

KINETIC COMPARISON OF A THREE-PHASE CATALYTIC HYDROGENATION REACTION CONDUCTED WITH AND WITHOUT SUPERCRITICAL CARBON DIOXIDE

F.P. Lucien*, **G. Zwolak**, **A. Bertucco[#]**

School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, UNSW Sydney, NSW 2052, Australia.

e-mail: f.lucien@unsw.edu.au, fax: +61-2-9385-5966

[#] Department of Chemical Engineering Principles and Plants, Università di Padova, via Marzolo 9, I-35131 Padova PD, Italy

The three-phase catalytic hydrogenation of an unsaturated ketone using a Pd/Al₂O₃ catalyst was investigated at high pressure. Kinetic experiments were performed using a Berty-type internal-recycle reactor. Temperature and pressure conditions ranged from 100 to 200°C and from 50 to 200 bar. Kinetic data were fitted to simple power-law models as well as more complex Langmuir-Hinshelwood models. An earlier study covered the experiments and modelling of the same system using supercritical carbon dioxide as a solvent. A kinetic comparison is presented in which the effect of supercritical carbon dioxide on reaction rate is considered in terms of its impact on reactor design.

INTRODUCTION

A striking feature of the open literature on reactions in SCFs is the relative absence of kinetic studies. A notable exception is the study by Palo and Erkey [1] on the rhodium-catalysed homogeneous hydroformylation of 1-octene. Phiong et al. [2] have also recently reported kinetic data on the three-phase catalytic hydrogenation (TPCH) of α -methylstyrene in supercritical carbon dioxide (scCO₂). Kinetic studies on high pressure reaction processes require careful consideration of the phase behaviour of the system since the number and types of phases have a direct impact on the reaction process [3-5]. In multiphase systems, such as TPCH, equations of state and related thermodynamic models are required for the estimation of phase equilibrium concentrations which appear in kinetic rate expressions. The coupling of phase equilibria with reactive events thus represents one of the challenges faced by researchers.

While it is often reported that SCFs such as CO₂ enhance reaction rates there is very little information which precisely quantifies the increase in reaction rate. Kinetic models provide the mathematical framework upon which the comparison of reaction rates can be made and from the industrialist perspective they are important in relation to reactor design and scale-up. In this work, we present a kinetic comparison of a reaction conducted with and without scCO₂, based on the TPCH of an unsaturated ketone. The kinetic study of this reaction in the presence of scCO₂ has been reported in earlier work [6,7]. Here we describe the measurement of kinetic data for the standard hydrogenation reaction and derive kinetic models in the form of Power-Law (PL) and Langmuir-Hinshelwood (LH) rate expressions. In making a kinetic comparison we have adopted an industrialist approach whereby the effect of scCO₂ on reaction rate is considered in terms of its impact on reactor design.

MATERIALS AND METHODS

Materials. The feed mixture consisted of an unsaturated ketone (component A) whose generic structure is represented as $R_1-CH=C=CH-C(=O)-R_2$. The reaction involves the hydrogenation of the two adjacent double bonds to form the corresponding saturated ketone (component C). The feed mixture also contains several isomers of the unsaturated ketone. As in previous work, the main reactant and its isomers were grouped together as a pseudo-component known as AD. Incomplete hydrogenation of the reactants leads to the formation of intermediates characterised by one double bond. These semi-hydrogenated isomers were also grouped together as a pseudo-component known as E. The reaction scheme can therefore be represented as:



The hydrogenation catalyst consisted of 0.5% Pd on alumina, in the form of 3 mm cylindrical pellets available commercially from Engelhard. The catalyst was found to contain Pd distributed as a thin layer (or egg-shell) on the alumina support.

The feed mixture has a normal boiling point well above 200°C, the maximum temperature employed, and can be considered as a nonvolatile liquid reactant under the reaction conditions. The reaction scheme therefore represents a catalytic hydrogenation system containing three-phases: a solid catalyst, a nonvolatile liquid phase and a gas phase consisting mainly of hydrogen. The reaction occurs primarily on that part of the catalyst which is wetted by the liquid reactant in view of the negligible concentration of organics in the gas phase.

Apparatus and Procedure. A suitable reactor for investigating the kinetics of a solid-catalysed three-phase hydrogenation reaction is one in which the liquid and gas reactants can be mixed intimately in the region surrounding the solid catalyst. This ensures that concentration gradients are eliminated in the bulk liquid phase. To achieve the required degree of mixing we employed a Berty-type internal-recycle reactor specifically designed for high temperature and pressure. A thorough description of the whole apparatus, its control system and the general operating procedure is given elsewhere [6].

In a typical experiment, the temperature, pressure, feed flow and reaction mass were held constant so as to attain steady-state conditions. The outlet stream was flashed to atmospheric pressure in a separator thereby removing most of the dissolved H_2 in the liquid. The composition of the outlet stream, on a H_2 -free basis, was then measured with an on-line GC unit. Steady-state conditions were confirmed with at least three sample analyses of the outlet stream with a relative standard deviation (RSD) of 5% or less. A minimum agitation speed of 1800 rpm was used to ensure the absence of external mass-transfer limitations. Pore diffusion effects were also found to be negligible, based on results obtained with crushed catalyst pellets. The ranges of temperature and pressure investigated were 100-200 °C and 50-200 bar.

By varying the feed flowrate (L) it was possible to obtain data which encompassed a wide range of reactant conversion (X). Values of the reaction rate (r) under a given set of conditions were obtained by applying the following component balances:

$$-r_{AD} = \frac{L(X_{AD}^{in} - X_{AD}^{out})}{M_{AD}W_{cat}} \quad (3)$$

$$r_C = \frac{L(X_C^{out} - X_C^{in})}{M_CW_{cat}} \quad (4)$$

where M is the molecular weight and W_{cat} is the mass of catalyst. Since the internal-recycle reactor operates as a CSTR [8] the composition at the outlet of the reactor is equivalent to the composition within the reactor. The composition of the outlet stream was therefore used as a basis for calculating concentrations of the various components in the liquid phase under reaction conditions. The composition of hydrogen in the liquid phase, under reaction conditions, was estimated using the Peng-Robinson equation of state. A full description of this calculation procedure is given elsewhere [6].

RESULTS AND DISCUSSION

Kinetic Models. A multivariable regression of the experimental rate data was performed with several types of PL models and LH models. Liquid-phase concentrations and temperature were used as the independent variables and reaction rates as the dependent variables. For the LH models, the surface reaction was assumed to be the rate-controlling step and adsorption equilibrium constants were made independent of temperature. Rate constants for the elementary surface reactions were assumed to be temperature dependent according to the standard Arrhenius law. The effect of pressure was only considered in terms of its effect on phase equilibria. The parameter values for each model were obtained using a standard least-squares routine (Micromath Scientist).

It should be emphasised at this point that the focus of this aspect of the study was to obtain mathematical expressions which satisfactorily described the kinetic data. Any rigorous attempt to elucidate the surface-reaction mechanism is hindered by the simplification of the reaction system with pseudo-components. A summary of some of the models considered is given in Table 1 and a list of the regressed parameters is shown in Table 2. The R^2 statistic shown in Table 2 is based on the calculated and experimental values of reaction rate.

The most successful model for the first hydrogenation step is a PL model which is first order with respect to the liquid reactant and zero order with respect to H_2 (PL-I-2). The most successful model for the second step is an LH model in which there is the dissociative adsorption of hydrogen (LH-II-2). It is interesting to note that for this reaction system, the first hydrogenation step is known to occur much more rapidly than the second hydrogenation step. Model LH-II-2 reflects the rapid conversion of AD to E in that the surface concentration of AD is not incorporated into the model, in contrast to model LH-II-1.

Table 1: Selected kinetic models for the first (I) and second (II) hydrogenation steps

Model	Model equation
PL-I-1	$-r_{AD} = kC_{AD}C_{H_2}, k = A\exp(-E_a / RT)$
PL-II-1	$r_C = kC_E C_{H_2}$
PL-I-2	$-r_{AD} = kC_{AD}$
PL-II-2	$r_C = kC_E$
LH-I-1	$-r_{AD} = \frac{kK_{AD}C_{AD}K_{H_2}C_{H_2}}{\left(1 + K_{AD}C_{AD} + K_EC_E + K_C C_C + K_{H_2}C_{H_2}\right)^2}$
LH-II-1	$r_C = \frac{kK_EC_EC_{H_2}C_{H_2}}{\left(1 + K_{AD}C_{AD} + K_EC_E + K_C C_C + K_{H_2}C_{H_2}\right)^2}$
LH-II-2	$r_C = \frac{kK_EC_EC_{H_2}C_{H_2}}{\left(1 + K_EC_E + K_C C_C + \sqrt{K_{H_2}C_{H_2}}\right)^3}$

PL - Power-Law model, LH - Langmuir-Hinshelwood model.

Table 2: Parameter values for the selected kinetic models

Model	A	E_a	K_{AD}	K_E	K_C	K_{H_2}	R^2
PL-I-1	1359	33471	-	-	-	-	0.947
PL-II-1	0.02467	5444	-	-	-	-	0.886
PL-I-2	10788	43678	-	-	-	-	0.948
PL-II-2	0.09715	13148	-	-	-	-	0.879
LH-I-1	0.4951	2601	155.6	56.17	16.20	179.4	0.909
LH-II-1	0.1010	6273	155.6	56.17	16.20	179.4	0.704
LH-II-2	2.150	8182	-	0.6843	0.4738	1.068	0.978

The units for rate are mol/min g. The units for concentration are mol/L. The units for E_a are J/mol.

Kinetic Comparison. Devetta et al. [7] found that the rate of hydrogenation of AD was strongly enhanced in the presence of scCO₂. Their experimental data was best described by models equivalent to PL-I-1 and LH-II-2. In making a kinetic comparison it is not intended to directly compare values for activation energy or adsorption equilibrium constants. Such parameters are, at best, fitted parameters and need to be treated with caution. For example, models PL-I-1 and PL-I-2 yield the same fit of the data, as indicated by R^2 , but the activation energies are substantially different. The point is even more evident with the second reaction step.

A practical way of assessing the impact that scCO₂ has on the rate of reaction is to consider its effect on the length of reactor required to achieve a given conversion. For this purpose, a trickle-bed reactor model was employed to calculate the length of reactor required to achieve 99% conversion of AD to C. The full details of the reactor model are described elsewhere [9]. Models PL-I-1 and LH-II-2 were used for calculating values of the reaction rate required by the trickle-bed model. Some simplifications to the original trickle-bed reactor model were made to simplify the kinetic comparison: the liquid reactant, H₂ and CO₂ flow over the packed bed of catalyst under plug flow and isothermal conditions; there are no internal or external mass-transfer limitations; the catalyst is completely wetted. Such simplifications are of course

unrealistic in industrial reactors so the results which follow really provide a qualitative comparison of the reaction processes.

The reactor length as a function of the CO₂ content in the feed to the reactor is shown in Figure 1. The calculations are based on a H₂ feed flow which is 20% in excess of that required to react stoichiometrically with the AD fed to the reactor. The results are presented in terms of a normalised reactor length. A value of 1 indicates the length required to achieve 99% conversion at 50 bar and 50°C in the absence of scCO₂. Over the range of conditions considered, the reactor length approaches a minimum value as the CO₂ content in the feed increases. The optimum CO₂ content is around 25-50 wt% with more CO₂ required at higher temperature and pressure. The impact of CO₂ on reactor length is quite significant: at 50°C/50 bar the reactor length is reduced by up to 50% while at 200°C/200 bar the corresponding reduction is 85%.

As a final comparison, the reactor length as a function of pressure is shown in Figure 2. The data for the reactor operated with CO₂ is based on a feed consisting of 50 wt% CO₂. At constant temperature, the reactor length decreases with pressure, with and without CO₂. This is attributed to the increase in the solubility of H₂ in the liquid phase, and therefore the reaction rate, as the total pressure increases. However, in both processes, there does appear to be a limit (~150 bar) to which pressure can be used to reduce the reactor length. It is also apparent from Figure 2 that the addition of CO₂ to the reaction process can greatly reduce the severity of the operating conditions. For example, at 200°C and 200 bar the normalised reactor length is around 0.13 for the standard hydrogenation reaction. In the presence of scCO₂, the same level of conversion can be achieved at 100°C and 100 bar.

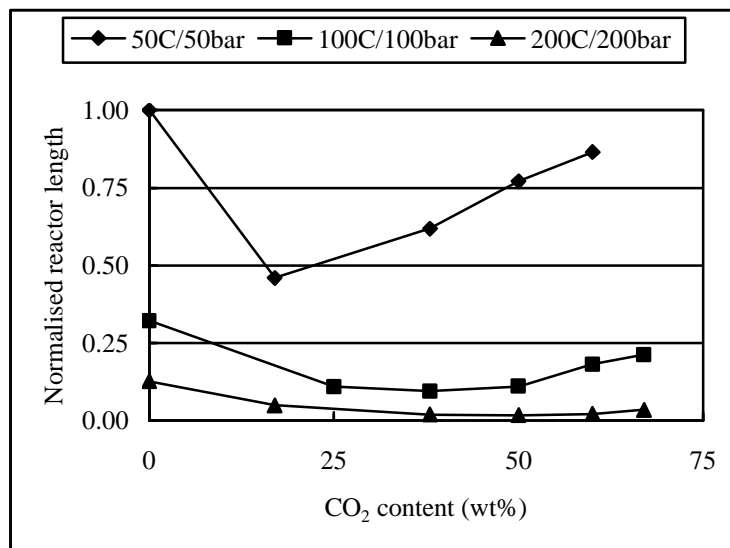


Figure 1: The effect of CO₂ content on reactor length.

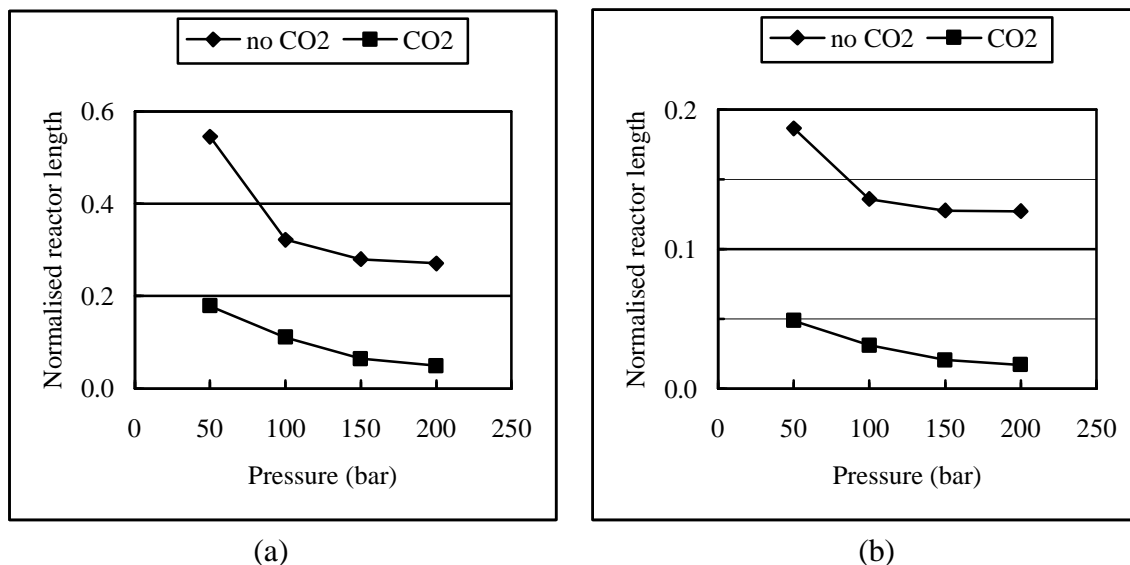


Figure 2: The effect of pressure on reactor length at a fixed CO₂ content of 50 wt% - (a) $T = 100$ °C; (b) $T = 200$ °C.

CONCLUSION

Supercritical CO₂ can be beneficial as a reaction solvent in catalytic hydrogenation processes in which the rate of reaction is typically limited by the interphase transport of hydrogen. The kinetic comparison reported here, in which it is assumed that there is thermodynamic equilibrium between liquid and vapour phases, demonstrates that the enhanced reaction rates obtained with scCO₂ lead to a significant reduction in reactor size. Furthermore, in catalytic hydrogenation processes which require the use of elevated pressure, scCO₂ can potentially reduce the severity of the operating conditions.

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