Investigating Hydrogenations at Different Catalyst Loadings using the ChemSCAN

Dr. Sina Ehsani, Joseph Willmot

H.E.L Group, 9-10 Capital Business Park, Manor Way, London, WD6 1GW

Abstract

In this study, a ChemSCAN is used to investigate the hydrogenation of nitrobenzene with a range of Pd/C catalyst loadings ranging from 4.0 mg to 9.3 mg. The experimental results showed that the hydrogenation reaction rate increases as the amount of catalyst in the reactor increases. The total volumetric uptake of this reaction was not affected by the amount of catalyst in the reactor and was in good agreement with the theoretical values. The results highlight how a ChemSCAN can be used for other similar catalytic studies.

Introduction

The ChemSCAN is a bench-top, automated parallel catalyst screening reactor system. It was designed for the rapid screening of reactions and catalysts at high pressures. The eight-reactor variant supports reactors ranging from 16 ml to 50 ml. The four-reactor variant can support direct agitation and reactors up to 500 ml. The independently controlled reaction zones are beneficial for design of experiment (DoE) studies and are found in other products such as the BioXplorer and PolyBLOCK 8. Typically, stainless steel (SS316) or hastelloy (HC276) reactors are used. The ChemSCAN operates at temperatures ranging from -40 ˚C (when used with a suitable chiller circulator) to 250 ˚C, and pressures up to 200 bargs. Each stirred reactor is independently controlled and monitored, allowing screening tests to be carried out concurrently, accelerating development time.

Aniline is a primary aromatic amine commonly used in the manufacture of polymers, rubber, agricultural chemicals, dyes and pigments, pharmaceuticals, and photographic chemicals [1]. The hydrogenation of nitrobenzene using precious metal catalysts such as copper (Cu), palladium (Pd), and platinum (Pt) is an important aniline synthesis route [2]. Palladium-supported catalysts are one of the most important groups of heterogenous catalysts, widely used in hydrogenation reactions [3]. Catalyst supports enhance the efficiency of the supported metals by acting as a catalytically active center [4]. Due to their large surface area and low intrinsic chemical activity,

activated carbons are frequently used as supports for noble metals [5]. The activated Pd/C materials are used as efficient catalysts for the hydrogenation of nitrobenzene [6].

In this study, the ChemSCAN was used to measure the volumetric uptake of hydrogen gas (H_2) during the hydrogenation reaction of nitrobenzene over a catalyst (palladium supported on activated carbon, Pd/C) loading range of 4.0 mg to 9.3 mg. The measured volumetric uptakes obtained from the ChemSCAN for each of the reactors were compared to the theoretical values.

Materials and Method

For this characterization, a ChemSCAN was used under standard laboratory conditions within a fume hood. A schematic of the ChemSCAN with eight reactor zones is shown in *Figure 1*.

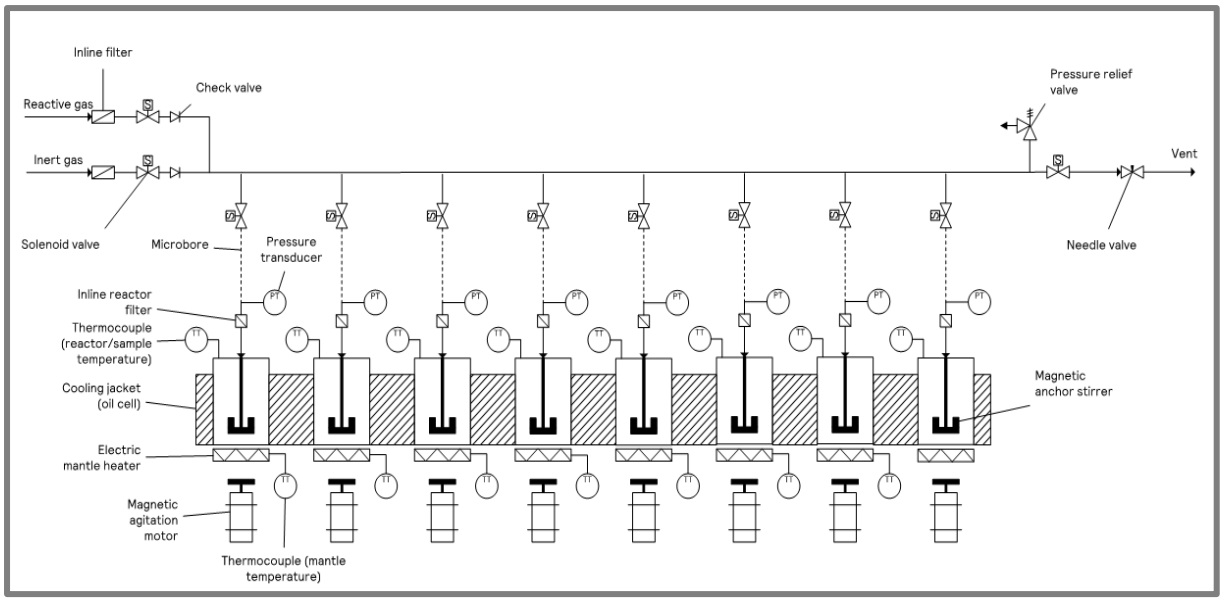

Figure 1: A schematic of HP ChemSCAN with 8 reactor zones.

This study aimed to investigate the catalytic hydrogenation of nitrobenzene (Sigma-Aldrich Code: N1,095-0) using 1% Palladium supported on activated carbon (Sigma-Aldrich Code: 20,567-2), under various catalyst loading levels. 1-Decanol (Sigma-Aldrich Code: 15,058-4) was selected as the solvent due to its low vapor pressure, high boiling point, and miscibility with nitrobenzene.

A solution of 4.75 mass% nitrobenzene was prepared by mixing 20.0 grams of nitrobenzene in 401.1 grams of 1-decanol. The required amount of the sample solution (nitrobenzene-decanol) along with the desired amount of catalyst (Pd/C) were added to each of the reactor vessels.

Table 1 shows the weight of the sample and the weight of the catalyst add to each of the reactors. All these reactions were performed at a constant temperature of 30 ˚C and a constant agitation speed of 500 rpm. A schematic of the 16 mL vessels is shown in *Figure 2*. The full experimental procedure is described in *Appendix B.*

Reactor Number	Weight of Sample (g)	Weight of Catalyst (mg)
1	4.23	9.30
2	4.23	6.80
3	4.25	5.50
4	4.22	4.00
5	4.24	9.10
6	4.22	8.50
7	4.23	5.80
8	4.22	4.80

Table 1: The amount of sample (nitrobenzene-decanol) and catalyst (Pd/C) used in each reactor.

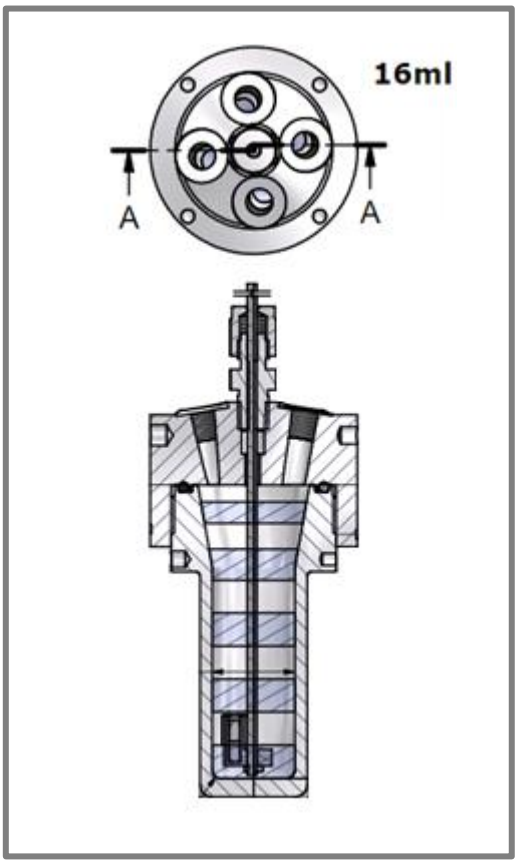

Figure 2: A schematic of the 16 mL stainless-steel reactor vessel.

Results and Discussion

The results of the hydrogenation experiments at various catalyst loadings (ranging from 4.0 mg to 9.3 mg) are shown in *Figure 3*. It should be noted that all volumetric uptake values, regardless of the amount of catalyst used, are within a maximum variation of 4.4 % of theoretical values. This demonstrates that the amount of catalyst only affected the reaction rate, not the final reaction or overall volumetric uptake.

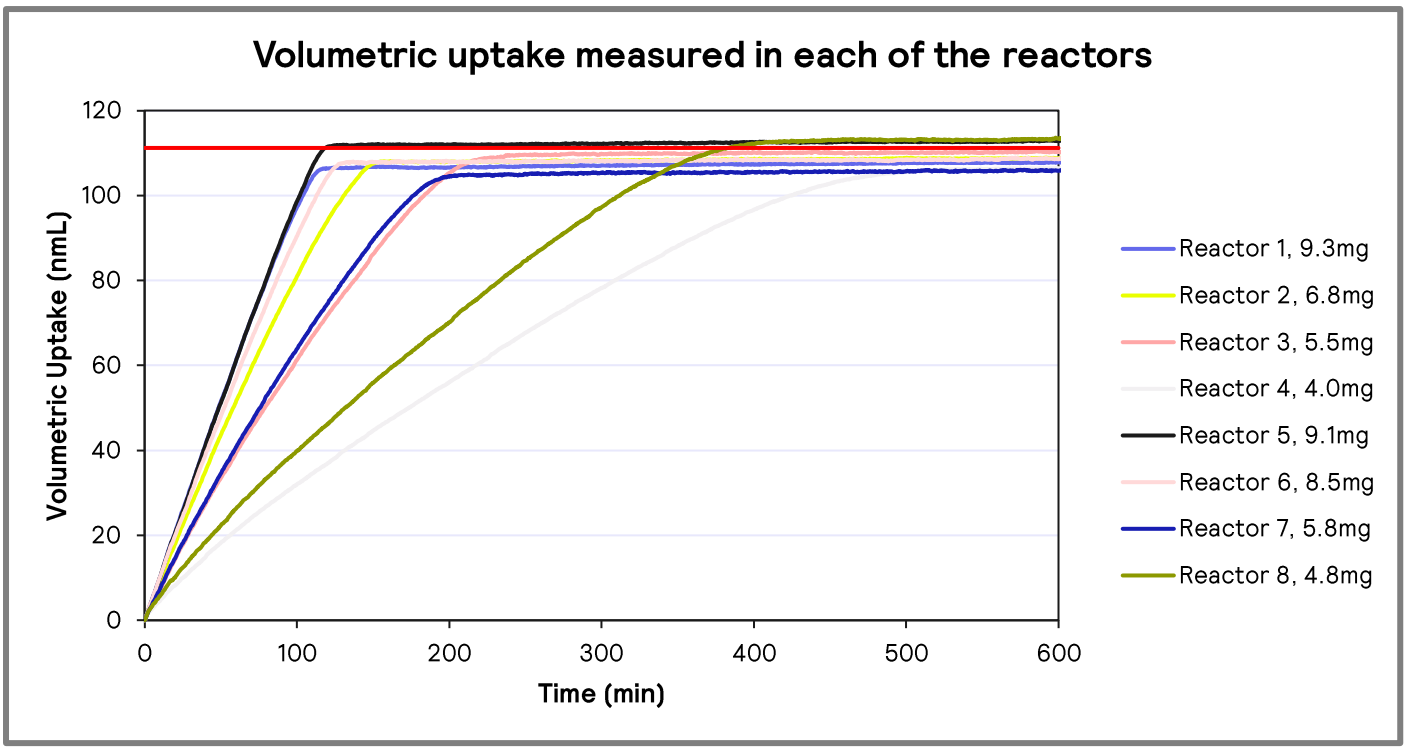

Figure 3: Volumetric uptake measured in each of the reactors.

Figure 3 also demonstrates that as catalyst loading increases, the rate of the hydrogenation reaction increases. That is, a catalyst loading of 9.3mg would result in the fastest hydrogenation process, which would be expected.

Table 2 shows the measured volumetric uptake in each of the reactors. It can be seen that the total volumetric uptakes in different reactors are similar to each other, indicating the degree of measurement precision obtained using the ChemSCAN. The measured volumetric uptakes have a mean value of 109.8 nmL and a standard deviation (σ) of 2.8 nmL. Considering there is approximately 0.20g of nitrobenzene in each reactor, the theoretical volumetric uptake in each reactor is 111.2 nmL (Appendix A – Sample Calculations). Therefore, the average measured volumetric uptake obtained using HP ChemSCAN is 98.8% of the theoretical value.

Reactor Number	Weight of Catalyst (mg)	Measured Volumetric Uptake (nmL)
1	9.3	108.4
2	6.8	109.2
3	5.5	110.9
4	4.0	106.8
5	9.1	113.5
6	8.5	109.4
7	5.8	106.5
8	4.8	113.9

Table 2: Measured volumetric uptake in each of the reactors.

Table 3 compares the measured volumetric uptake in each reactor to the theoretical (normalized) volumetric uptake. The results in *Table 3* show that the minimum difference between the measured volumetric uptake and the theoretical volumetric uptake is obtained in reactor #3 of 0.6 %. In contrast, reactor #7 has the maximum difference of 4.4% to theoretical values.

Reactor Number	Measured Volumetric Uptake (nmL)	Theoretical Volumetric Uptake (nmL)	Percent Difference (%)
1	108.4	111.2	2.6
2	109.2	111.1	1.7
3	110.9	111.6	0.6
4	106.8	111.0	3.9
5	113.5	111.5	1.7
6	109.4	110.9	1.4
7	106.5	111.3	4.4
8	113.9	111.0	2.5

Table 3: A comparison between the measured volumetric uptake and the theoretical volumetric uptake.

Conclusions

The purpose of this study was to investigate the hydrogenation reaction of nitrobenzene with different catalyst loadings using the ChemSCAN. Different amounts of the catalyst, palladium supported on activated carbon, were added to each of the eight reactors, and the volumetric uptakes were measured using the ChemSCAN. These experiments demonstrated that an increase in the amount of catalyst inside the reactor results in a faster hydrogen gas (H_2) uptake, presumable due to a quicker hydrogenation reaction.

In addition, the results demonstrated that the total hydrogen volumetric uptake is not affected by the amount of catalyst inside the reactor. Rather, the amount of the catalyst inside the reactor would only affect the reaction kinetics.

A comparison between the measured volumetric uptakes using the ChemSCAN and the theoretical uptakes calculated using the ideal gas law demonstrated that the ChemSCAN can be used to accurately characterize hydrogenation reactions. This is essential information when screening catalysts, as the ChemSCAN can easily and readily differentiate the performance of each set of reaction conditions. For example, defining optimal reaction conditions by keeping the chemistry the same and changing the reaction parameters in a DoE study.

References

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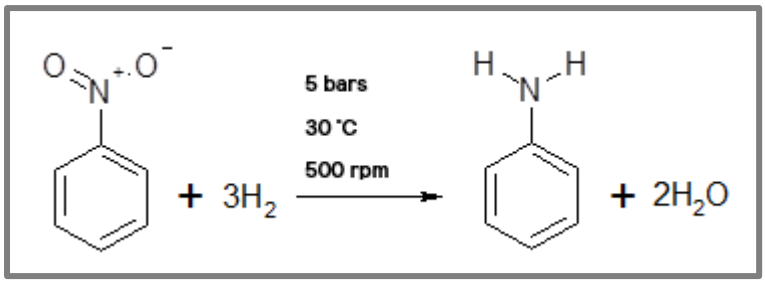
Appendix A

Reaction



Sample Calculations

Mass of nitrobenzene in the original solution: $20.0\ \mathrm{g}$

Density of nitrobenzene: $1.20\ \mathrm{g/mL}$

Volume of nitrobenzene in the original solution: $\frac{20.0\ \mathrm{g}}{1.2\ \frac{\mathrm{g}}{\mathrm{mL}}} = 16.7\ \mathrm{mL}$

Volume of the nitrobenzene-decanol mixture: $500.0\ \mathrm{mL}$

Volume of 1-decanol: $500.0 - 16.7 = 483.3\ \mathrm{mL}$

Density of 1-decanol: $0.83\ \mathrm{g/mL}$

Mass of 1-decanol: $0.83\ \frac{\mathrm{g}}{\mathrm{mL}} \times 483.3\ \mathrm{mL} = 401.1\ \mathrm{g}$

Mass fraction of nitrobenzene in the original solution: $\left(\frac{20.0\ \mathrm{g}}{401.1\ \mathrm{g}+20.0\ \mathrm{g}}\right) \times 100\ \% = 4.75\ \%$

Weight of sample in Reactor #1, m_1: $4.23\ \mathrm{g}$

Weight of nitrobenzene in Reactor #1: $4.23\ \mathrm{g} \times 4.75\% = 0.20\ \mathrm{g}$

Molar Mass of nitrobenzene: $123.11\ \frac{\mathrm{g}}{\mathrm{mol}}$

Number of Moles of nitrobenzene in Reactor #1: $\frac{0.20\ \mathrm{g}}{123.11\frac{\mathrm{g}}{\mathrm{mol}}} = 1.63 \times 10^{-3}\ \mathrm{moles}$

In this hydrogenation reaction, per 1 mole of nitrobenzene, 3 moles of hydrogen gas are required, therefore:

Number of Moles of hydrogen in Reactor #1: $(1.63 \times 10^{-3}) \times 3 = 4.90 \times 10^{-3}\ \mathrm{moles}$

Standard Volumetric Uptake for Solution:

where, $\mathrm{P} = 10^5\ \mathrm{Pa}$, $\mathrm{T} = 273.15\ \mathrm{K}$, $\mathrm{R} = 8.314\ \frac{\mathrm{m^3 \times Pa}}{\mathrm{K \times mol}}$

Based on the ideal gas law, $\mathrm{V} = \frac{\mathrm{nRT}}{\mathrm{P}} = \left(\frac{4.90\times10^{-3}\times8.31\times273.15}{10^5}\right)\mathrm{m^3} \times \frac{10^6\ \mathrm{mL}}{1\ \mathrm{m^3}} = 111.2\ \mathrm{nmL}$

Temperature Control

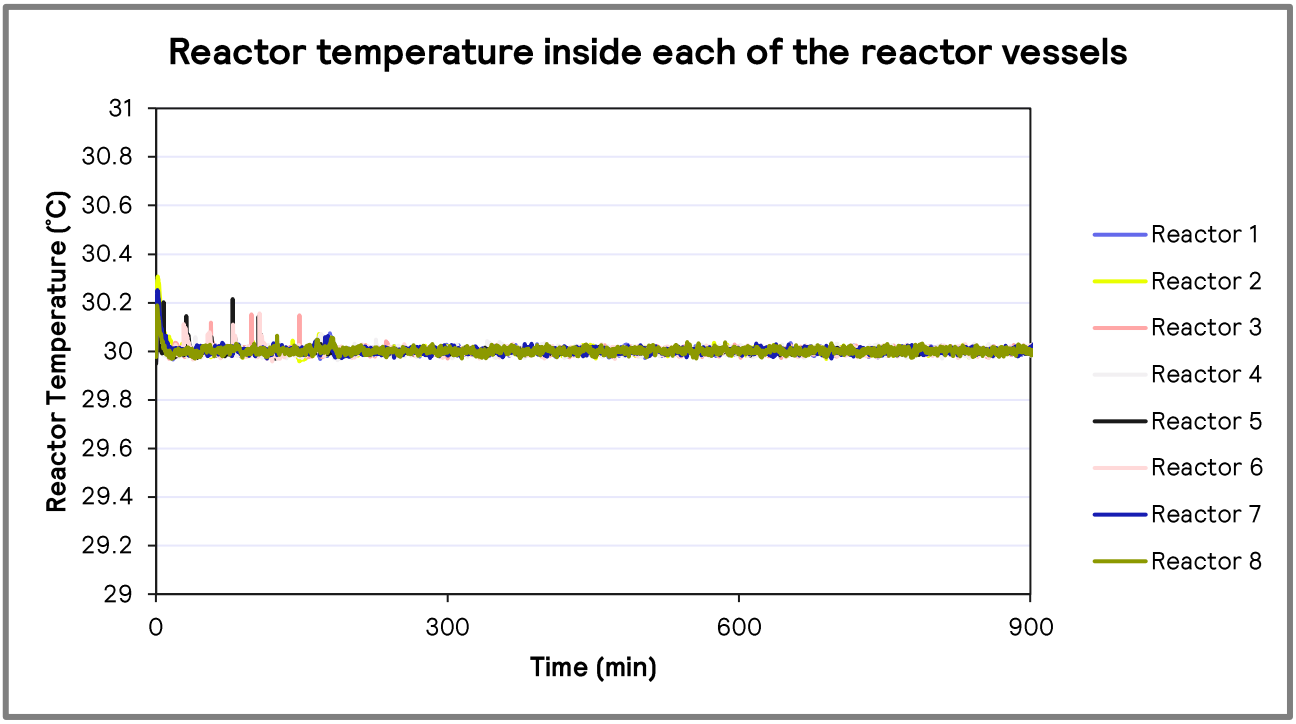


Figure A1: Reactor temperature inside each of the reactor vessels during the hydrogenation reaction.

Agitation Control

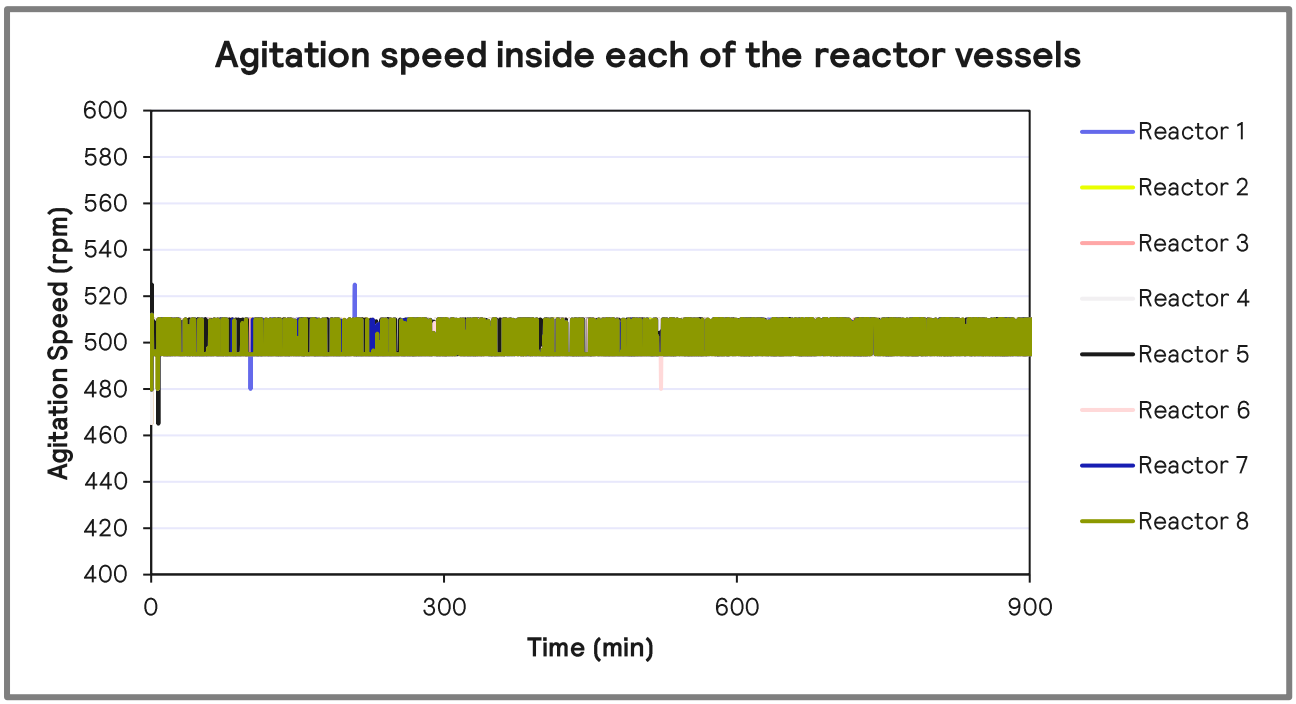


Figure A2: Agitation speed inside each of the reactor vessels during the hydrogenation reaction.

Appendix B – Experimental Procedure

Chemicals

- Nitrobenzene 99% (Sigma-Aldrich Code: N1,095-0)
- 1-Decanol (1 decyl alcohol) 99% (Sigma-Aldrich Code: 15,058-4)
- 1% Pd Catalyst on activated carbon (Sigma-Aldrich Code: 20,567-2)
- Hydrogen gas 99.9%

4% w/v Nitobenzene Solution Preparation

To prepare 500 cm^3 of the stock nitrobenzene in 1-decanol solution:

- Weighed out 20 g of nitrobenzene into a 500 cm^3 glass volumetric flask.
- Added 1-decanol to the 500 cm^3 mark.
- Inserted stopper and shake vigorously to mix.
- Transferred the solution to an appropriately labelled container.

Procedure

- Checked that there is adequate bottle pressure and inventory in the hydrogen supplies.
- Ensured that the reactor stirrer/magnets are clean and spin easily.
  NOTE: It is good practice to take them off the stirrer shaft and fully clean them after every test.
- Placed the required amount of the 1 % Pd on activated carbon catalyst in each reactor.
- Using a 5 cm^3 measuring pipette, added 5 cm^3 of the previously prepared nitrobenzene solution to the reactor.
- Assembled the reactors. Ensured the O-rings are clean, in good condition, and lightly greased. Used C spanners to tighten and seal the reactors.
- Write/configure a plan

NOTE: To ensure good results, three inert and reactive purges are recommended (two as a minimum). **If this is not done thoroughly, then air may still be in the reactor headspace at the start of the reaction, and as a result, the reaction will partially or totally stall.**