APPENDIX A. Experimental Detail for Reaction Study

The trickle bed reactor facility is shown schematically in Figure 80. The inner diameter of the reactor was 0.05 m. Pre-purified hydrogen from a rack of two cylinders was fed into the reactor at a controlled flow rate. Liquid was charged into the feed tank which was subsequently pressurized with nitrogen. The liquid feed was made up of α-methyl styrene, AMS, (99%, Aldrich) in hexane (95%, Aldrich) as solvent with AMS concentrations from 1 to 9 % v/v (70 to 680 mol/m^3). The AMS concentration was determined by a Gas Chromatograph (Varian) that was pre-calibrated for a range of AMS concentrations between 7.7 and 680 mol/m^3. Analytical reproducibility was within approximately 2% on AMS concentration. The pressure difference between the feed tank and the reactor was kept at 340 kPa and was used to supply liquid into the reactor. The pump was used only to circulate the feed prior to operation in order to ensure a uniform feed concentration. Experiments were conducted for liquid velocities ranging from 1.4 to 4.4 mm/s (maximum liquid velocity used for pulsing pre-wetting was 9.4 mm/s) and the gas velocity was set at 3.4 mm/s at 790 kPa for all the runs (hydrogen is therefore in stoichiometric excess for all experiments except the most severely gas limited condition – excess between 4 and 1100 % depending on the liquid velocity and concentration). A differential pressure transducer (Validyne DP15-30) was used to measure the pressure drop over the entire reactor (i.e. catalyst bed, glass bead beds, the entrance and the exit). A thermocouple capable of registering intervals of 0.5 degrees Centigrade is located at the exit of the bed. The liquid is funnelled at the bed exit by a metallic sieve and the thermocouple is placed in the liquid stream. The feed was always introduced at 19 degrees Centigrade. The column itself is insulated with ceramic material to reduce heat losses to the environment.

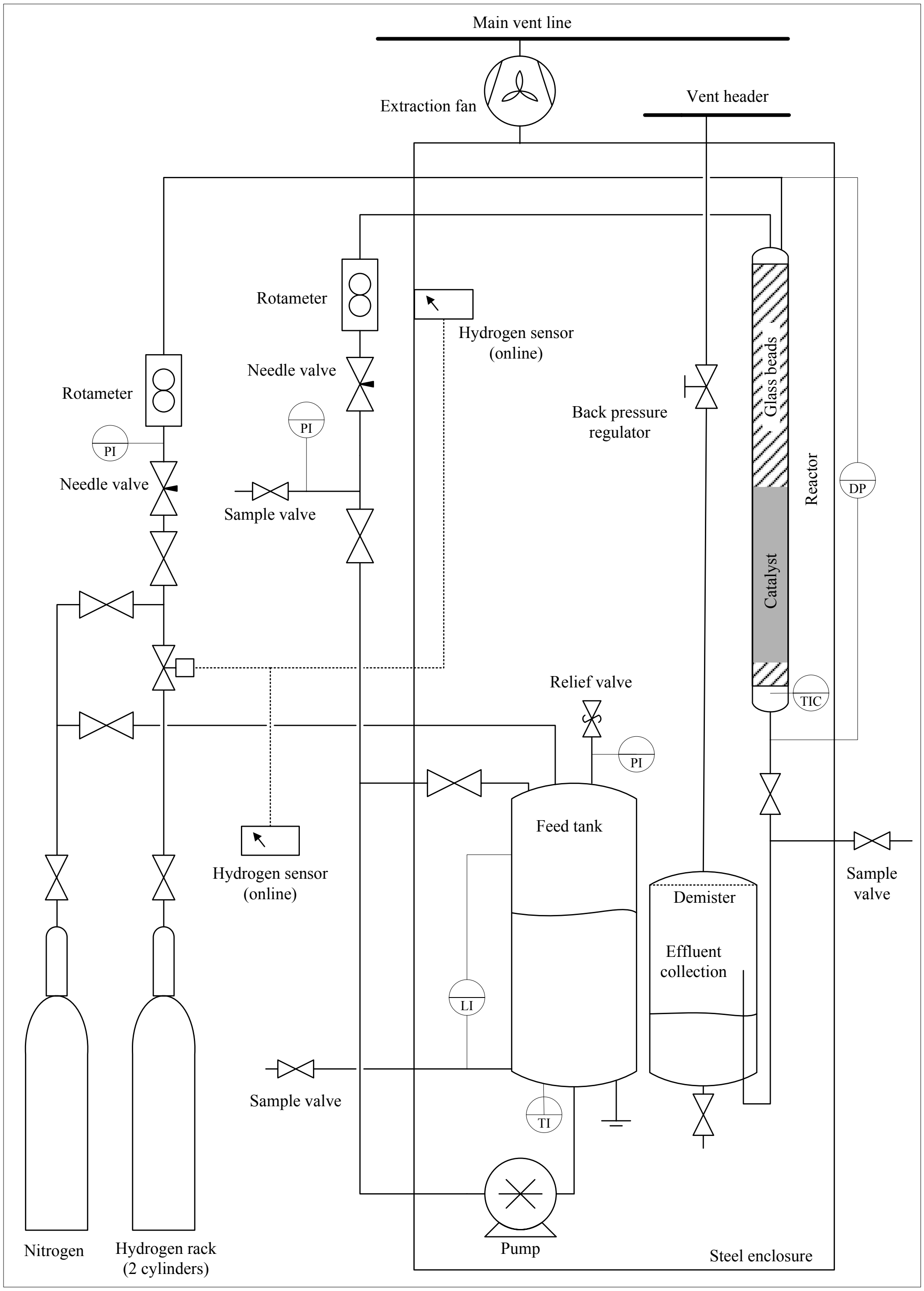

Figure 80. Experimental setup for reaction study

A heater was used to heat the catalyst for activation purposes, but was turned off during the reaction run. A bed of glass beads at the reactor entrance ensures that the liquid is saturated with hydrogen prior to it entering the catalyst bed. This was confirmed by estimating the hydrogen concentration in the liquid at the catalyst bed entrance by assuming plug flow of the liquid and a gas-liquid mass transfer rate characterized by a volumetric coefficient. Using either the Goto & Smith (1975) or the Larachi et al. (1999) correlation to estimate the coefficient, the concentration at the catalyst bed entrance was determined to be within 1% of the saturated concentration. The glass beads also serve as a distributor for the gas and liquid phases prior to it entering the catalyst bed. All experiments reported here were conducted at 790 kPa absolute pressure. Although it is possible to increase γ by operating at a lower pressure, there is indication that the intrinsic kinetics is dependent on the pressure (Khadilkar, 1998) which makes comparison between the gas- and liquid limited runs difficult. At 800 kPa the kinetics are usually taken to be dependent on both reactant concentrations (Khadilkar, 1998). Operating at a single pressure for all the runs eliminates any hydrodynamic differences that might have occurred due to changes in the pressure. At this pressure, γ ranged between 0.48 and 4.6 for the different AMS concentrations. For each condition, liquid samples were taken at intervals of 5 minutes. Steady state was assumed once the pressure drop, temperature rise and conversion had all stabilized. Steady state was usually achieved in about 10-15 minutes but sampling continued to 25 minutes in each case.

The catalyst bed height was either 337 mm or 148 mm depending on the degree of liquid limitation. That is, it was necessary to reduce the bed height of the cases where $\gamma < 2$ in order to keep the conversion in the measurable range (10 - 90%). For the shortest bed, the bed height was approximately 70 times the equivalent particle diameter (1.9 mm).

The catalyst was 1% Pd egg-shell on porous cylindrical alumina extrudate (Engelhard) with diameter 1.5 mm and length 4.3 ± 1.8 mm (equivalent diameter 1.9 mm, particle to column diameter ratio approximately 26). It was activated in situ at 120 ^{o}C for 5 hours with hydrogen flowing at the operating velocity. After activation the catalyst activity decreases before it stabilizes (compare Wu et al., 1996). Consequently, it was necessary to operate the reactor for a prolonged period (approximately 9 hours) at a liquid velocity of 3.4 mm/s in the Kan-Liquid mode in order to reach stable operation. During this time the activity was monitored by sampling the reactor effluent intermittently and calculating the conversion. After an initial decrease the conversion stabilized at approximately 6 hours. As a final check, the conversion of a Kan-Liquid mode experiment at the end of the experimental program yielded approximately the same conversion as the initial stabilization run, thereby confirming that the catalyst was stable throughout the experimental program.

Additional experimental precautions were taken as follows:

- The absence of homogeneous side reactions was confirmed by operating the setup with only glass beads (no catalyst) loaded into the reactor. No reaction was detected. A polimerization inhibitor (p-tert-butylcatechol) present in the feed is likely to be responsible for the absence of oligomeric or polymeric activity (Meille et al., 2002).
- At the reaction conditions, the vapour pressures of AMS, cumene and hexane are well below 30 kPa (Watson & Harold, 1993). Therefore there is little expectation of liquid vaporization.
- The presence of hydrodynamic effects on the reaction rate was confirmed by performing two liquid limited reaction experiments. In the first, 158 grams of catalyst were loaded and the liquid superficial velocity was set to 2.7 mm/s (yielding a weight hourly space velocity of 0.12). The conversion was 44%. Another bed was then packed with 500 grams of catalyst and the liquid velocity was set to 8.4 mm/s (again the weight hourly space velocity was 0.12). The conversion for this run was 81%. For a chemically controlled reaction rate, the conversion is a function of the space velocity and not the superficial velocity (as shown in Wu et al., 1996). These two experiments therefore show that

hydrodynamic effects are present – the high superficial velocity in the second run facilitates transport to the catalyst and therefore yields a higher conversion.

Since hysteresis is involved, the exact operating procedure needs to be reported. The catalyst was saturated internally with feed by leaving the reactor flooded with feed overnight. Due to capillary action the catalyst interior is expected to remain filled throughout the experiments. The bed was then drained with the gas flowing at the operating velocity for 15 minutes. The liquid was introduced at the lowest velocity and steady state was achieved. After the last steady state sample had been taken, the liquid flow rate was increased to the next higher setting. This was repeated until the highest setting had been completed (i.e. the Levec mode). The liquid flow rate was then increased to 9.4 mm/s (pulsing flow) for 20 seconds and reduced to the 4.4 mm/s. After that operating condition had been completed, the liquid flow rate was reduced to the next lowest setting and so on until the Kan-Liquid mode had been completed. Several of the runs (five in each mode) were repeated in order to determine the reproducibility of results. These runs were conducted by establishing a Levec point (i.e. increasing the flow rate from zero to the operating velocity, e.g. 1.9 mm/s), then increasing the flow rate to 9.4 mm/s (pulsing) and then decreasing it directly back to 1.9 mm/s (i.e. the Kan-Liquid point). The repeat runs are shown on the figures in the results section. In most instances the reproducibility was within a few percent. Although there were differences in a limited number of cases, the trends of which pre-wetting mode yielded higher conversions were never reversed.

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