

Development of hydrogenation reaction using parallel processing

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INTRODUCTION

From test tube to production – rapidly. That is the objective of most chemical companies and realisation of this objective consists of two parts: speed so that much data can be generated quickly and quality so that the data is good enough to eliminate the need for extensive piloting.

The issue of parallel processing (or high throughput) has certainly been tackled with some success and a range of tools are available covering many process applications. Now effort is also being made in generating data that is likely to be scalable and in this article we will investigate how heterogeneous hydrogenations from 8 x 10 ml vessels can be scaled up without any problem by comparing the results with data from 100 and 1000 ml vessels.

PARALLEL HYDROGENATION

Governing Variables

The rate of hydrogenation in heterogeneous catalytic systems depends on large number of variables. Typically, the substrate to be hydrogenated is dissolved in a solvent and the proposed reaction with hydrogen is catalysed by small amounts of a finely divided metal coated to a support (such as carbon). To promote reaction, the hydrogen must first dissolve in the solvent; the dissolved gas together with the substrate must then come into contact with the catalyst so that product can be formed – at a rate determined by the kinetics. Fresh liquid must be continuously exposed to catalyst surface by agitation so the further reaction can occur.

The rate at which hydrogenation occurs depends on the relative rates of these steps – solubility, agitation and kinetics (hence catalyst choice and process conditions) – the slowest will govern the overall rate.

For a given solvent, solubility is favoured by increased pressure and reduced temperature. Rate of reaction on the other hand is favoured by higher temperature – as indicated by the Arrhenius relationship between temperature and rate. Given the availability of hydrogen and



HP Chemscan (10 ml)



HP auto-MATE (100 ml)



SIMULAR
reaction calorimeter (1000 ml)

Figure 1 – The three experimental systems used for hydrogenation studies

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Figure 2 – Internals for the three reactor types studied

good agitation (i.e. rapid exposure of fresh catalyst to liquid), the reaction rate will be governed by kinetics. Under these conditions, changes in temperature, pressure or the amount of catalyst will affect the reaction rate. In fact the system will behave very much like a homogeneous one – allowing the chemist to alter the process conditions to optimize important parameters such as selectivity and yield.

On the other hand, if the mixing is poor, changes in process conditions will have no influence on the rate – the process being said to be mixing (or mass transfer) limited. This is not an ideal region in which to operate as there is very little scope for the chemist to influence the process.

It is important that conditions under which experimental data is generated are known so that if the process is scaled up, any differences in the results can be correctly interpreted.

Experimental Evaluation

In a recent study by HEL, laboratory scale equipment covering two orders of magnitude in volume was compared: High Pressure Chemscan 10 ml, High pressure auto-MATE 100 ml, and the SIMULAR reaction calorimeter 1000 ml. A systematic study was performed to demonstrate the consistency of data across this wide range. The equipment in question is shown in Figure 1.

To give a better idea of the difference in scales in the intervals of the vessels, stirrer, baffle etc are shown in Figure 2.

In order to compare hydrogenation data, a simple approach was used involving only the time to reaction (either time to completion – especially for fast reactions – or else up to some arbitrary extent, such as 50%). This can be determined easily if the hydrogen uptake rate and/or heat release are obtained from experiments.

The reference reaction used to make the comparisons was reduction of nitrobenzene with hydrogen using a 1% palladium on carbon catalyst. At moderate conditions, this reaction takes around 60 minutes for completion.

The equipment used in this study was

fully instrumented with control of agitation, temperature and pressure. Most importantly for hydrogenation reactions, the uptake of hydrogen was evaluated in real time – thus the broad results were available quickly and reliably. Typical data from the smallest scale (10 ml with the HP Chemscan) is shown in Figure 3. This is a plot of the hydrogen uptake as a function of time for different catalyst loadings.

Comparison of Systems

The ideal situation is for the mixing “rate” to exceed the kinetic rate – so that the process is not mass transfer limited. The first objective is to ascertain what is controlling.

In Figure 4, reaction time is plotted against catalyst loading from a whole range of experiments based on a variety of stirrer types and on reactor sizes that differ by two orders of magnitude; the results have been produced over several months on many different vessels so can be considered to be a

good representation of the equipment performance. The data (at 40°C and 6.9 bar) shows a classic trend – as the catalyst amount is increased, the reaction time is reduced (i.e. the rate is increased). This indicates a kinetic controlled region.

Eventually, when the catalyst loading is sufficiently high, there is no reduction in reaction time – hence, the process is mass transfer limited.

These two regions are quite distinct in Figure 4. At a catalyst concentration of 4 g l⁻¹ and above, the reaction time does not reduce with increased catalyst loading, indicating a mass transfer limited reaction. At lower catalyst concentrations, the reaction time increases with reducing catalyst loading, indicating that the process is kinetic controlled.

The data in Figure 4 plus additional results at 60°C, in other equipment are combined in Figure 5; another classic check for kinetic control becomes clear: the

40°C data is quite separate from the 60°C data in the kinetic controlled region but the two data sets merge at the high catalyst loading.

CONCLUSIONS

Heterogeneous hydrogenation reactions can be performed in parallel and quantitative data can be generated in real time – as the reaction proceeds. This is an important component of parallel processes development as it allows rapid evaluation of the results.

Equally, important, it has been shown that with well designed and fully instrumented reactors, performance at different scales – varying by two orders of magnitude – can be directly compared. This shows that for the three systems studied – HP Chemscan, HP auto-MATE and SIMULAR, the data is perfectly consistent.

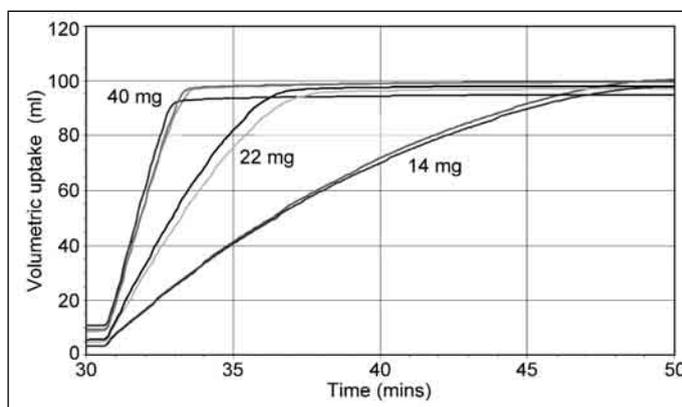


Figure 3 – Hydrogen uptake with time for HP Chemscan, for different catalyst amounts

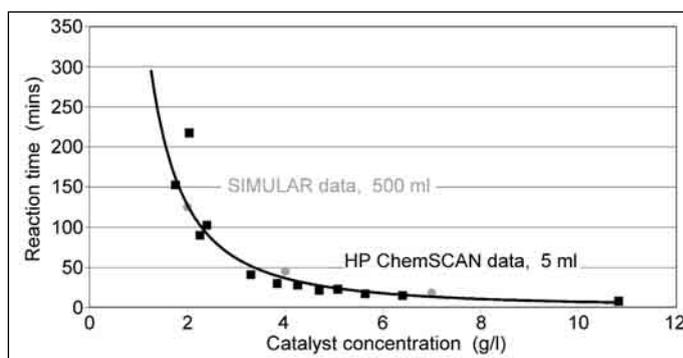


Figure 4 – Comparison of experiments based on different reactor sizes: 5 ml (Chemscan) and 500 ml (SIMULAR)

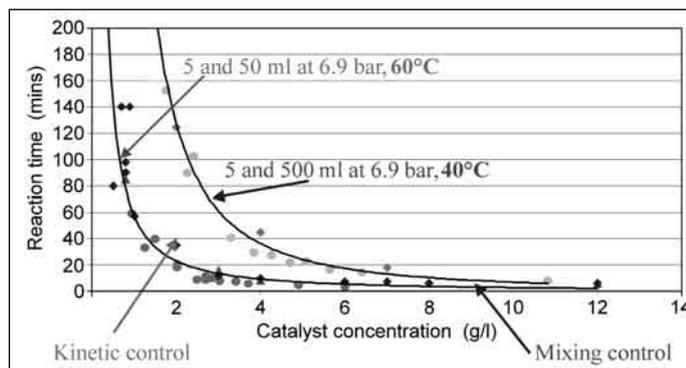


Figure 5 – Combined data at 40°C and 60°C at different scales