersion
θ	relative adsorption strength
r	rate of conversion, [mole s ⁻¹ kg _{cat} ⁻¹]
R _i	dimensionless reaction rate: $r_i / \rho_b k_{1,S}$
R _{prod,i}	dimensionless production rate of component i
St _{mod,i}	modified Stanton number (also called NTU) [K]
T	temperature
T _s	standard temperature
TAT	2,4,6-triaminotoluene
TNT	2,4,6-trinitrotoluene
V _{r,l}	liquid volume in the reactor, [m ³]
x _{i,l}	liquid mole fraction of species i
X _i	dimensionless mole fraction of component i: $x_i / x_{A,0}$
y _i	mole fraction of component i in the gas phase
Z	dimensionless axial coordinate = h/L
α	hydrogen supply ratio: ratio of the number of moles of hydrogen fed to the reactor per unit of time to the number of moles of TNT fed to the reactor per unit of time
α _i	hydrogen supply ratio based on component i
β	ratio of heat capacities of the gas and the liquid phase in the feed
γ	molar ratio of methanol to hydrogen in the feed
ΔH _{ev}	enthalpy of evaporation [kJ/mole]
ΔH _{r,i}	reaction enthalpy [kJ/mole of component i converted]
ΔH _{vap}	heat of evaporation, [kJ mole ⁻¹]
ΔT _{ad,i}	dimensionless adiabatic temperature rise for reaction i
ΔT _{ev,i}	dimensionless heat effect of evaporation for component i
ε _G	hold up of the gas phase [m ³ gas/m ³ reactor]
ζ _{H₂,ζ}	hydrogen conversion, defined as the amount of hydrogen consumed by the reaction over the amount required for complete conversion
η	catalyst activity
η _o	scaling factor from the Pd on Carbon slurry catalyst to the Pd on Alumina catalyst used in the packed bed reactor: 1.28×10^{-3}
θ	relative surface concentration
Θ	dimensionless temperature: $-(E_1/RT_s)(1 - T/T_s)$
λ _{eff}	effective axial thermal conductivity [W/m ² K]
ν _{H₂}	stoichiometric coefficient of hydrogen of the overall reaction
ρ	density [kg/m ³]
ρ _b	specific catalyst mass [kgcat/m ³ reactor]
φ	molar flow rate per unit of cross sectional area of the reactor [kmol/m ² s]
φ	dimensionless flow: ϕ / ϕ_o
φ _{H₂in}	feed rate of hydrogen gas, [mole s ⁻¹]
φ _{H₂out}	flow rate of the hydrogen off-gas, [mole s ⁻¹]
φ _{v,l}	total liquid feed rate to the reactor, [m ³ s ⁻¹]

sub- and super-scripts

ax	in axial direction	sol	solvent
b	referring to catalyst bed	G	gas
cat	catalyst, catalyst feed stream	H	hydrogen
cf	cold feed streams	L	liquid
cond	condensate returned	O	feed conditions
ev	evaporation of the solvent	S	referring to standard conditions
feed	reagent feed stream	S	solvent, methanol
l	liquid	W	reaction water
o	initial		