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Technoeconomic Analysis of Hydrogen Storage using 1,4-Butanediol (BDO)/ γ -Butyrolactone (GBL) as a Stationary Backup Power System

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Abstract

Liquid organic hydrogen carriers (LOHCs) are compounds that store and release hydrogen in stable forms at high density. While one-way carriers such as methanol and ammonia have gained attention, their economic advantages are often realized from their use as an export product and direct use as a fuel. Liquid carrier materials that can instead be cycled for energy storage have promise for stationary power applications. In particular, the reversible LOHC system 1,4-butanediol (BDO, H₂-rich) and gamma-butyrolactone (GBL, H₂-lean) has a lower enthalpy of dehydrogenation compared to conventional cyclic hydrocarbons and can utilize non-precious metal copper-based catalysts. In this study, BDO/GBL system capital and operating expenses are characterized for vapor phase versus liquid phase hydrogenation and dehydrogenation in a 10 megawatt backup power application corresponding to sizing of Tier 2 datacenters as well as other critical infrastructure such as hospitals. Costs are benchmarked against two incumbent technologies: a well-established methylcyclohexane/toluene carrier system and compressed gas storage. BDO/GBL storage costs are found to differ substantially between operating modes, with liquid phase hydrogenation coupled with liquid phase dehydrogenation leading to the lowest LCOS of \$4.58/kg H₂ in the absence of byproduct formation. In this bounding case, LCOS for the BDO/GBL system is lower than for MCH/TOL (\$6.97/kg H₂) and compressed gas (\$8.48/kg H₂ at 170 bara and \$12.05/kg H₂ at 350 bara). However, escalating costs of carrier replacement due to byproduct formation (ranging from an added \$6-11/kg H₂) illustrate the need for highly selective catalysts to ensure BDO/GBL carrier viability.

Keywords

Liquid organic hydrogen carriers; hydrogen storage; technoeconomic analysis; BDO/GBL

1 Introduction

Hydrogen generated from a wide range of resources can be used as an energy carrier or feedstock across many sectors with applications ranging from emergency backup power for critical infrastructure to use as a chemical reductant in large scale industrial processes [1-3]. Hydrogen storage is a key enabler to couple hydrogen production to hydrogen utilization, allowing temporal or spatial shift of hydrogen supply to more economically match demand requirements.

Current methods of storage using compressed H₂ gas or cryogenic liquefied H₂ are challenged by low volumetric storage density, high replacement and capital costs, energy requirements and gas losses for compression and liquefaction, respectively. In contrast, liquid organic hydrogen carriers (LOHCs) are a class of materials that store hydrogen in chemical bonds. There are two broad categories of LOHCs: one-way carriers (e.g., ammonia, formic acid, and methanol) where hydrogen is fixed chemically to a suitable molecule, and cycling or two-way carriers (e.g. methylcyclohexane (MCH), perhydro-dibenzyltoluene (H18-DBT), and 1,4-butanediol (BDO)), where the carrier molecule can be regenerated after the release of hydrogen. General advantages of LOHCs compared to physical methods of hydrogen storage include (i) enhanced volumetric and gravimetric density of stored hydrogen, (ii) stability at ambient temperatures and pressures, and (iii) compatibility with current petrochemical infrastructure for material storage and transport.

Previous analyses suggest that some LOHCs can be cost-competitive with physical H₂ storage for specific large scale applications such as long distance storage and transport [4,5] or seasonal energy storage [6]. However, each LOHC system must be assessed individually, since process energy efficiency and cost drivers vary widely depending on unique thermodynamic properties and reaction kinetics [4,7-9].

Commercially relevant LOHCs such as MCH (with toluene (TOL) as H₂-lean form) and H18-DBT (dibenzyltoluene (H0-DBT) as H₂-lean form) exhibit high enthalpies of dehydrogenation and high reaction temperatures, causing reduced energy efficiency and increased equipment costs for process heat exchange [7,10-12]. Due to these

challenges, prior work by some of the authors has focused on materials that have lower enthalpies of hydrogen release and lower dehydrogenation reaction temperatures than the aforementioned cyclic hydrocarbons [13-15]. H₂-rich BDO and H₂-lean gamma-butyrolactone (GBL) are one such two-way carrier pair whose thermodynamic properties are summarized in Table 1.1. Other advantages of the BDO/GBL pair include a high boiling point that facilitates product H₂ separation and a volumetric energy density (for H₂-rich form) on par with carriers such as MCH/TOL. GBL hydrogenation and BDO dehydrogenation reactions can utilize lower cost, earth-abundant Cu-based catalysts, as compared to the Ni or Pt-group metal catalysts applied for alternate LOHC systems [16]. Additionally, BDO is a widely available commodity chemical produced at over 3.6 MM MT/y globally, and can optionally be bio-derived via direct fermentation of sugars or conversion of bio-based succinic acid and bioethanol precursors [17,18].

Table 1.1 Comparison of reversible LOHC candidate properties [8,19,20]

LOHC pair (H ₂ -rich/H ₂ -lean)	Gravimetric storage density	H ₂ energy density	ΔH_{rxn}°	Normal melting point	Normal boiling point	Standard density
	wt% H ₂	g/L	kJ/mol H ₂	°C	°C	kg/m ³
1,4-butanediol / gamma-butyrolactone	4.5%	48	43	20 / -44	229 / 204	1017 / 1130
Ethanol / ethyl acetate	4.3%	36	36	-114 / -84	78 / 77	789 / 902
Methylcyclohexane / toluene	6.2%	51	68	-126 / -95	101 / 110	770 / 862
Perhydro-dibenzyltoluene / dibenzyltoluene	6.2%	60	65	-45 / -39	354 / 390	910 / 1040
Perhydro-N-ethylcarbazole / N- ethylcarbazole	5.8%	58	53	20 / 68	280 / 270	940 / 1100

Previous studies have focused primarily on the kinetics of BDO/GBL dehydrogenation and hydrogenation [21-24] or process energy efficiency [13] without addressing design and cost considerations, which are critical for ensuring carrier viability. In this study, baseline costs are established for the BDO/GBL carrier pair for a 10 MW stationary backup power application. Vapor versus liquid phase hydrogenation and dehydrogenation are modeled under a range of operating conditions to identify process tradeoffs and mode of operation that results in lowest LCOS. Costs are compared to the MCH/TOL carrier system as well as compressed gas H₂ storage benchmarks which were modeled for the same end user operation size and cycle.

2 Methodology

2.1 System design basis and system boundary

The backup power system design basis used in this study is described in Peng et al. [25] and summarized here. In the modeled backup power scenario, enough energy is stored in the form of H₂-rich carrier to meet 10 MW of demand for a 4-day demand duration assuming a 50% fuel cell efficiency [26], aligning with requirements for current diesel backup power systems [27]. Hydrogenation is assumed to occur over a conservatively shorter 2-day period due to inherent unpredictability in the interval between consecutive backup power events. The number of “charge” and “discharge” (i.e. H₂ storage and release) cycles is fixed at 12 per year.

Table 2.1 Design basis for 10 MW stationary backup power case

Hydrogenation duration	h	48
Dehydrogenation duration	h	96
Charge cycles per year		12
Backup power demand requirement	MW	10
Hydrogenation sizing basis	MT H ₂ /h	1.2
Dehydrogenation sizing basis	MT H ₂ /h	0.6
Hydrogenation average operating capacity	%	6.6%
Dehydrogenation average operating capacity	%	13.2%

The system boundary is set at the generation of hydrogen from an electrolyzer at 30 bara and 80 °C and ends at the delivery of hydrogen to a fuel cell at 3 bara and 80 °C. These hydrogen outlet conditions are typical for commercially available alkaline water electrolyzers and proton exchange membrane (PEM) electrolyzers [28-31].

2.2 Process modeling

2.2.1 BDO/GBL system

Process modeling approach

The BDO/GBL process is modeled using Aspen Plus V14.0, a rigorous commercial process simulator. The PR-BM equation of state property method is used with selected pure component and binary interaction parameters regressed against experimental data for improved prediction of vapor pressures, densities, vapor-liquid equilibrium, and reaction equilibrium constants.

Experimental data and kinetic models for hydrogenation and dehydrogenation in vapor and liquid phase are reported in the literature, involving the primary reversible GBL/BDO reaction as well as formation of 1-butanol (1-BuOH), tetrahydrofuran (THF), 2-hydroxytetrahydrofuran (2-HTHF), 4-hydroxybutyl 4-hydroxybutanoate (4-HHB), and dibutylene glycol (DG). Vapor phase hydrogenation kinetics were implemented according to Gautier et al. [21,22,32], and vapor phase dehydrogenation kinetics were implemented based on Javaid et al. [33] with kinetic parameters for byproduct formation reactions fitted against the original experimental data from Ichikawa et al. [24]. Liquid phase hydrogenation and dehydrogenation kinetics are based on models described in Qasmi et al. [23] with kinetic parameters re-regressed to account for differences in physical properties used in modeling.

For calculating equilibrium conversion constraints for each case, an equilibrium reactor (REquil block) calculating simultaneous phase and chemical equilibrium is modeled in parallel with the kinetic plug flow reactor model at the same reactor operating conditions (feed composition, temperature, and pressure).

A simplified process flow diagram for the BDO/GBL system is shown in Figure 2.1.

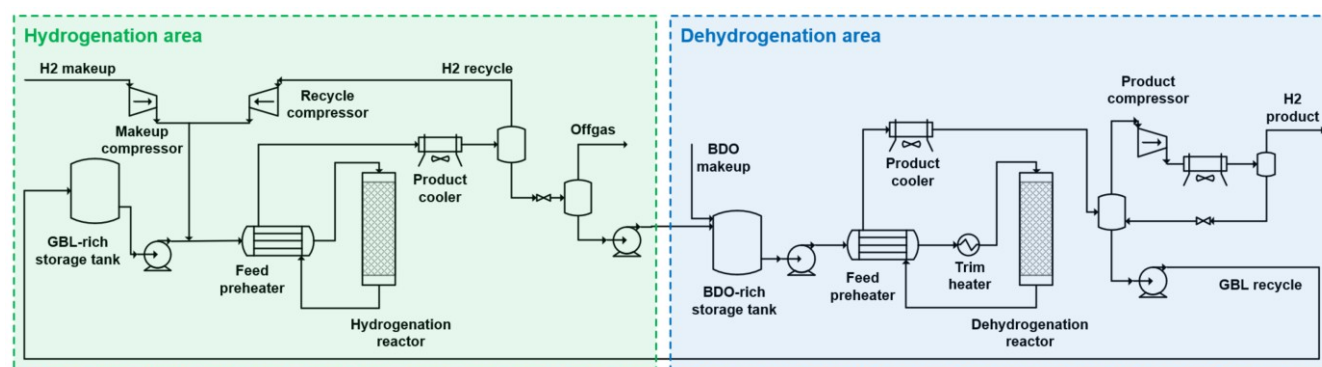


Figure 2.1 Process flow diagram for the 1,4-butanediol and gamma-butyrolactone (BDO/GBL) storage system (shown for vapor phase hydrogenation, vapor phase dehydrogenation).

Hydrogenation area process description

Inlet hydrogen is fed to the system from co-located electrolyzers at 30 bara and further compressed to hydrogenation reactor operating pressure prior to mixing with recycled H_2 . Carrier feed from the GBL-rich storage tank is almost pure GBL due to the near complete conversion of BDO to GBL that can be attained in dehydrogenation. GBL is mixed with combined hydrogen feed at a target H_2 :GBL molar ratio and fed to a heat exchanger which preheats feed against hot reactor effluent.

The hydrogenation reactor is represented as a heterogeneous catalytic plug flow reactor where GBL and H_2 are partially converted to BDO. Fully vapor phase reactor systems assume adiabatic fixed bed reactors. Liquid phase reactions are assumed to take place using multitube reactors to sufficiently manage heat of reaction at higher conversion points which otherwise can cause issues such as localized reactor hot spots leading to catalyst deactivation, reaction runaway/quenching, or undesirable reactant vaporization [34,35].

Exit feed is cooled to separate condensed carrier from excess H_2 , which is recycled and recompressed to account for small pressure losses. Carrier material is flashed to atmospheric pressure with a small vent stream of >99.9 vol% H_2 before being fed to the BDO-rich storage tank for later dehydrogenation. A significant quantity of GBL may be present in the BDO-rich storage tank due to limited equilibrium conversions at the high reaction temperatures required for sufficiently fast reaction rates. Makeup carrier required due to byproduct formation in either hydrogenation or dehydrogenation is fed as BDO to the BDO-rich storage tank.

Dehydrogenation area process description

During periods where hydrogen is required, the BDO-rich carrier feed is preheated using hot reactor effluent and passed through a trim heater to further raise the feed temperature to reactor temperature for endothermic dehydrogenation. The effluent of the multitube dehydrogenation reactor consists of GBL, small amounts of unconverted BDO, and H_2 . Following effluent heat recovery, carrier material is condensed out of the product stream and separated from H_2 , then returned to the GBL-rich storage tank.

For lower pressure vapor phase dehydrogenation, H_2 is compressed to 3 bara outlet pressure sufficient for fuel cell operation [36,37] and cooled to remove residual GBL carrier material. H_2 product exits at greater than 99.95

vol% purity. Since the liquid phase dehydrogenation system operates at higher 4-6 bara pressure, the product compressor and associated downstream separation equipment are not required and H₂ is throttled to target product pressure.

2.2.2 MCH/TOL benchmark system

The system design for the MCH/TOL system with vapor phase hydrogenation and dehydrogenation was adapted from the process models developed by some of the authors, described in detail for a significantly larger stationary storage system [6]. Similar to the BDO/GBL system, the MCH/TOL system was modeled in Aspen Plus and scaled to the same 10 MW backup power system for comparison.

2.2.3 CG benchmark system

Compressed gas (CG) hydrogen storage systems are modeled at two nominal pressure levels (170 bara and 350 bara) using the Tankinator model developed by the Pacific Northwest National Laboratory (PNNL) [38]. The 170 bara configuration employs Type I aluminum pressure vessels, whereas the 350 bara configuration utilizes Type IV composite tanks consisting of carbon fiber-reinforced polymer with aluminum liners. A release efficiency of 95% is assumed for both systems, implying that 5% of the stored hydrogen is considered unrecoverable due to losses. The storage tanks are maintained at ambient temperature (25 °C), and discharged hydrogen is preheated to 80 °C prior to entering the fuel cell system.

2.3 Process performance metrics

Key process metrics used to evaluate system performance are defined below.

Levelized cost of H₂ storage

Levelized cost of H₂ storage (LCOS) is calculated according to the method presented in Breunig et al. [6], and summarized in Equation 2.1 where TCI is Total Capital Investment, CCF is Capital Charge Factor, OC_{fix} are fixed Operating Costs per year, OC_{var} are variable Operating Costs per year, and AS is Annual Storage of H₂.

$$\text{Levelized Cost of Storage } \left(\frac{\$}{\text{kg}} \right) = \frac{(TCI \cdot CCF + OC_{fix} + OC_{var})}{(AS)} \quad \text{where } AS \neq 0 \quad \text{Equation 2.1}$$

TCI is the sum of fixed capital investment (FCI, including total direct and indirect costs), land, and working capital. Installed equipment costs were estimated using Aspen Process Economic Analyzer or a factored estimate approach using installation factors specific to equipment type [39,40], with sizing information derived from simulation mass and energy balances. Equipment sparing philosophy is not considered at this stage. All equipment is costed as carbon steel based on current industrial practice [41,42]. Additional direct costs and indirect costs are calculated as a factored estimate of total installed costs (TIC) and total direct costs (TDC) respectively. Capital charge factor (CCF) is based on the financing structure detailed in Table 2.2.

Fixed operating costs (OC_{fix}) include operating and supervisory labor, maintenance materials, and insurance/taxes which are estimated based on an equipment module approach and factored estimates, whereas variable operating costs for raw materials and utilities (OC_{var}) are calculated directly from simulation results.

Annual storage (AS) of hydrogen is 692 MT/y based on the design basis for backup power (i.e. rate, duration, and number of cycles per year). Note that AS is the number of cycles multiplied by the maximum storage size of hydrogen, determined based on end user requirements (here 58 MT H₂).

Key economic assumptions are summarized in Table 2.2, with additional costing methodology provided in Table S2 through S4. All material, equipment, and labor costs were updated to a pricing basis of 2024 using the producer price index for chemical manufacturing [43], chemicals manufacturing labor cost index [44], and Chemical Engineering Plant Cost Index [45].

Table 2.2 Economic assumptions

Assumption	Value
Pricing basis	2024
Working capital	5% of FCI
Depreciation method	150% declining balance
Recovery period (y)	20
Equity financing (%)	36%
Loan interest rate (%)	5%
Internal rate of return (%)	10%
Plant life (y)	30
Construction period (y)	3
Income tax rate (%)	21% federal, 6% state

Process energy efficiency

Process energy efficiency is calculated based on natural gas (lower heating value (LHV) basis) and electricity consumption according to Equation 2.2, assuming 33.3 kWh/kg H₂ LHV [46].

$$eff = 1 - \frac{\text{Hydrogenation energy required} + \text{dehydrogenation energy required}}{\text{LHV of H}_2 \text{ product}} \quad \text{Equation 2.2}$$

3 Technoeconomic analysis

Both hydrogenation and dehydrogenation can occur in vapor or liquid reacting phase. Three classes of process configurations were assessed over the range of operating conditions noted in Table 3.1:

- Case 1: vapor phase hydrogenation, vapor phase dehydrogenation**
Sensitivity analysis for this case explores how vapor phase hydrogenation conditions affect system costs. Dehydrogenation operating conditions are held fixed.
- Case 2: liquid phase hydrogenation, vapor phase dehydrogenation**
Sensitivity analysis is conducted on liquid phase hydrogenation operating conditions for comparison to previous vapor phase hydrogenation results. Dehydrogenation operating conditions are held fixed.
- Case 3: liquid phase hydrogenation, liquid phase dehydrogenation**
Sensitivity analysis is conducted on liquid phase dehydrogenation operating conditions for comparison to previous vapor phase dehydrogenation results. Hydrogenation operating conditions are held fixed.

The primary independently varied sensitivity variables are reactor temperature and pressure: for each case, temperature is varied across a range at two pressure levels. Additional operating variables of interest are the reactor conversion target and the H₂:GBL molar ratio in feed (for hydrogenation only) which are specified as follows. For all process variants, reactor conversion is set as a dependent variable based on the equilibrium conversion at each given temperature and pressure. Conversions to desired product (BDO or GBL) are targeted at a specified fraction below the equilibrium conversion threshold since required reactor volumes and costs increase steeply as the extent of conversion approaches equilibrium. As discussed further in the following sections, H₂:GBL molar ratio is set as a dependent variable for vapor phase hydrogenation (varies with temperature and pressure) and assumed as a fixed variable for liquid phase hydrogenation.

For subsequent baseline system modeling and costing, only the main hydrogenation and dehydrogenation reactions were considered. The effect of byproduct formation is discussed in Section 3.5.

Table 3.1 BDO/GBL cases and operating condition ranges

		Case 1	Case 2	Case 3
Hydrogenation specifications		Vapor phase hydrogenation	Liquid phase hydrogenation	Liquid phase hydrogenation
Temperature	°C	180-240 ^a	180-240 / 160-220 ^a	200
Pressure	bara	35 / 50 ^a	50 / 120 ^a	50
H ₂ to GBL molar ratio in feed	ratio	140-20 / 200-30	4 / 50	4
Conversion to BDO	% of feed GBL	61-19% / 74%-33%	83-42% / 89-81%	71-74% / 67-74%
Equilibrium conversion to BDO	%	68-21% / 82-36%	92-47% / 99-90%	79-82% / 75-82%
Dehydrogenation specifications		Vapor phase dehydrogenation	Vapor phase dehydrogenation	Liquid phase dehydrogenation
Temperature	°C	260	260	160-220 ^a
Pressure	bara	2	2	4 / 6 ^a
Conversion to GBL	% of feed BDO	99%	99%	77-95% / 59-95%
Equilibrium conversion to GBL	%	~100%	~100%	95%

^a denotes independent sensitivity variables for each case

3.1 Summary of baseline results

Operating parameters and selected results for the conditions that result in lowest cost are summarized in Table 3.2 and Figure 3.1 for each BDO/GBL system operating mode: vapor/vapor, liquid/vapor, and liquid/liquid hydrogenation and dehydrogenation. Lowest LCOS and highest process energy efficiency is attained for liquid phase hydrogenation combined with liquid phase dehydrogenation (Case 2). This is due to high hydrogenation conversion with minimal H₂ diluent, as well as lack of dehydrogenation H₂ product compression. The upstream hydrogenation area generally drives system costs for reasons that include slower reaction rates, incomplete conversion, and shorter 2-day charging duration. With the exception of vapor phase

hydrogenation/dehydrogenation which has higher costs, baseline LCOS for other BDO/GBL modes is significantly lower than for MCH/TOL and CG benchmarks.

Results for each individual BDO/GBL case are further discussed in the subsequent sections. A detailed comparison between BDO/GBL and MCH/TOL systems is also provided.

Table 3.2 Results summary for lowest cost operating conditions in each operating mode

		Case 1	Case 2	Case 3
Process conditions resulting in lowest LCOS				
Hydrogenation specifications		Vapor phase hydrogenation	Liquid phase hydrogenation	Liquid phase hydrogenation
Temperature	°C	220	220	200
Pressure	bara	50	50	50
H ₂ :GBL molar ratio	ratio	50:1	4:1	4:1
Conversion target	% of feed GBL	47%	60%	74%
Dehydrogenation specifications		Vapor phase dehydrogenation	Vapor phase dehydrogenation	Liquid phase dehydrogenation
Temperature	°C	260	260	220
Pressure	bara	2	2	6
Conversion target	% of feed BDO	99%	99%	95%
Process energy balance				
Natural gas consumption	kWh/kg H ₂	13.3	11.7	8.7
Electricity consumption	kWh/kg H ₂	3.2	1.1	0.5
Process energy efficiency	%	50%	62%	72%
Key process and economic results				
GBL-rich/BDO-rich storage quantity	MT	2645 / 2697	2058 / 2114	1742 / 1799
Fixed operating costs	\$/y	\$1,552,300	\$1,141,700	\$1,079,700
Variable operating costs	\$/y	\$382,600	\$221,600	\$146,400
Total installed costs, hydrogenation	\$	\$16,048,900	\$6,939,700	\$8,754,400
Total installed costs, dehydrogenation	\$	\$6,646,000	\$6,266,500	\$3,019,700
Total capital investment	\$	\$51,152,100	\$30,968,000	\$27,406,100
Levelized cost of storage	\$/kg H ₂	\$8.03	\$5.14	\$4.58

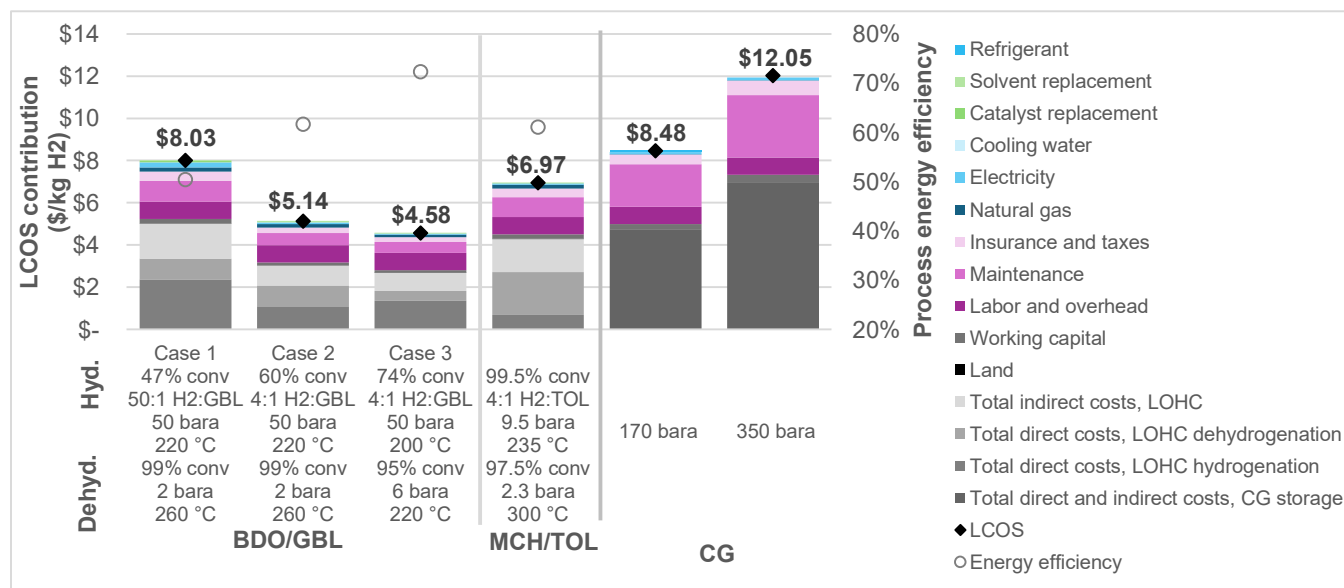


Figure 3.1 LCOS and process energy efficiency comparison for all BDO/GBL cases at conditions resulting in lowest cost, no byproducts. Results are compared with MCH/TOL as well as 170 and 350 bara CG.

3.2 Case 1: vapor phase hydrogenation, vapor phase dehydrogenation

3.2.1 Objective and scope

This case establishes costs for vapor phase hydrogenation in combination with vapor phase dehydrogenation. Hydrogenation temperature is varied in the sensitivity analysis from 180-240 °C at a fixed 35 bara and 50 bara (extrapolated) reactor pressure. H₂:GBL molar ratio in feed is set at the minimum ratio required to maintain 100% vapor phase conditions at reactor inlet. The lower-cost dehydrogenation area is modeled as vapor phase with reactor conditions held constant. Operating temperature is selected above the range of feed dew points corresponding to upstream hydrogenation conversions. The reactor operates at slightly elevated operating pressure to overcome downstream pressure drops.

3.2.2 Key results

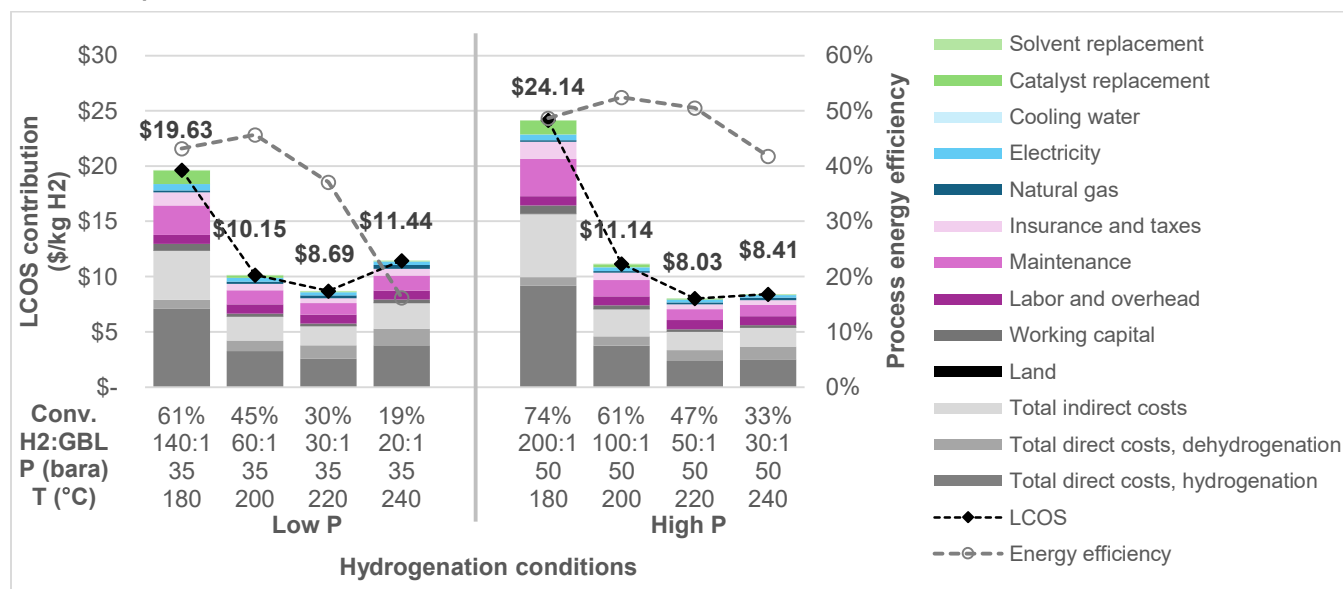


Figure 3.2 LCOS breakdown and process energy efficiency for Case 1 across a range of hydrogenation temperatures at 35 and 50 bara. Vapor phase hydrogenation conditions varied, with vapor phase dehydrogenation fixed at 260 °C and 2 bara.

LCOS and process energy efficiency results for Case 1 are shown in Figure 3.2 as a function of reactor operating conditions. Vapor phase hydrogenation is characterized firstly by lower feasible equilibrium conversions of GBL to BDO and secondly by higher H₂ dilution. These two factors decrease process energy efficiency and additionally increase operating and capital expenses by way of increased equipment throughput and storage volumes. This is applicable to not only upstream hydrogenation, but also the downstream dehydrogenation area through which unconverted GBL is carried.

For all conditions, direct and indirect capital costs (Figure S1) make up the majority of LCOS with the hydrogenation area accounting for 70% or more of total installed equipment costs. The largest contributors to hydrogenation equipment costs (H₂ recycle compressor, feed preheater, and product coolers) all have costs tied to the choice of vapor phase hydrogenation due to the aforementioned low conversions and high H₂ flowrates compared with liquid phase operation. Except at very low temperatures, the hydrogenation reactor itself does not constitute a large portion of equipment costs. Low per pass conversions and large excess of H₂ allow for vapor phase hydrogenation using lower cost adiabatic fixed bed reactors with a small temperature rise of 10-20 °C from reactor inlet to outlet.

Although dehydrogenation area capital costs are a small proportion of LCOS, operating pressure of the dehydrogenation reactor could be increased beyond the current 2 bara to eliminate the H₂ product compressor, which represents the largest single cost component in the dehydrogenation section. However, such a change would necessitate higher operating temperatures to maintain vapor phase conditions, thereby precluding the use of saturated steam at conventional supply pressures, which typically provide heat only up to 260–270 °C [34,47].

The small fixed and variable cost contributions stem mainly from maintenance materials and cost of labor. Natural gas and electrical utilities contribute negligibly to LCOS. Similarly, catalyst degradation rate and catalyst cost have minor influence on LCOS.

Process tradeoffs

Equilibrium conversion for the exothermic hydrogenation reaction increases at lower temperatures according to Le Chatelier's principle. However, the higher conversion possible at low temperature is countered by higher H₂ feed ratios required to maintain vapor phase. This has the net effect of a BDO product stream concentration that, at a given pressure, is relatively comparable across the temperature range assessed. The cost tradeoff between conversion and H₂ ratio as a function of temperature results in lowest LCOS of \$8.69/kg H₂ (at 35 bara) and \$8.03/kg H₂ (at 50 bara) at an intermediate 220 °C operating point. This corresponds to an intermediate H₂:GBL ratio in feed but importantly the lowest absolute H₂ recycle flowrate, since for the fixed design basis of 1.2 MT H₂/h, GBL feed rate (to which H₂ is ratioed) varies at differing conversion points. Also of note is that operation at overly low temperatures is additionally disfavored due to slow reaction rates, which translate to increased costs for hydrogenation reactor volume and catalyst replacement quantity.

Process energy efficiency is dramatically lower at higher temperature on account of escalating natural gas consumption, despite heat integration via feed-effluent heat exchange. As conversion drops with higher temperature, larger flowrates of unconverted GBL must be heated to reaction temperature and vaporized for dehydrogenation. As shown in the subsequent section, this effect is less pronounced if dehydrogenation is instead performed in liquid phase.

At a given temperature, higher hydrogenation operating pressure favors increased equilibrium conversion and reaction rate due to dependence on H₂ partial pressure. At higher temperatures, LCOS is slightly lower for 50 bara operation compared to 35 bara operation since GBL and H₂ flowrates are both decreased. The opposite is true at lower temperatures owing to higher H₂ ratios.

3.3 Case 2: liquid phase hydrogenation, vapor phase dehydrogenation

3.3.1 Objective and scope

The objective of this case is to assess potential cost reductions that can be attained by switching to liquid phase hydrogenation.

Sensitivity analysis on liquid phase hydrogenation first varies hydrogenation temperature from 180-240 °C at an operating pressure of 50 bara, consistent with the original experimental data upon which kinetics are based. Only a small 100% excess of H₂ feed is assumed (i.e. a 4:1 H₂:GBL ratio). Alternate liquid phase reaction conditions described in the patent literature favor even higher pressures (preferably 80-160 bara) to increase feasible equilibrium conversion, and high H₂:GBL ratios (around 50-100) to improve selectivity to BDO [48]. Liquid phase hydrogenation is therefore also explored at a higher 120 bara pressure and a 50:1 H₂ ratio, with temperature varied at a slightly lower range of 160-220 °C to suppress vaporization of condensables. For all conditions, vapor phase dehydrogenation conditions are held fixed as in Case 1.

3.3.2 Key results

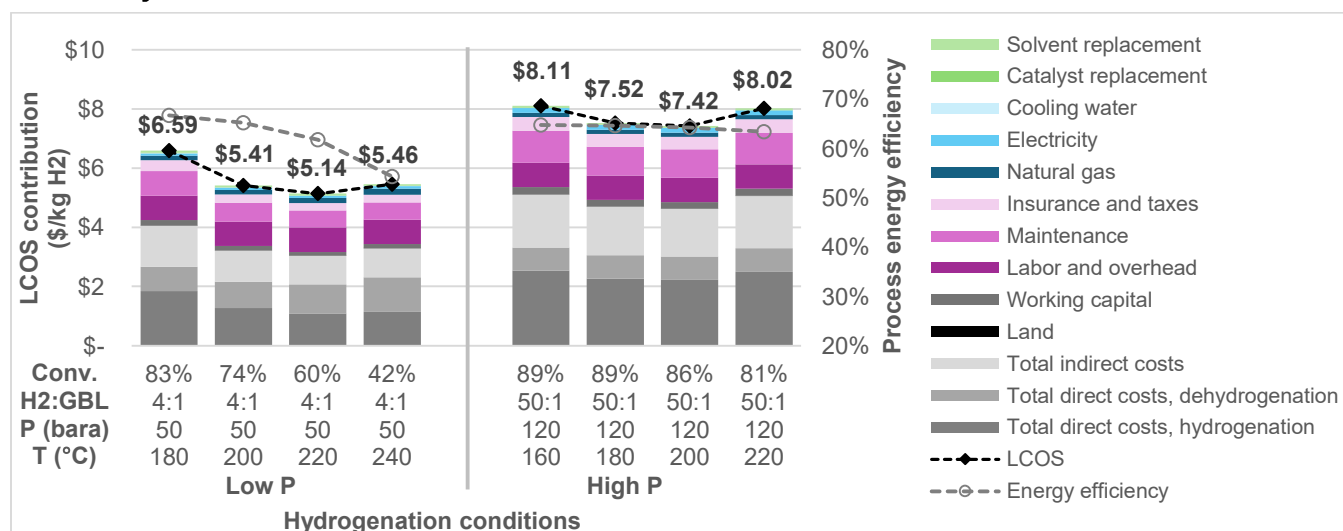


Figure 3.3 LCOS breakdown and process energy efficiency for Case 2 across a range of hydrogenation temperatures at 50 and 120 bara. Liquid phase hydrogenation conditions varied, with vapor phase dehydrogenation fixed at 260 °C and 2 bara.

Results for Case 2 involving liquid phase hydrogenation are shown in Figure 3.3. As expected, higher conversions combined with substantially lower H₂ flowrates serve to reduce key hydrogenation area equipment costs (e.g. feed preheater and H₂ recycle compressor). This translates to up to a 36% decrease in LCOS when

compared to the lowest storage costs attained in Case 1 for vapor phase hydrogenation. Higher cost of multitube reactor construction is more than offset by reduced liquid phase reactor volumes relative to vapor phase reaction, though reactor design must additionally account for adequate H₂ mass transfer and avoid liquid maldistribution. Process energy efficiency is higher for liquid phase operation than for vapor phase cases at similar conversion points due to savings on compression electricity for lower H₂ flowrates.

Process tradeoffs

The inverse relationship between conversion and temperature is similarly applicable to liquid phase hydrogenation. Despite the diminishing conversion, LCOS decreases as a function of higher temperatures up to a certain point since increased rates of reaction substantially lower hydrogenation reactor costs. However, as reactor temperature increases, the lower conversion also corresponds to increase in H₂ feed flowrate (at a fixed H₂:GBL ratio) as well as higher overall carrier flowrate (since H₂ production is fixed). This is mainly reflected in increased feed heat exchanger costs, with the net effect being a slight increase in LCOS at the higher temperature bound. Process energy efficiency again closely follows conversion (both decreasing as a function of temperature).

At 50 bara hydrogenation pressure with small excess of H₂ feed, lowest LCOS is \$5.14/kg H₂ at an intermediate 220 °C temperature. At this operating point, hydrogenation area capital costs are minimized such that they are almost equal to dehydrogenation capital costs despite the shorter 2-day hydrogenation duration. For operation at elevated 120 bara pressure with increased H₂ feed ratio, lowest LCOS is \$7.42/kg H₂ at 200°C. A cost penalty is incurred from additional capital and operating expenses of the feed heat exchanger and H₂ makeup compressor (now requiring 3-stage compression with intercooling). Even so, liquid phase operation in this mode is still slightly cost advantaged compared to vapor phase hydrogenation.

3.4 Case 3: liquid phase hydrogenation, liquid phase dehydrogenation

3.4.1 Objective and scope

The objective of this case is to evaluate implications of conducting dehydrogenation in liquid phase.

Sensitivity analysis is performed on liquid phase dehydrogenation operating conditions by varying temperature across a range of 160-220°C at a reactor pressure of 4 and 6 bara. Upstream hydrogenation is assumed as liquid phase to allow for lower system costs. Operating conditions are held fixed at a slightly higher conversion point than the previous lowest LCOS conditions for liquid phase hydrogenation. This is to reduce unconverted light GBL carrier in the downstream dehydrogenation area that would unfavorably lower feed bubble point.

3.4.2 Key results

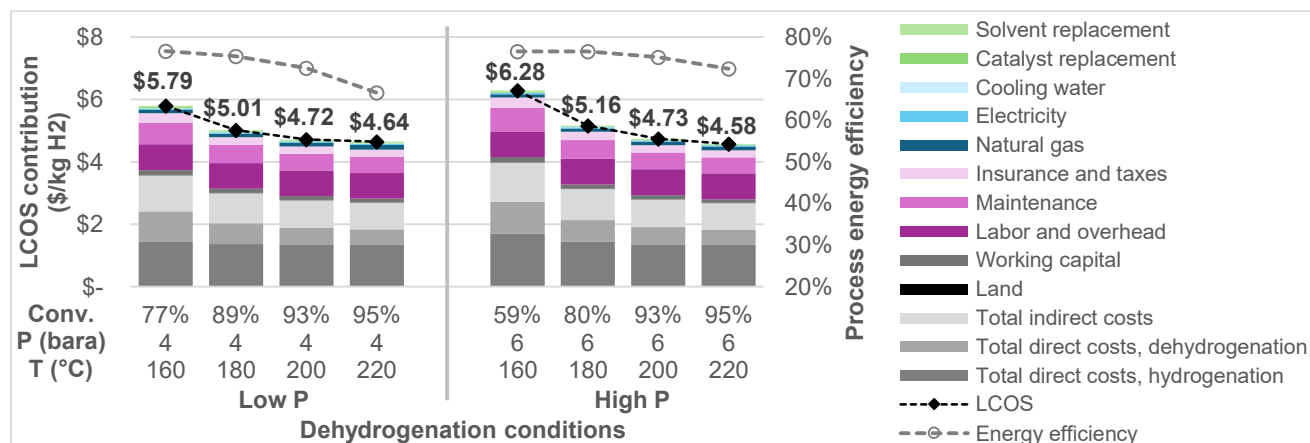


Figure 3.4 LCOS breakdown and process energy efficiency for Case 3 across a range of dehydrogenation temperatures at 4 and 6 bara. Liquid phase dehydrogenation conditions varied, with liquid phase hydrogenation conditions fixed at 200 °C, 50 bara, 4:1 H₂:GBL ratio.

Results for Case 3 are documented in Figure 3.4. As previously established, the dehydrogenation area has less of an effect on overall system costs relative to hydrogenation for the present design basis. Nonetheless, small reductions in cost can still be achieved via the choice of liquid phase dehydrogenation as opposed to vapor phase. Operation in liquid phase requires either higher pressures or lower temperatures which both shift equilibrium undesirably towards BDO reactant. However, the primary cost benefit of the modestly higher pressure levels evaluated here is that further H₂ product compression is not needed, as opposed to vapor phase operation where product compression is the largest contributor to dehydrogenation area capital costs.

Process energy efficiency is improved over vapor phase dehydrogenation but not drastically so. As discussed in Mevawala et al [13], though vapor phase operation requires complete feed stream vaporization, a large portion of heat needed for vaporization can be recovered via effluent heat exchange prior to the reactor which is not the case for liquid phase operation.

Process tradeoffs

Higher dehydrogenation temperature has a favorable effect on reaction rate and equilibrium conversion, thus minimizing dehydrogenation reactor and system costs. Minimum LCOS is \$4.64/kg H₂ at 4 bara and \$4.58/kg H₂ at 6 bara. However, feasible operating window is approximately bounded by the 220 °C maximum temperature assessed here to avoid full vaporization of the reacting liquid phase along the reactor (note slightly higher temperatures can be tolerated at 6 bara). Process energy efficiency decreases across this range since higher temperatures increase the partial pressure of BDO and GBL carrier (with partial pressure of the latter also increasing with conversion). Thus, additional natural gas consumption is required to compensate for heat of vaporization in addition to the enthalpy of dehydrogenation.

Increasing reactor pressure from 4 to 6 bara suppresses reactant vaporization, thereby increasing reacting liquid phase fraction and reducing heating demand. In terms of LCOS, at low temperatures this positive effect of pressure on reactor sizing is outweighed by significantly decreased equilibrium conversions. However, on the upper end of temperatures modeled where conversions is only marginally lower with pressure, costs at 6 bara are slightly reduced relative to 4 bara operation. For applications requiring H₂ product pressures higher than the 3 bara basis assumed in this analysis, higher pressure dehydrogenation operation would provide additional savings in downstream compression equipment and operating costs.

3.5 Effect of byproduct formation

3.5.1 Objective and scope

For baseline results shown previously, byproduct formation reactions were excluded to identify a minimum threshold for LCOS as a function of reaction phase and operating conditions only. As a result, carrier replacement cost is negligible across all cases, with only small losses in H₂ offgas stream from hydrogenation and in the H₂ product stream from dehydrogenation. However, compared to other LOHC systems such as MCH/TOL which demonstrates high selectivity at near complete conversions [5,49,50], appreciable byproduct formation for the BDO/GBL pair has been reported in the literature for certain catalysts under both hydrogenation and dehydrogenation conditions.

The cases shown in Section 3.1 were reassessed with experimentally observed byproduct formation reactions now included. Byproducts formed are a mix of 1-BuOH and THF for vapor phase hydrogenation [22], 4-HHB in liquid phase hydrogenation, THF and 2-HTHF in vapor phase dehydrogenation, and 4-HHB and DG in liquid phase dehydrogenation [22-24]. A minor degree of reversible byproduct formation may generally be tolerated depending on the steady state concentration within a storage system, but irreversibly formed byproducts must be largely removed to avoid accumulation (e.g. via conventional distillation). In the current modeling, all species are assumed to be completely separated from BDO/GBL carrier material prior to storage, but design and costing of those downstream separations is not conducted here for reasons discussed below.

Makeup carrier is assumed to be fed as H₂-lean BDO, due to the more limited global production and higher price point of GBL [51]. To maintain system GBL inventory, dehydrogenation area sizing is increased to account for additional GBL production.

3.5.2 Key results

LCOS and key process results are shown in Table 3.3 and Figure 3.5. Under respective case conditions, selectivity to byproducts is higher for vapor phase hydrogenation compared to liquid phase hydrogenation, and higher for liquid phase dehydrogenation than for vapor phase dehydrogenation. The net effect of byproduct formation is a doubling or tripling of LCOS, not yet including additional costs of equipment, utility, and added solvent loss associated with byproduct separation. Makeup solvent alone incurs a significant LCOS penalty of \$6-11/kg H₂ on top of previous system costs.

The quantity of excess H₂ produced in dehydrogenation to avoid GBL depletion ranges from 8-22% over the minimum target H₂ production rate. The equivalent H₂ energy content constitutes 28-39% of dehydrogenation heat demand (assuming conservative 90% efficiency on LHV basis [52,53]). Energy could conceivably be recovered from this stream to offset natural gas consumption, albeit at the expense of additional capital equipment. However, LCOS would be relatively unaffected since process heating only accounts for a small fraction of costs.

For all operating modes when taking into account carrier replacement cost only, LCOS is already comparable to or higher than for physical H₂ storage or MCH/TOL benchmark costs. As a result, further separations modeling

and a full sensitivity study across temperatures and pressures were not performed. System costs would remain prohibitively high for the BDO/GBL system in any combination of reaction phase or operating conditions without substantial improvements to reaction selectivity over the observed kinetics applied in this study (Table S1).

Table 3.3 BDO/GBL case results with byproduct formation modeled

		Case 1	Case 2	Case 3
Hydrogenation area				
Phase		Vapor	Liquid	Liquid
Target conversion to BDO	%	46.8%	60.2%	73.8%
Selectivity to BDO	%	81.2%	89.0%	94.2%
Hydrogenation conversion, total	%	57.7%	67.6%	78.4%
Dehydrogenation				
Phase		Vapor	Vapor	Liquid
Target conversion to GBL	%	98.4%	98.4%	84.0%
Selectivity to GBL	%	99.4%	99.4%	88.8%
Dehydrogenation conversion, total	%	99.0%	99.1%	94.5%
System costs (excluding separations)				
Total capital investment	\$	\$51,685,600	\$32,184,100	\$28,802,100
	\$/kg H ₂	\$5.29	\$3.29	\$2.95
	% increase	1.0%	3.9%	5.1%
Fixed and variable operating costs	\$/y	\$9,866,800	\$5,698,700	\$7,697,400
	\$/kg H ₂	\$14.26	\$8.24	\$11.13
	% increase	410%	318%	528%
Levelized cost of storage	\$/kg H ₂	\$19.55	\$11.53	\$14.07
	% increase	143%	124%	208%

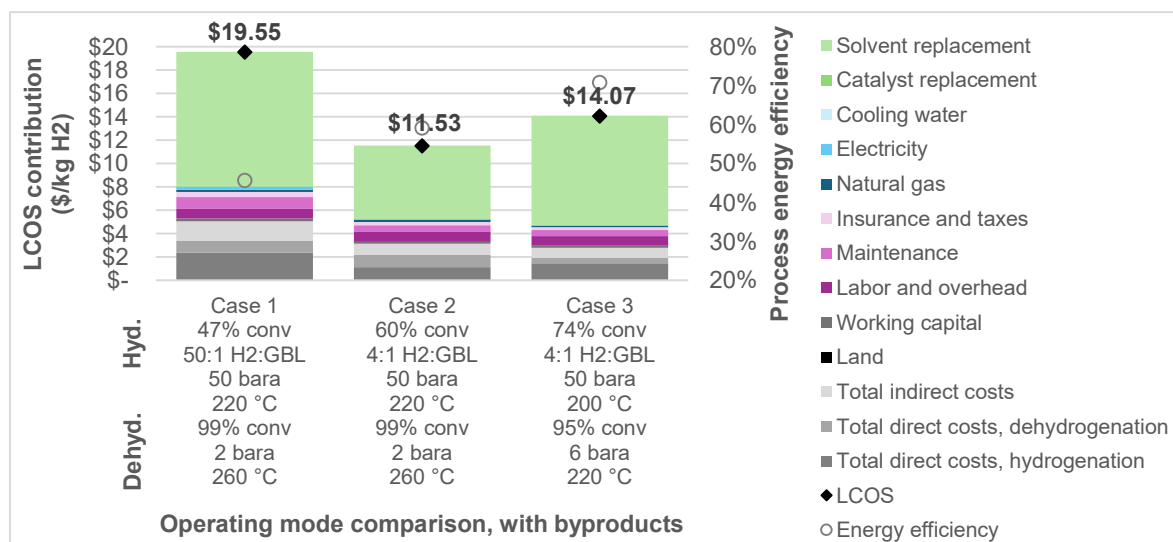


Figure 3.5 LCOS breakdown and process energy efficiency comparison for all operating modes at conditions resulting in lowest cost, byproduct formation modeled

3.5.3 Recent advances in catalyst development

There has been interest in developing bimetallic copper-based catalysts on non-acidic oxide supports to increase the catalyst stability and enhance the selectivity for GBL hydrogenation. Copper based catalysts are prone to deactivation through sintering and aggregation under reducing conditions [54] and the presence of a second metal enhances stability. Acidic sites on supports are assumed to be responsible for the irreversible dehydration reactions leading to THF and DG, thus supports that minimize acidic sites, e.g., SiO₂ and reduced TiO₂ will provide greater selectivity. Huang et al. first reported the enhanced selectivity of bimetallic cobalt-copper catalysts on reduced TiO₂ supports [55]. They found that cobalt rich catalysts, Cu_{0.1}Co_{0.9}-TiO₂-R, provided a high BDO production rate with 100% selectivity at 100 °C from GBL diluted in 1,4-dioxane, which resulted in highest catalyst activity among solvent candidates examined. Kim et al. similarly reported high selectivity for BDO exceeding 90% from a copper rich phase on a SiO₂ support, Cu_{0.8}Co_{0.2}-SiO₂, at 200 °C and 40 bara H₂ in the presence of 1,4-dioxane [56]. Both sets of experiments were performed at low concentrations of 10-20 wt% GBL in solvent where the lower effective H₂ storage density would scale equipment costs upwards and reduce process energy

efficiency [57], suggesting additional study is warranted to investigate whether high selectivity can be maintained at higher GBL loadings.

To address the selectivity and stability of copper-based catalysts for cycling BDO/GBL in the absence of solvent, Chen et al. compared the activity of a series of catalysts on a series of oxide supports prepared by three different methods [58]. High hydrogenation and dehydrogenation average rates were attained up to 0.43 mg H₂ uptake/g cat/min and 0.37 mg H₂ release/g cat/min for five of the catalysts with highest selectivity (>99.6%), with no observed catalyst degradation over multiple cycles. Notably, they demonstrated that both Cu/ZnO and Cu/Cr₂O₃ prepared by a co-precipitation method provided 100% selectivity for both H₂ uptake by GBL and H₂ release from BDO.

3.6 Comparison to MCH/TOL

MCH/TOL is a more mature LOHC pair that has progressed from demonstration stage to commercialization [59,60]. This carrier material is used as a benchmark system (see Figure 3.1) to illustrate how differences in carrier properties and observed kinetics can change system design and costs.

Capital costs are found to be the predominant driver of LCOS differences. MCH vapor phase dehydrogenation capital costs dwarf vapor phase hydrogenation capital cost, as opposed to the BDO/GBL system where the opposite is true. For TOL hydrogenation, a H₂ makeup compressor is not required due to lower 10 bara reactor operating pressure, thus reducing hydrogenation area capital cost. This contrasts with the GBL/BDO reaction equilibria which favors higher pressure operation to achieve sufficient hydrogenation conversion at viable (i.e. not unreasonably low) reaction temperatures. Due to the lower boiling points of the MCH/TOL pair, both recycle H₂ and product H₂ streams are cooled to -30 °C to condense out residual solvent, whereas heavier BDO/GBL system streams are only cooled to 40 °C. Chiller electricity represents a negligible overall cost contribution per kg H₂ stored, but refrigeration system capital comprises 11% of total installed equipment costs.

Another key difference between the two LOHC systems is the higher enthalpy of reaction for MCH dehydrogenation (68 kJ/mol H₂ at standard conditions) compared to BDO dehydrogenation (43 kJ/mol H₂ at standard conditions). However, actual dehydrogenation heat demand for the process as-modeled not only includes enthalpy of dehydrogenation but also sensible and latent heat required to bring feed up to reactor temperature (less feed/effluent heat recovery). 3 mols of H₂ are released per mol MCH compared to the 2 mol H₂ released per mol GBL, resulting in reduced flowrate of H₂-rich carrier feed relative to H₂ produced. In addition, the enthalpy of vaporization of MCH is about 318 kJ/kg MCH compared to a higher 627 kJ/kg BDO [61,62] (at respective normal boiling points), further reducing vapor phase dehydrogenation heat demand for the MCH/TOL system despite the higher reaction temperatures.

Natural gas requirement for the BDO/GBL case involving analogous vapor phase hydrogenation (Case 1 in Section 3.1) is actually 10% higher than for the MCH/TOL system (which consumes 12.0 kWh/kg H₂). In this case, the BDO/GBL system operates at lower upstream hydrogenation conversion and therefore requires heating and vaporization of the excess unreacted GBL in dehydrogenation feed. Natural gas consumption for the BDO/GBL case with liquid phase hydrogenation and vapor phase dehydrogenation (Case 2) is 3% lower than for MCH/TOL, and 28% lower with liquid phase hydrogenation and dehydrogenation (Case 3), due to the lower reaction temperatures and notably no vaporization heat duty.

Process heating costs make up a relatively small portion of LCOS for both LOHC systems due to low assumed cost of natural gas utility. However, MCH dehydrogenation, which is modeled at 360 °C, uses higher pressure steam utility at a more challenging 164 barg supply pressure [6], contributing to escalated capital costs (21% of total) for the steam boiler system.

The MCH/TOL system utilizes Ni-based catalyst for hydrogenation (\$68/kg) and Pt-based catalyst for dehydrogenation (\$135/kg), whereas lower cost Cu-based catalyst (\$14/kg) is used for both GBL hydrogenation/BDO dehydrogenation reactions. Costs for initial catalyst fill and average yearly replacement cost are only a small fraction of overall LCOS for both the MCH/TOL system (\$0.02/kg H₂, or 0.2% of total LCOS) and the BDO/GBL system (\$0.004-0.05/kg H₂, or 0.1-0.7% of LCOS across cases), suggesting that selection of higher cost (e.g. platinum group metal) catalysts may be warranted if reaction rates or selectivity can be materially improved to lower reactor or makeup carrier costs which are a larger component of LCOS.

Use cases requiring significantly higher rates of hydrogenation relative to dehydrogenation (e.g. seasonal storage for industrial H₂ consumers [6]) are better suited for application of MCH/TOL due to faster TOL hydrogenation kinetics compared to GBL hydrogenation. Scenarios where slower hydrogenation may be tolerated relative to required dehydrogenation rates (e.g. for backup power with a longer allowable charge time or large centralized hydrogenation facilities for LOHC export) will tend to favor BDO/GBL since system costs for this pair are much more sensitive to hydrogenation duration.

4 Conclusions

4.1 Key conclusions

Analysis of the BDO/GBL system for 10 MW backup power shows that choice of phase is more critical for upstream hydrogenation for reasons that include slower reaction rates, incomplete conversion, and shorter charging duration. In the absence of byproduct formation, there is a clear cost preference for liquid phase hydrogenation as opposed to vapor phase hydrogenation. Reducing LCOS involves limiting diluent flowrates in the area that drives costs (in this case hydrogenation). Vapor phase hydrogenation is inherently challenged in this regard since unreacted GBL and excess H_2 cannot be minimized simultaneously by only adjusting temperature and pressure, due to reaction equilibrium and vapor phase constraints.

LCOS for vapor phase hydrogenation coupled with vapor phase dehydrogenation is in the range of \$8.03/kg H_2 to \$24.14/kg H_2 . In contrast, hydrogenation reactor operation in liquid phase with higher achievable conversions provides cost reductions over the operating range evaluated, even at H_2 feed ratios in large excess of the stoichiometric requirement. LCOS for liquid phase hydrogenation ranges from \$5.14/kg H_2 (for lower pressure and minimal H_2 excess) to \$8.11/kg H_2 (for higher pressure operation with higher H_2 dilution).

Though LCOS is less sensitive to dehydrogenation area costs, liquid phase dehydrogenation at moderately elevated pressure provides a further benefit over vapor phase dehydrogenation by avoiding product H_2 compression. Lowest overall LCOS of \$4.58/kg H_2 is attained for liquid phase dehydrogenation coupled with upstream liquid phase hydrogenation, with an upper range of \$6.28/kg H_2 .

Process conditions that result in lowest LCOS do not necessarily maximize process energy efficiency due to low assumed utility costs, but liquid phase hydrogenation/dehydrogenation coincidentally has highest process efficiency which is attributed again to low diluent flowrates, high conversions in each reactor, and reduced heating requirements for vaporization in dehydrogenation. Process energy efficiency for this variant ranges from 67% to 77% depending on operating conditions, with the lowest LCOS conditions corresponding to 72% efficiency.

Importantly, the minimum LCOS of \$4.58/kg H_2 calculated for BDO/GBL is lower than storage costs for MCH/TOL (\$6.97/kg H_2) and compressed gas benchmarks (\$8.48/kg H_2 at 170 bara, \$12.05/kg H_2 at 350 bara). This represents a bounding case for the BDO/GBL storage system without formation of reaction byproducts, which could be achieved by continued catalyst development targeted in particular at liquid phase hydrogenation. Across all operating modes, insufficient reaction selectivity remains the largest risk to BDO/GBL carrier viability. When incorporating byproduct formation based on the reaction kinetics utilized in the current study, LCOS increases to \$11.53/kg H_2 to \$19.55/kg H_2 even before the added cost of required separations.

4.2 Limitations of this study and recommendations for future work

As previously mentioned, alternate Cu-based catalysts for hydrogenation and dehydrogenation have been newly reported in the literature with near 100% selectivity. For these better performing catalysts, a comprehensive sensitivity analysis and cost optimization could be conducted that crucially includes detailed separations modeling, which was omitted from the present study. Another limitation is that thus far these novel catalyst preparations have not been demonstrated beyond lab scale. Factors such as minimum levels of H_2 dilution (for hydrogenation), potential accumulation of trace impurities from carrier makeup, or long-term catalyst stability are not well characterized experimentally.

Additionally, in this analysis, H_2 fuel cell costs were not assessed as part of system scope. The H_2 product stream contains low levels of residual BDO/GBL and the exact effect of these hydrocarbon impurities on operation and lifetime for various types of stationary fuel cells is not known. Evaluation of the cost tradeoff between impurity cleanup (e.g. via further cooling and condensation, or use of fixed adsorbent beds) and fuel cell capital and operating costs is left as an area for future study. Dehydrogenation integration with available waste heat from fuel cell operation is a potential strategy for improving process energy efficiency. This approach is particularly critical for scenarios with limited on-site fuel utility available during times of backup power demand and is similarly suggested as a topic for further modeling and analysis.

The steady state analysis here does not address the cost or efficiency implications of system startup, shutdown, or other operational transients (e.g. fluctuating H_2 feed rates from electrolysis). Findings from this study also pertain specifically to the 10 MW backup power scenario assumed as a design basis. For alternate stationary storage use cases, differing requirements for charge and discharge rates could materially change hydrogenation versus dehydrogenation area costs as a proportion of LCOS. Choice of reaction conditions for the BDO/GBL system may therefore be less critical: e.g. higher costs of vapor phase hydrogenation operation may be tolerated for the sake of reduced operational complexity. Precise knowledge of design requirements for industrially relevant use cases is necessary to confirm optimal configuration and value proposition of the BDO/GBL cycle and thereby encourage larger scale system validation.

5 CRediT authorship contribution statement

Jocelyn Shyong: Writing – original draft, Methodology, Investigation, Formal analysis, Visualization, Conceptualization. **Mark Bowden:** Writing – review and editing, Validation, Conceptualization. **Tom Autrey:** Writing – review and editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Syed Saqline:** Methodology, Investigation, Writing – review and editing. **Hanna Breunig:** Methodology, Writing – review and editing

6 Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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8 References

1. Griffiths, S., Sovacool, B. K., Kim, J., Bazilian, M., & Uratani, J. M. (2021). Industrial decarbonization via hydrogen: A critical and systematic review of developments, socio-technical systems and policy options. *Energy Research & Social Science*, 80. <https://doi.org/10.1016/j.erss.2021.102208>
2. U.S. Department of Energy. (2024). *Pathways to Commercial Liftoff: Clean Hydrogen*.
3. National Petroleum Council. (2024). *Harnessing Hydrogen: Role of Low Carbon Intensity Hydrogen in the United States*.
4. Niermann, M., Drünert, S., Kaltschmitt, M., & Bonhoff, K. (2019). Liquid organic hydrogen carriers (LOHCs) – techno-economic analysis of LOHCs in a defined process chain. *Energy & Environmental Science*, 12(1), 290-307. <https://doi.org/10.1039/c8ee02700e>
5. Papadias, D. D., Peng, J.-K., & Ahluwalia, R. K. (2021). Hydrogen carriers: Production, transmission, decomposition, and storage. *International Journal of Hydrogen Energy*, 46(47), 24169-24189. <https://doi.org/10.1016/j.ijhydene.2021.05.002>
6. Breunig, H., Rosner, F., Saqline, S., Papadias, D., Grant, E., Brooks, K., Autrey, T., Ahluwalia, R., King, J., & Hammond, S. (2024). Achieving gigawatt-scale green hydrogen production and seasonal storage at industrial locations across the U.S. *Nature Communications*, 15(1), 9049. <https://doi.org/10.1038/s41467-024-53189-2>
7. Tsogt, N., Gbadago, D. Q., & Hwang, S. (2024). Exploring the potential of liquid organic hydrogen carrier (LOHC) system for efficient hydrogen storage and Transport: A Techno-Economic and energy analysis perspective. *Energy Conversion and Management*, 299. <https://doi.org/10.1016/j.enconman.2023.117856>
8. Niermann, M., Beckendorff, A., Kaltschmitt, M., & Bonhoff, K. (2019). Liquid Organic Hydrogen Carrier (LOHC) – Assessment based on chemical and economic properties. *International Journal of Hydrogen Energy*, 44(13), 6631-6654. <https://doi.org/10.1016/j.ijhydene.2019.01.199>
9. Müller, K., Völkl, J., & Arlt, W. (2013). Thermodynamic Evaluation of Potential Organic Hydrogen Carriers. *Energy Technology*, 1(1), 20-24. <https://doi.org/10.1002/ente.201200045>
10. Rao, N., Lele, A. K., & Patwardhan, A. W. (2022). Optimization of Liquid Organic Hydrogen Carrier (LOHC) dehydrogenation system. *International Journal of Hydrogen Energy*, 47(66), 28530-28547. <https://doi.org/10.1016/j.ijhydene.2022.06.197>
11. Naseem, M., Usman, M., & Lee, S. (2021). A parametric study of dehydrogenation of various Liquid Organic Hydrogen Carrier (LOHC) materials and its application to methanation process. *International Journal of Hydrogen Energy*, 46(5), 4100-4115. <https://doi.org/10.1016/j.ijhydene.2020.10.188>
12. Müller, K., Skeledzic, T., & Wasserscheid, P. (2021). Strategies for Low-Temperature Liquid Organic Hydrogen Carrier Dehydrogenation. *Energy & Fuels*, 35(13), 10929-10936. <https://doi.org/10.1021/acs.energyfuels.1c01170>
13. Mevawala, C., Autrey, T., Brooks, K., Bowden, M., Tran, B. L., & Müller, K. (2022). 1,4-Butanediol as a Hydrogen Carrier: Liquid- versus Gas-Phase Dehydrogenation. *Energy & Fuels*, 37(1), 560-566. <https://doi.org/10.1021/acs.energyfuels.2c03355>

14. Mevawala, C., Brooks, K., Bowden, M. E., Breunig, H. M., Tran, B. L., Gutiérrez, O. Y., Autrey, T., & Müller, K. (2022). The Ethanol–Ethyl Acetate System as a Biogenic Hydrogen Carrier. *Energy Technology*, 11(1). <https://doi.org/10.1002/ente.202200892>
15. Gutiérrez, O. Y., Grubel, K., Kothandaraman, J., Lopez-Ruiz, J. A., Brooks, K. P., Bowden, M. E., & Autrey, T. (2023). Using earth abundant materials for long duration energy storage: electro-chemical and thermo-chemical cycling of bicarbonate/formate. *Green Chemistry*, 25(11), 4222-4233. <https://doi.org/10.1039/d3gc00219e>
16. Modisha, P. M., Ouma, C. N. M., Garidzirai, R., Wasserscheid, P., & Bessarabov, D. (2019). The Prospect of Hydrogen Storage Using Liquid Organic Hydrogen Carriers. *Energy & Fuels*, 33(4), 2778-2796. <https://doi.org/10.1021/acs.energyfuels.9b00296>
17. Bermudez Aponte, N. A., & Meille, V. (2024). Use of Biosourced Molecules as Liquid Organic Hydrogen Carriers (LOHC) and for Circular Storage. *Reactions*, 5(1), 195-212. <https://doi.org/10.3390/reactions5010008>
18. Zhu, Y., Yang, J., Mei, F., Li, X., & Zhao, C. (2022). Bio-based 1,4-butanediol and tetrahydrofuran synthesis: perspective. *Green Chemistry*, 24(17), 6450-6466. <https://doi.org/10.1039/d2gc02271k>
19. National Institute of Standards and Technology. (2025). *NIST Chemistry WebBook, SRD 69*. <https://webbook.nist.gov/chemistry/>
20. Rao, P., & Yoon, M. (2020). Potential Liquid-Organic Hydrogen Carrier (LOHC) Systems: A Review on Recent Progress. *Energies*, 13(22), 6040. <https://doi.org/10.3390/en13226040>
21. Schlender, J. H., & Turek, T. (1999). Gas-Phase Hydrogenolysis of Dimethyl Maleate to 1,4-Butanediol and γ -Butyrolactone over Copper/Zinc Oxide Catalysts. *Industrial & Engineering Chemistry Research*, 38(4), 1264-1270. <https://doi.org/10.1021/ie980606k>
22. Gautier, V., Champon, I., Chappaz, A., & Pitault, I. (2022). Kinetic Modeling for the Gas-Phase Hydrogenation of the LOHC γ -Butyrolactone–1,4-Butanediol on a Copper-Zinc Catalyst. *Reactions*, 3(4), 499-515. <https://doi.org/10.3390/reactions3040033>
23. Qasmi, C., Mochel, R., Gautier, V., Champon, I., Thomas, S., Chappaz, A., & Anne-Cécile, R. (2023). GBL/BDO pair as a bio-based liquid organic carrier: Kinetic modeling of liquid phase hydrogenation and dehydrogenation over copper-based catalyst. *International Journal of Hydrogen Energy*. <https://doi.org/10.1016/j.ijhydene.2023.11.232>
24. Ichikawa, N., Sato, S., Takahashi, R., Sodesawa, T., & Inui, K. (2004). Dehydrogenative cyclization of 1,4-butanediol over copper-based catalyst. *Journal of Molecular Catalysis A: Chemical*, 212(1-2), 197-203. <https://doi.org/10.1016/j.molcata.2003.10.028>
25. Peng, P., Anastasopoulou, A., Brooks, K., Furukawa, H., Bowden, M. E., Long, J. R., Autrey, T., & Breunig, H. (2022). Cost and potential of metal–organic frameworks for hydrogen back-up power supply. *Nature Energy*, 7(5), 448-458. <https://doi.org/10.1038/s41560-022-01013-w>
26. U.S. Department of Energy. (2015). *Fuel Cells Fact Sheet*. https://www.energy.gov/sites/default/files/2015/11/f27/fcto_fuel_cells_fact_sheet.pdf
27. National Fire Protection Association. (2022). NFPA 110: Standard for Emergency and Standby Power Systems. In.
28. Jin, X., You, S., Petersen, M., Riofrio, J., Thakur, S., Træholt, C., & Feng, Z. (2024). Exploring commercial water electrolyser systems: a data-based analysis of product characteristics. *Clean Energy*, 8(1), 126-133. <https://doi.org/10.1093/ce/zkad072>
29. Haug, P., Kreitz, B., Koj, M., & Turek, T. (2017). Process modelling of an alkaline water electrolyzer. *International Journal of Hydrogen Energy*, 42(24), 15689-15707. <https://doi.org/https://doi.org/10.1016/j.ijhydene.2017.05.031>
30. Brauns, J., & Turek, T. (2020). Alkaline Water Electrolysis Powered by Renewable Energy: A Review. *Processes*, 8(2).
31. Wong, C. Y., Wong, W. Y., Ramya, K., Khalid, M., Loh, K. S., Daud, W. R. W., Lim, K. L., Walvekar, R., & Kadhum, A. A. H. (2019). Additives in proton exchange membranes for low- and high-temperature fuel cell applications: A review. *International Journal of Hydrogen Energy*, 44(12), 6116-6135. <https://doi.org/https://doi.org/10.1016/j.ijhydene.2019.01.084>
32. Schlender, J. H. (2000). *Gasphasenhydrierung von Maleinsäuredimethylester zu 1,4-Butandiol, γ -Butyrolacton und Tetrahydrofuran an Kupfer-Katalysatoren* Universität Karlsruhe]. Karlsruhe, Germany.
33. Javadi, A., & Bildea, C. S. (2014). Design and Control of an Integrated 1,4-Butanediol Dehydrogenation and Furfural Hydrogenation Plant. *Chemical Engineering & Technology*, 37(9), 1515-1524. <https://doi.org/10.1002/ceat.201400210>
34. Turton, R., Shaeiwitz, J. A., Bhattacharyya, D., & Whiting, W. B. (2018). *Analysis, Synthesis, and Design of Chemical Processes*. Pearson Education.

35. Joshi, S. S., & Ranade, V. V. (2016). *Industrial catalytic processes for fine and specialty chemicals*. Elsevier.
36. Zhang, J., Zhang, H., Wu, J., & Zhang, J. (2013). PEM Fuel Cell Fundamentals. In *Pem Fuel Cell Testing and Diagnosis* (pp. 1-42). <https://doi.org/10.1016/b978-0-444-53688-4.00001-2>
37. Ferriday, T. B., & Middleton, P. H. (2021). Alkaline fuel cell technology - A review. *International Journal of Hydrogen Energy*, 46(35), 18489-18510. <https://doi.org/10.1016/j.ijhydene.2021.02.203>
38. Klymyshyn, N. A., Brooks, K., & Barrett, N. (2023). Methods for Estimating Hydrogen Fuel Tank Characteristics. *Journal of Pressure Vessel Technology*, 146(1). <https://doi.org/10.1115/1.4063884>
39. Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., Schoen, P., Lukas, J., Olthof, B., Worley, M., Sexton, D., & Dudgeon, D. (2011). *Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover*. <https://www.osti.gov/biblio/1013269>
40. Woods, D. R. (2007). *Rules of thumb in engineering practice*. John Wiley & Sons.
41. American Petroleum Institute. (2004). Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants.
42. Johnson Matthey. (2020). DAVY butanediol and co-products process.
43. U.S. Bureau of Labor Statistics. (2025). *Producer price index industry data for chemical manufacturing*. <http://data.bls.gov/cgi-bin/srgate>
44. U.S. Bureau of Labor Statistics. (2025). *Employment, Hours, and Earnings from the Current Employment Statistics survey (National)*. <http://data.bls.gov/cgi-bin/srgate>
45. Chemical Engineering. (2024). *Chemical Engineering Plant Cost Index*. <https://www.chemengonline.com/pci-home>
46. Hydrogen Tools. (2025). *Hydrogen Analysis Resource Center*. <https://h2tools.org/hyarc/hydrogen-data/lower-and-higher-heating-values-hydrogen-and-other-fuels>
47. Koch Applied Solutions. (2025). *Steam & Hot Water Boilers*. <https://www.kochapplied.com/steam-hot-water-boilers/>
48. Hesse, M., Schlitter, S., Borchert, H., Schubert, M., Rosch, M., Bottke, N., Fischer, R.-H., Weck, A., Windecker, G., & Heydrich, G. (2003). *Method for the production of 1,4- butanediol* US 2005O182281A1). United States Patent and Trademark Office.
49. Kurosaki, D. (2018). *Introduction of Liquid Organic Hydrogen Carrier and the Global Hydrogen Supply Chain Project*.
50. Honeywell International Inc. (2025). *Honeywell Liquid Organic Hydrogen Carrier*. <https://uop.honeywell.com/en/energy-transition/hydrogen-solutions/liquid-organic-hydrogen-carrier>
51. IHS Markit. (2020). *Process Economics Program: Butyrolactone from 1,4-Butanediol*.
52. Rosenow, J. (2024). A meta-review of 54 studies on hydrogen heating. *Cell Reports Sustainability*, 1(1), 100010. <https://doi.org/https://doi.org/10.1016/j.crsus.2023.100010>
53. Lara, G. (2022). *Boilers running on hydrogen: What you need to know*. <https://www.power-eng.com/hydrogen/boilers-running-on-hydrogen-what-you-need-to-know/>
54. Twigg, M. V., & Spencer, M. S. (2001). Deactivation of supported copper metal catalysts for hydrogenation reactions. *Applied Catalysis A: General*, 212(1), 161-174. [https://doi.org/https://doi.org/10.1016/S0926-860X\(00\)00854-1](https://doi.org/https://doi.org/10.1016/S0926-860X(00)00854-1)
55. Huang, Z., Barnett, K. J., Chada, J. P., Brentzel, Z. J., Xu, Z., Dumesic, J. A., & Huber, G. W. (2017). Hydrogenation of γ -Butyrolactone to 1,4-Butanediol over CuCo/TiO₂ Bimetallic Catalysts. *ACS Catalysis*, 7(12), 8429-8440. <https://doi.org/10.1021/acscatal.7b03016>
56. Kim, B.-S., Hidajat, M. J., Lee, S. W., Seo, J. G., Hwang, D. W., & Yun, G.-N. (2025). A Mechanistic Study on the Selective Hydrogenation of γ -Butyrolactone over the Rationally Designed Bimetallic CuCo Catalysts. *ACS Sustainable Chemistry & Engineering*, 13(2), 1017-1030. <https://doi.org/10.1021/acssuschemeng.4c08880>
57. Tran, B. L., Bowden, M. E., Autrey, T., Byun, M. Y., & Müller, K. (2024). Roles of Solvent in the Catalytic Hydrogen Release from Liquid Organic Hydrogen Carriers: Chemical, Thermodynamical and Technological Aspects. *Topics in Catalysis*, 67(13-14), 892-899. <https://doi.org/10.1007/s11244-024-01950-8>
58. Chen, Y., Kong, X., Yang, C., Liao, Y., Gao, G., Ma, R., Peng, M., Shao, W., Zheng, H., Zhang, H., Pan, X., Yang, F., Zhu, Y., Liu, Z., Cao, Y., Ma, D., Bao, X., & Zhu, Y. (2025). A catalytic cycle that enables crude hydrogen separation, storage and transportation. *Nature Energy*. <https://doi.org/10.1038/s41560-025-01806-9>
59. Chiyoda Corporation. (2014). *Performance Summary of Demonstration Tests of SPERA Hydrogen Process*. <https://www.chiyodacorp.com/en/service/spera-hydrogen/demo-plant/>

60. Honeywell International Inc. (2025). Honeywell Technology Is Selected For First Commercial Hydrogen Supply Chain via MCH. <https://ess.honeywell.com/us/en/about-ess/newsroom/press-release/2025/05/honeywell-technology-is-selected-for-first-commercial-hydrogen-supply-chain-via-mch>
61. Majer, V. (1985). *Enthalpies of Vaporization of Organic Compounds; A Critical Review and Data Compilation*. Oxford, Blackwell Scientific Publications.
62. Gräfe, H., Körnig, W., Weitz, H. M., Reiß, W., Steffan, G., Diehl, H., Bosche, H., Schneider, K., & Kieczka, H. (2000). Butanediols, Butenediol, and Butynediol. In. https://doi.org/10.1002/14356007.a04_455