Heterogeneous Catalytic Hydrogenation of Polystyrene in Liquids Expanded with Supercritical Fluids

Cain, N. A., Carbonell, R. G., Kiserow, D. J., Roberts, G. W.[*]

North Carolina State University, Department of Chemical & Biomolecular Engineering, Kenan CO$_2$ Center, Campus Box 7565, Raleigh, NC 27695.
Fax: 001-919-513-1655; contact e-mail: *groberts@ncsu.edu*

1.   Introduction

The use of organic solvents expanded with supercritical fluids (ScF) as chemical process media has been investigated for more than two decades. During the past 7 years, ScF/solvent combinations have received increased attention with recognition of their versatility as fluid phase chemical reaction solvents [1]. ScF expanded liquids often provide an otherwise difficult to achieve range of solute solubilities obtained by mixing a good solvent (the organic liquid) with a much poorer solvent (the ScF). The enhanced transport properties introduced by the addition of a ScF can be exploited to improve the rates of reactions that must be carried out under mass transfer controlled conditions. As examples, solvents expanded by supercritical and subcritical ScFs have been used in homogeneous catalytic oxidations [2], heterogeneous catalytic oxidations [3], and heterogeneous hydrogenations [4].

A pronounced example of mass transfer control during reaction is offered by the heterogeneously catalyzed hydrogenation of unsaturated polymers in organic solvents. The unmanageably high viscosities in the reactions can be mitigated by the addition of a ScF co-solvent. Judicious choice of the ScF can simultaneously give increased liquid-phase hydrogen concentrations so the mixed solvent system can be doubly beneficial for increasing hydrogenation rates. Additionally, ScF based mixed solvents can often penetrate otherwise inaccessible pores in the solid catalyst.

Recently, the hydrogenation of polystyrene (PS) has been investigated in decahydronapthalene (DHN) expanded by supercritical carbon dioxide (scCO$_2$) [4]. Although, scCO$_2$ showed improvements on the rate of hydrogenation, carbon monoxide (CO) was produced via the reverse water gas shift reaction (RWGSR). To alleviate the formation of CO, propane (C3) has been explored as an alternative ScF cosolvent for the hydrogenation of PS. Two different reactor configurations were employed to investigate the influence of C3 on the rate of PS hydrogenation; semi-batch stirred tank reactor (STR) and a semi-batch presaturated one liquid flow integral recycle reactor (POLF-IRR).

2.   Materials and Methods

Phase equilibria, density and viscosity measurements on mixtures of C3 and DHN were conducted with 99.99% purity research grade propane (National Welders) and 99 +% purity 76/24 wt% *trans/cis*-DHN (Sigma-Aldrich). The phase behavior and density of C3/DHN mixtures were measured in a variable-volume view cell completely enclosed within a thermostable (± 0.2 $^{\circ}$C) oven. The cell was equipped with a linear variable displacement gauge used for simultaneous measurement of density during a phase behavior experiment. Agitation was supplied by a magnetically driven stir bar immersed in the fluid sample. Temperature was

measured in the oven and directly inside the view cell. Thermal equilibrium was assumed when both temperatures were the same for two hours.

Viscosity measurements were taken with a Cambridge Applied Systems SPL440 viscometer equipped with a variable-volume view cell and an external recirculation pump used for mixing. The viscosity of the sample fluid was calculated from an internal calibration based on the time required to move a magnetically driven piston through a fluid between two sensing coils. Temperature was measured in the view cell, in the viscometer, and in the oven. Fluid circulation was maintained at all times other than during the viscosity measurements.

The hydrogenation of PS in DHN and a mixture of C3 and DHN were carried out in two different reactor configurations; a STR and POLF-IRR. The catalyst used was a 5 wt% palladium on silica support prepared by wet impregnation using a palladium chloride precursor. The palladium chloride used was 99.9% purity (Alfa Aesar). The silica support (Fuji Sylisia) was 99.9% purity and was used as-received as 3.5 mm spheres for the POLF-IRR and ground to 50 μm powder for the STR. The H_2 partial pressure was maintained above 52 bar for the duration of each hydrogenation reaction. For the hydrogenation experiments conducted with C3 as a cosolvent, C3 was initially charged in the vessel to reach a partial pressure of 18 bar, equating to approximately 20 mol% C3 in the liquid phase at 150 ^{o}C.

For the STR (Autoclave Engineers), the reduced catalyst was ground into a powder before addition to the reactor. The agitation speed was maintained at 2500 rpm and a temperature of 150 ^{o}C was used for all experiments. For the POLF-IRR, the reduced catalyst was present as a packed bed and the solution was presaturated with H_2 and C3 before contacting the catalyst. The recirculation rate through the bed was maintained at 65 mL/min and the temperature in the packed bed was held at 150 ^{o}C.

3.   Results

The solution viscosities were analyzed using a recently developed small molecule free-volume model (FVM) for dynamic viscosity [5]. The FVM (Equation 3.1) contains three terms which are characteristic of the molecule, a term characteristic of the energy barrier (α) that molecules have to cross in order to diffuse, a term related to the characteristic molecular length (ℓ), and a term characteristic of the molecular overlap of the free-volume (B). In Equation 3.1, R is the gas constant, T is temperature, P is pressure, and M is molecular weight.

$$\eta = \rho \ell \left[\frac{\alpha\rho + (PM/\rho)}{\sqrt{(3RTM)}} \right] \exp\left\{ B \left[\frac{\alpha\rho + (PM/\rho)}{RT} \right]^{3/2} \right\} \tag{3.1}$$

The FVM can be applied to mixtures; the details can be found elsewhere [6]. The FVM pure component parameters were obtained from the literature and are reported in Table 3.1.

Component	α (J mol^{-1} m^3 kg^{-1})	B x 10^3	ℓ (Å)
Propane	59.5	7.39	0.848
t-DHN	100.7	10.51	0.909
c-DHN	103.8	12.03	0.749

Table 3.1   Pure component FVM parameters [5, 7]

For complex mixtures like C3 in DHN, the density used in the FVM was either measured or it was computed by using the Sanchez-Lacombe equation of state (SLEOS) as an interpolation vehicle. The SLEOS is shown in Equation 3.6 in the form of the reduced density, $\tilde{\rho}$.

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r_{mix}}\right)\tilde{\rho}\right] = 0 \tag{3.2}$$

In Equation 3.6, $\tilde{T}$ and $\tilde{P}$ are the reduced temperature and pressure. The reduced parameters are defined in Equation 3.7 through Equation 3.9.

$$\tilde{T} = T/T^* \qquad\qquad T^* = \varepsilon_{mix}^*/R \tag{3.3}$$

$$\tilde{P} = P/P^* \qquad\qquad P^* = \varepsilon_{mix}^*/v_{mix}^* \tag{3.4}$$

$$\tilde{\rho} = \rho/\rho^* \qquad\qquad \rho^* = M_{mix}/\left(r_{mix}v_{mix}^*\right) \tag{3.5}$$

In Equation 3.7 through Equation 3.9, ε_{mix}^* is the characteristic interaction energy for the mixture, v_{mix}^* is the characteristic close-packed molar volume of a mer of the mixture, r_{mix} is the number of sites occupied by a molecule of the mixture, M is the molecular weight, and R is the universal gas constant. The mixing rules, described elsewhere, assume random mixing of all components [8]. The pure component characteristic parameters for the SLEOS are reported in Table 3.2.

Component	ρ^* (g/cm^3)	P^* (bar)	T^* (K)
Propane	0.690	3140	371
t-DHN	0.935	3150	621
c-DHN	1.105	3570	735

Table 3.2   Pure component characteristic parameters for SL-EOS [9]

The SLEOS calculations used the binary interaction parameters shown in Table 3.3. These were obtained by fitting the SLEOS to measurements of bubble point pressures for C3/DHN mixtures at 150 $^\circ$C. The SLEOS captures the volume expansion behavior of DHN and PS solutions when pressurized with scCO$_2$ [4]. Figure 3.1 shows the volume expansion calculations and data taken for the saturated liquid of C3/DHN mixtures at 150 $^\circ$C. The volume expansion is defined as the ratio of the specific volume of the C3/DHN mixture at T and P over the specific volume of saturated liquid DHN at T and P^{sat}.

Components	k_{ij}
C3/t-DHN	0.055
C3/c-DHN	0.055
t-DHN/c-DHN	0

Table 3.3   Binary interaction parameters for SLEOS
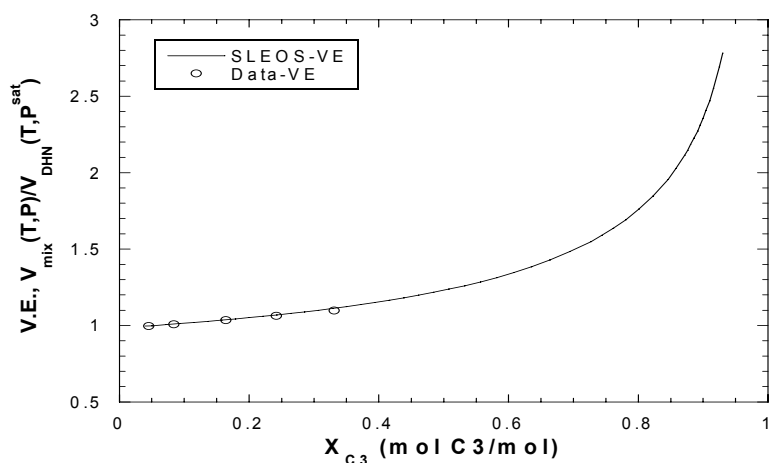
Figure 3.1 Volume expansion measurements and SLEOS predictions at the C3/DHN bubble point pressure and 150 ^{o}C

C3/DHN mixture viscosity data is shown in Figure 3.2 for a pressure of 74 bar and compared to the FVM prediction for 76/24 wt% *t/c*-DHN at 74 bar. For reference, the known viscosity of C3 at 74 bar is also compared to values calculated from the FVM (Figure 3.2).
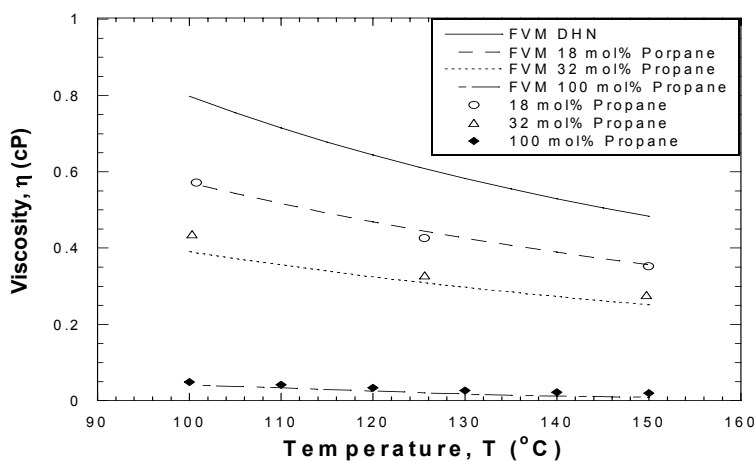

Figure 3.2 Measured viscosity and FVM predictions for C3, DHN, and C3/DHN mixtures at 74 bar

The rate of hydrogenation of polystyrene in the STR was investigated with 1 wt% PS in DHN and with 1 wt% PS in a mixed solvent of C3/DHN at 150 ^{o}C. The H_2 partial pressure was maintained above 750 psig and the agitation speed was kept at 2500 RPM. Previous investigators obtained an apparent first order rate with respect to aromatic concentration. For PS concentration less than 3.5 wt%, the reaction rate was independent of agitation speed and H_2 concentration above ~2000 rpm and above ~700 psig partial pressure H_2, respectively [4].

Integration of the material balance for aromatic concentration in the STR yields the relationship shown in Equation 3.6. In Equation 3.6, X_A is the fractional conversion at time, t, and X_A^0 is the fractional conversion at time zero. A non-zero value of X_A^0 accounts for any hydrogenation that occurs during heatup of the reactor. C_{cat} (g cat/mL) is the concentration of the catalyst in the expanded liquid phase and k_A (mL/g cat/min) is a first-order rate constant. The effect of the product of catalyst concentration and time on the left side of Equation 3.6 for hydrogenations carried out in an STR under our conditions is plotted in Figure 3.3. As suggested by Equation 3.6, the conversion data are plotted versus the product of C_{cat} and t to test for linearity. The straight lines in Figure 3.3 are the best-fit lines to the data and first-order rate constants were computed from the slope as per Equation 3.6. The rate of hydrogenation of PS in a C3/DHN mixture was 74% higher than the rate of PS hydrogenation in neat DHN.

$$-LN\left[\left(1-X_A\right)/\left(1-X_A^0\right)\right] = k_A C_{cat} t \qquad (3.6)$$
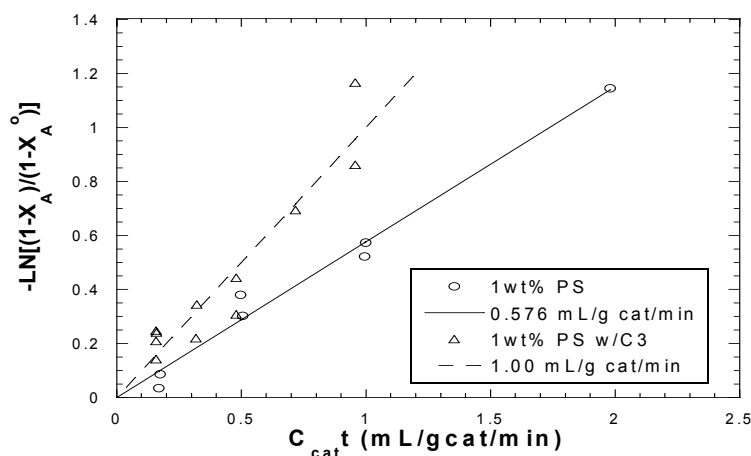
Figure 3.3   Hydrogenation results for 1 wt% PS in DHN and C3/DHN at 150 ^{o}C

In the POLF-IRR, the single-pass conversion in the packed bed was kept small enough that the change in concentration of aromatics in the recirculation loop was negligibly small. Under these conditions, Equation 3.2 could be used to evaluate the hydrogenation kinetics. Since the catalyst was a spherical pellet, the diffusion distance for the polymer molecules was increased significantly compared to the diffusion distance when the catalyst is present as a powder and the influence of internal mass transfer limitations was expected to be exacerbated. As a result, the hydrogenation rate of 1 wt% PS in DHN was almost 90% slower in the POLF-IRR as compared to the STR (Figure 3.4). As would be expected, slower hydrogenation rates in the POLF-IRR are observed when the viscosity of the reaction medium increases; the rate of hydrogenation for a 10 wt% PS/DHN solution is 14 times slower than for a 1 wt% PS/DHN solution. Thus, the rate increase expected for the higher concentration of PS (mass action effect) is overwhelmed by the rate decrease due to higher viscosity (mass transfer effect). The extent of the mass transfer limitation can be mitigated somewhat by the addition of C3 to the reaction mixture. Thus, when 20 mol% C3 was added to the DHN, the rate of hydrogenation of a 10 wt% PS solution increased by 50%.
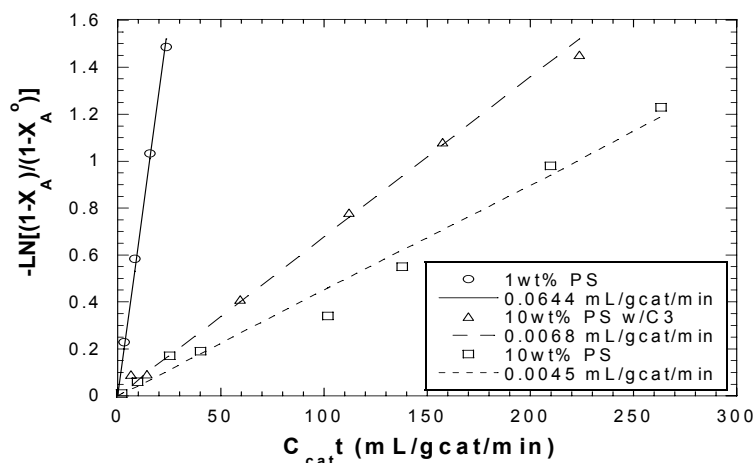
Figure 3.4   Hydrogenation results for a 1 wt% PS in DHN and 10 wt% PS in DHN and C3/DHN at 150 $^{\circ}$C.

4.   Conclusions

The addition of scC3 as a cosolvent for the hydrogenation of PS in DHN increases the hydrogenation rate compared to reactions carried out in the absence of C3. The increase in the rate can be attributed to the reduction in the solution viscosity leading to higher rates of mass transfer of the polymer molecules to the catalyst surface and into the porous support. When a powdered catalyst is used instead of a spherical pellet, the distances required for PS molecules to migrate to active catalytic sites is shortened and a concomitant increase in the hydrogenation rate is measured.   The highest achievable hydrogenation rates might be obtained by combining powdered catalysts with scC3 modified reaction solvents. Unhappily, post-reaction separation of powders from viscous PS/DHN solutions is apt to be difficult and costly. The combination of pelletized catalysts with scC3/DHN overcomes this objective, but the decrease in hydrogenation rate compared to the powdered catalyst somewhat lessens the positive economic impact of using pellets in a POLF-IRR. Nevertheless, the trade-off may be acceptable since similar polymer product quality is obtained with either reactor.

5.   References

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