Maximising opportunities in supercritical chemistry: the continuous conversion of levulinic acid to γ-valerolactone in CO_2

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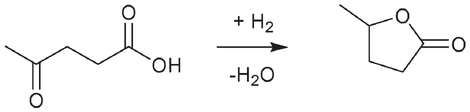
Phase behaviour is manipulated during the hydrogenation of aqueous levulinic acid in supercritical CO_2 to separate almost pure γ-valerolactone from water and unreacted acid with reduced energy requirements compared to conventional processing.

Several research groups have now demonstrated that supercritical CO_2 ($scCO_2$), is a highly effective medium for continuous catalytic reactions,[1] including alkylation,[2] etherification,[3] hydroformylation,[4] oxidation[5] and particularly hydrogenation.[6] These reactions have been very successful in terms of process intensification and scale-up. Indeed, conditions have sometimes been optimised to give products sufficiently pure to eliminate completely the need for downstream purification.[6] However, there are definite limitations. In particular, the relatively poor solvent power of $scCO_2$ and the need to pump the substrate into the reactor means that it is often necessary to use a co-solvent, which has then to be separated from the product, considerably compromising the efficiency of the process and entailing increased energy costs.

In this communication, we describe a new approach that combines the use of water as a co-solvent with phase manipulation using $scCO_2$ to integrate reaction and separation into a single process with reduced energy requirements compared to conventional distillation. We illustrate our approach with the conversion of levulinic acid (LA) to γ-valerolactone (GVL) (Scheme 1). LA can be obtained from renewable biomass by the acid catalysed dehydration of hexose sugars.[7] Its conversion to GVL involves hydrogenation followed by intramolecular cyclisation, with the loss of water.[7,8] GVL has been proposed as a sustainable liquid and as a precursor to a biomass-derived acrylic monomer.[9,10]

A recent patent[11] describes the continuous hydrogenation of LA to GVL in $scCO_2$. GVL is a liquid but LA is a solid (mp 30 °C) which had to be pumped into the reactor dissolved in 1,4-dioxane. At the end of the reaction the GVL had to be separated from the dioxane solvent, the H_2O produced in the reaction and any unreacted LA, processes which are potentially energy intensive. A variety of conditions were reported but *ca.* 98% conversion could be achieved with a tubular reactor at 200 °C and 20 MPa with a 20% excess of H_2 over a 5% Ru on Al_2O_3 catalyst.[11]



Scheme 1 Conversion of levulinic acid (LA) to γ-valerolactone (GVL).

We have found that the co-solvent can be replaced by water; a concentrated mixture of LA and H_2O (75% w/w LA, *ca.* 1 : 2 mol/mol) is an easily pumpable liquid. Surprisingly, this aqueous solution of LA can be converted into GVL, even though the second stage of the reaction involves elimination of H_2O. We used an automated reactor[12] to identify the optimal conditions and at 200 °C; almost quantitative conversion can be obtained, see Table 1.

Compared to the patent,[11] our reaction involves lower pressures (10 MPa *vs.* 20 MPa) and a higher concentration of LA (LA : CO_2 *ca.* 1 : 10 *vs.* 1 : 28). However we require a larger excess of H_2 (H_2 : LA = 3 : 1), possibly because of reduced mass transport across the gas/liquid interface. Since GVL is miscible with H_2O, it is obtained in aqueous solution at the end of the reaction, (*ca.* 3 : 1 H_2O : GVL, mol/mol) and separation is required. It is here that $scCO_2$ offers a real advantage.

The advantage derives from the work of Lazzaroni *et al.* who showed that adding a moderate, sub-critical pressure of CO_2 to aqueous THF causes liquid/liquid separation into THF-rich and H_2O-rich phases.[13] This is quite distinct from supercritical extraction since the THF remains in a separate, "gas-expanded" liquid phase (THF + CO_2) which is immiscible with H_2O but does not dissolve substantially in the gaseous CO_2 phase at these pressures.[14] We therefore investigated whether a similar phase separation occurs when aqueous GVL is pressurised with CO_2. Our results, Fig. 1, show that apart from a slightly unusual phase inversion, GVL behaves just like THF. Since GVL and H_2O separate at a pressure of CO_2 similar to that inside our reactor, we have the basis for a process which combines reaction and separation. The phase inversion is a bonus which simplifies the equipment needed but is not inherent to the principle.

Therefore, we reconfigured our apparatus to incorporate a simple liquid separator between the reactor and back pressure regulator, see Fig. 2. The modified system was tested first by

Table 1 Reaction optimisation of LA to GVL in $scCO_2$

Expt. no.	*T*/°C	H_2 equiv.	Yield of GVL (%)
1	180	4.5	73
2	190	4.5	74
3	200	4.5	>99
4	200	3.0	>99
5	200	1.5	52

[a] All reactions performed at 10 MPa system pressure with 2.76 g of 5% Ru on SiO_2 (Degussa H 3036 XH/D). Flow rates 1.0 ml min^{-1} liquid CO_2, 0.3 ml min^{-1} LA–H_2O (75% w/w LA).

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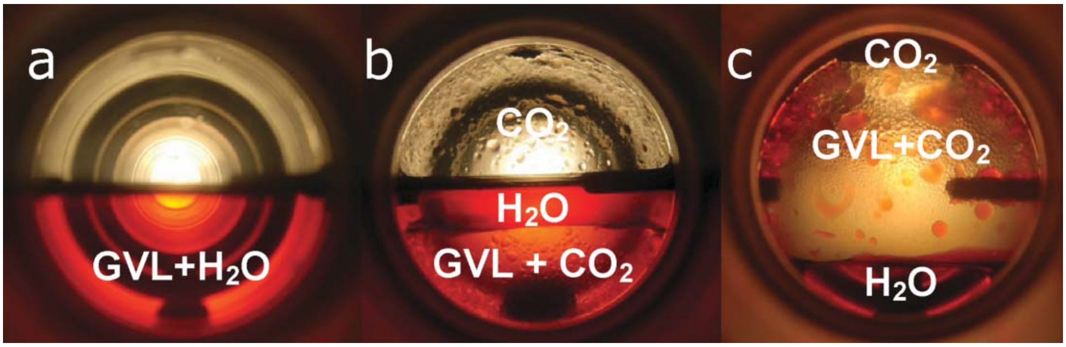

Fig. 1 Three photographs of different stages of the same experiment demonstrating how a pressure of CO_2 induces the phase separation of aqueous GVL (GVL–H_2O, 1 : 3.15 mol/mol). To aid visualisation, the mixture has been doped with a dye, Direct Red 23, which partitions preferentially into the water-rich phase. (a) the mixture in the cell without any CO_2. (b) The same mixture under a pressure of 2.7 MPa CO_2 at 21 °C. The system has now split into three phases with CO_2 at the top, H_2O plus dye in the middle and GVL + CO_2 at the bottom. The reason why the organic layer is at the bottom is that, unusually for a non-halogenated organic compound, pure GVL is denser than H_2O. (c) Under a much higher pressure of CO_2 9.3 MPa at 44 °C. There are still three phases but the H_2O phase is at the bottom because the density of the GVL + CO_2, is now lower than that of H_2O since, at this pressure, liquid/supercritical CO_2 is much less dense than either GVL or H_2O. The importance of this experiment is that it shows that GVL and H_2O can be separated using a pressure of CO_2 similar to that which already exists inside our reactor.

pumping a mixture of LA + H_2O through the system pressurised with CO_2 but without H_2 or heating the catalyst bed. Then, a second mixture of GVL + H_2O was tested similarly.† The results were encouraging with the separator working well; aqueous LA could be drained from the bottom separator while GVL *free* from H_2O was recovered from the BPR.

The apparatus was then run as normal, pumping LA + H_2O through the heated reactor with CO_2 and H_2. The separator performed excellently. Unlike our previous reactor which delivered a 1 : 3 GVL–H_2O mixture, the separator gave a product stream of virtually pure GVL (0.4% H_2O w/w by coulometric Karl Fischer determination) even without optimisation. In addition, the GVL contained no LA detectable by gas chromatography, while the aqueous stream from the bottom of the separator contained a modest amount of unreacted LA (see Fig. 3).

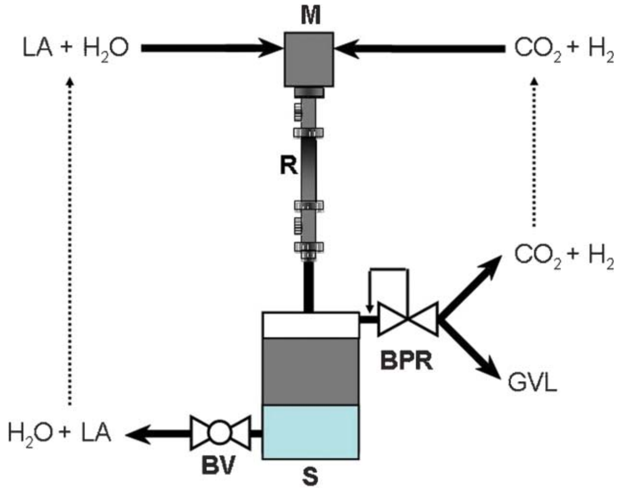

Fig. 2 Schematic diagram of the reactor with downstream separator. The reactant streams (LA + H_2O) and (CO_2 + H_2) are pumped through a static mixer, M, into the fixed bed reactor, R, and then, after cooling, to a 100 ml separator, S. If the product mixture is triphasic (L + L + V, see Fig. 1), the two liquid phases will begin to collect in S with the GVL-rich phase on top. When S is full, the GVL-rich layer will pass through S and on to the back pressure regulator, BPR, where the pressure is released and GVL recovered. The aqueous phase, (containing any unreacted LA) continues to accumulate in S and can periodically be drained *via* the ball valve, BV, without significant loss of system pressure.†

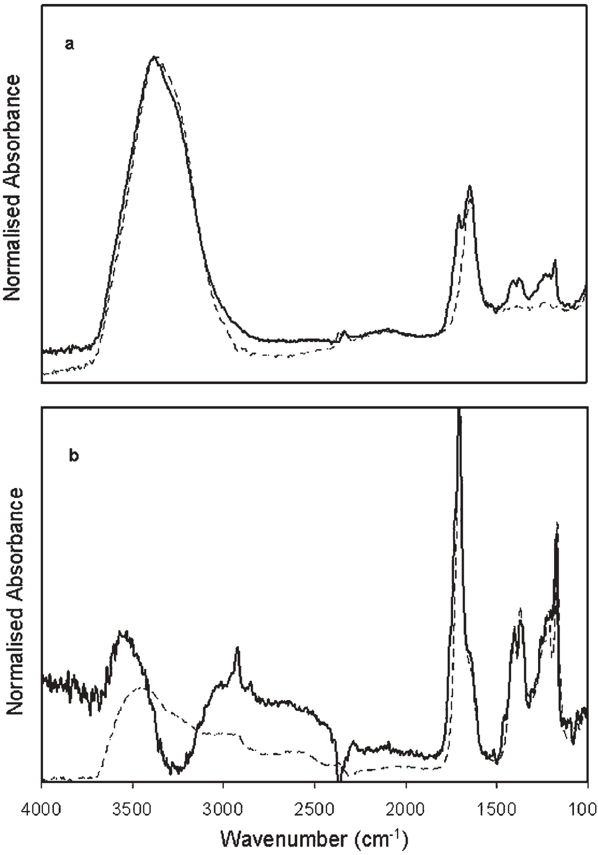

Fig. 3 IR Spectra demonstrating the presence of LA in the aqueous stream recovered from the separator during the hydrogenation of LA in the apparatus shown in Fig. 2. (a) Solid line, ATR spectrum of liquid recovered from separator; dashed line, pure water. (b) Solid line, spectrum obtained by subtraction of the two spectra in (a); note the similarity of the spectrum to the dashed line, ATR spectrum of aqueous LA reactant originally pumped into the reactor.

Not only does this separation eliminate the need for purifying the GVL by distillation but also it does so without any *additional* input of energy. The separation merely exploits the phase equilibrium which already exists downstream of the reactor. This saving in energy is significant. Supercritical reactions are more energy intensive than many conventional processes. If separation can be integrated into a supercritical reactor, the high pressure process becomes considerably more attractive from an energy point of view. Indeed, in principle, the recovery of GVL does not even require a full release of pressure since liquid GVL is present in the system even under high pressure conditions. In practice a substantial amount of CO_2 would still be released as a component of the GVL-rich phase.‡

Several important points emerge from these experiments:

- Our reactor/separator delivers pure GVL, *even when the hydrogenation reaction is incomplete*.
- H_2O should be considered more widely as a co-solvent for reactions in $scCO_2$ even though H_2O is immiscible with $scCO_2$.
- Our strategy for separation/purification could probably be applied to a range of reactions in addition to hydrogenation (*e.g.* oxidation or etherification), which generate H_2O as one of the products.
- Phase separation within high pressure reactors should be viewed as a potential resource to be manipulated for product recovery.

We are currently investigating the wider applications of our approach to other reactions.

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Notes and references

† All equipment was constructed from 316SS (Swagelok®). Liquid materials were delivered *via* HPLC pumps, JASCO PU-980 for organic substrate, PU-1580-CO2 for carbon dioxide. H_2 was dosed *via* an automated Rheodyne switching unit built at the University of Nottingham. Synthetic mixtures were prepared with the following compositions: (a) CO_2–GVL–H_2O solution (9.45 : 1 : 3.15 mol/mol) representing the product stream and (b) CO_2–LA–H_2O solution (9.45 : 1 : 2.15 mol/mol) as the reactant stream.

‡ Recycling of CO_2 will be rendered somewhat more complicated by the presence of excess H_2

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