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Research Article

Improving Productivity, Heat Transfer, and Catalyst Stability in the Dehydrogenation of Perhydro Benzyl Toluene through Internal Product Recycling

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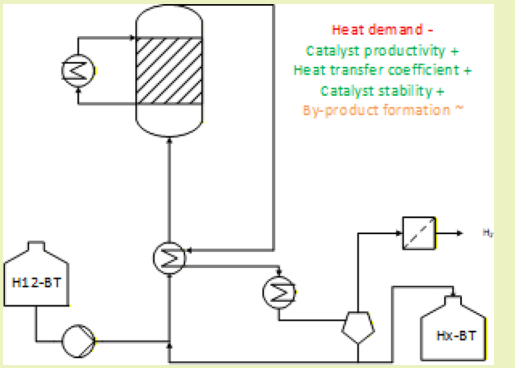
ABSTRACT: The liquid organic hydrogen carrier (LOHC) technology enables efficient hydrogen storage under ambient conditions by chemically binding hydrogen to organic molecules. Among the various LOHC systems, the perhydro benzyl toluene/benzyl toluene (H12-BT/H0-BT) pair stands out due to its low vapor pressure, favorable thermal stability, and high volumetric storage density. Continuous dehydrogenation of H12-BT in fixed-bed reactors, however, is typically characterized by rapid evaporation of the LOHC once a significant part of the bound hydrogen has been released. The resulting gas-phase dehydrogenation suffers from reduced heat transfer efficiency and catalyst wetting. In this study, we introduce a reactor concept that suppresses full LOHC evaporation through an internal recycling of the hydrogen-lean liquid product. We compare this recycling concept with the classical once-through reaction mode regarding heat demand, heat transfer, hydrogen release productivity, by-product formation, and catalyst stability. Although the recycling concept exhibits a moderately higher heat demand due to its higher overall amount of LOHC evaporation, it significantly improves heat transfer in the reactor, leading to higher average catalyst bed temperatures. As a result, hydrogen release productivity increases by up to 50%, while by-product formation remains comparable to the classical concept. Furthermore, the enhanced liquid holdup reduces coke precursor accumulation at the catalyst and markedly improves catalyst stability.



KEYWORDS: *LOHC, hydrogen storage, perhydro benzyl toluene, liquid holdup, product recycling reactor, multiphase reactor, dehydrogenation*

1. INTRODUCTION

Liquid Organic Hydrogen Carrier (LOHC) technologies enable safe and efficient hydrogen storage under ambient conditions by chemically binding hydrogen to an organic carrier molecule.[1,2] A LOHC system comprises at least one hydrogen-lean and one hydrogen-rich species. In the exothermic hydrogenation step, hydrogen reacts with the hydrogen-lean molecule to form the hydrogen-rich counterpart. Hydrogen can subsequently be released from the hydrogen-rich molecule via endothermic dehydrogenation. In the case of aromatic/alicyclic LOHC systems, both reactions rely on supported precious-metal catalysts. Ideally, the hydrogen-rich and hydrogen-lean compounds remain liquid at ambient conditions and are fully compatible with existing fossil-fuel logistics, thereby avoiding costly and time-consuming investments in new hydrogen infrastructure.

The overall energy efficiency of LOHC-based hydrogen storage depends strongly on thermal integration between hydrogenation and dehydrogenation.[3] In ideality, the heat released during hydrogenation equals the heat required for hydrogen release, enabling very high cycle efficiencies—provided that hydrogenation heat can be effectively utilized. In practice, however, hydrogenation frequently occurs at energy-rich sites or during renewable generation peaks, making full utilization of this heat a challenge.

Among currently available LOHC systems, the benzyl toluene/perhydro benzyl toluene (H0-BT/H12-BT) pair stands out due to its low vapor pressure, moderate viscosity, high density, and excellent hydrogen storage capacity of 6.2 wt % or 1.81 kWh L^{-1} at ambient conditions.[4] Furthermore, repeated hydrogenation and dehydrogenation can be carried out with minimal by-product formation, with methyl fluorene (MF) being the main byproduct.[4] Continuous dehydrogenation of H12-BT is typically conducted in fixed-bed reactors[5−7] and

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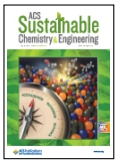

requires detailed understanding of the thermodynamic equilibrium,[8] process-dependent reaction kinetics,[9,10] heat transfer,[11] and reactor hydrodynamics. Dehydrogenation proceeds at temperatures between 280 and 350 °C.[6,7] Because hydrogen formation substantially increases the total molar flow in the reactor, elevated pressures adversely shift the equilibrium. To achieve near-quantitative hydrogen release, reactor pressures below 10 bar are mandatory at the typical dehydrogenation temperatures.[4,8]

The operating pressure in the dehydrogenation reactor determines the vapor−liquid equilibrium (VLE) of the LOHC mixture. To feed H12-BT in liquid form, the reactor pressure must exceed its vapor pressure. As hydrogen is released, its increasing partial pressure lowers the partial pressure of the LOHC components (summarized as Hx-BT), thereby inducing progressive evaporation. Reducing temperature or increasing pressure can suppress evaporation, but both approaches negatively affect reaction kinetics and equilibrium conversion.[10] Therefore, temperature−pressure combinations must be chosen that balance equilibrium limitations with the degree of Hx-BT evaporation. Figure 1 shows the vapor pressure of H12-BT and H0-BT. Additionally, the highest possible pressure to achieve a degree of dehydrogenation (DoDH) of 0.9 ($P^{EQ}_{DoDH=0.9}$) is shown in Figure 1. Furthermore, the lowest pressure to suppress complete evaporation of Hx-BT at a DoDH of 0.9 ($P^{Liquid}_{DoDH=0.9}$) is shown. This shows that complete evaporation cannot be suppressed for a technically relevant DoDH by adjusting process conditions.

Another factor governing evaporation is the ratio of liquid LOHC to hydrogen. Along the reactor, the rising hydrogen partial pressure continuously decreases the partial pressure of Hx-BT.[13] Under typical fixed-bed conditions, complete evaporation of the LOHC occurs already at a DoDH below 0.4, meaning that most of the reactor operates in the gas phase.[14] Poor catalyst wetting reduces productivity compared to liquid-phase or batch systems, where complete condensation of Hx-BT maintains full wetting.[14−16] Alternative reactor architectures—such as coated heat exchangers,[17−19] reactive distillation,[9,20,21] or membrane reactors[22,23]—can mitigate these limitations but introduce substantial extra complexity and scale-up challenges.

Maintaining liquid-phase dehydrogenation offers several advantages over gas-phase operation. First, the higher density of liquids results in longer residence times, which enhances hydrogen release.[14] Second, the thermal conductivity of liquids exceeds that of gases by at least an order of magnitude, yielding significantly higher heat-transfer coefficients.[24] In typical H12-BT dehydrogenation reactors, heat-transfer coefficients range from 200 to 1500 W m^{-2} K^{-1} in liquid−gas biphasic flow, but drop to roughly 150 W m^{-2} K^{-1} under fully gaseous conditions.[11,14] Third, carbonaceous by-products formed during dehydrogenation can dissolve in hot liquid LOHC and can be removed in this way from the catalyst surface.[25,26] The formation of methyl fluorene (MF) is a key indicator of coke precursor generation.[27] In gas-phase operation, coke precursors exhibit low volatility and thus accumulate on the catalyst surface and accelerate deactivation.[28−30]

In this study, we evaluate the concept of internal recycling of the hydrogen-lean, liquid LOHC fraction during H12-BT dehydrogenation, which has not been reported for LOHC dehydrogenation to the best of the authors' knowledge. Increasing the LOHC-to-hydrogen ratio suppresses full evaporation and improves catalyst wetting. From hydrogenation studies, it is known that internal liquid recycling also increases heat-transfer coefficients and accelerates heat removal from the reactor.[31] These effects suggest significant potential for improving dehydrogenation performance. However, dilution of the feed with hydrogen-lean product lowers the concentration of H12-BT and this reduces the intrinsic reaction rate.[10]

The aim of this work is therefore to compare a classical once-through dehydrogenation reactor with a reactor employing internal product recycling, examining differences in heat demand, heat-transfer, hydrogen release productivity, by-product formation, and catalyst stability. The results serve to provide guidance for the design and operation of dehydrogenation reactors that use liquid-phase product recycling.

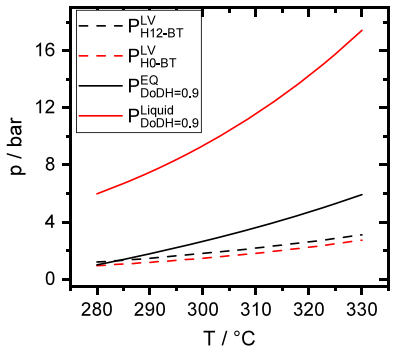

Figure 1. Dependency of H12-BT and H0-BT vapor pressure P^{LV}_{H12-BT} and P^{LV}_{H0-BT}, the highest pressure to enable thermodynamically a DoDH of 0.9 $P^{EQ}_{DoDH=0.9}$ and the lowest pressure to suppress complete evaporation for a DoDH of 0.9 $P^{Liquid}_{DoDH=0.9}$.[4,12]

2. MATERIAL AND METHODS

2.1. Conceptual Design

Figure 2 illustrates the process flow scheme of a classical H12-BT dehydrogenation unit. The hydrogen-rich LOHC is stored in a feed tank and pumped through a feed−product heat exchanger, where it is preheated by the hot product flow. Typically, the feed cannot be heated fully to reaction temperature, since complete heat recuperation would require an infinitely large heat-exchange surface. As a consequence, H12-BT enters the reactor slightly below the target reaction temperature and is further heated in situ by the external heat transfer medium.

After preheating, the liquid feed passes through the fixed-bed reactor containing the dehydrogenation catalyst, where hydrogen is released. The heat required for the endothermic reaction is supplied through the reactor wall via a circulating heat-transfer medium that is reheated in an external loop. Dehydrogenation is typically carried out at a thermal oil temperature between 290 and 350 °C, a pressure between 3 and 6 bar and a liquid hour space velocity of 0.3 and 2.5 h^{-1}.[6] The product flow—comprising Hx-BT and hydrogen—flows back through the feed−product heat exchanger and is cooled by the incoming feed. Because partial or complete evaporation of Hx-BT increases the enthalpy of the product stream, additional cooling is typically required in a secondary air-cooled heat exchanger. After cooling to near-ambient temperature, hydrogen and the hydrogen-lean LOHC are separated in a gas−liquid separator. The liquid, hydrogen-lean Hx-BT mixture is routed to a product tank, while the hydrogen is purified, for example by adsorption, if higher purity is required for downstream applications.[32]

The modifications necessary to implement the recycling concept are highlighted in red in Figure 2. In this process configuration, the H12-BT feed is mixed with a defined fraction of the hydrogen-lean LOHC product flow prior to entering the preheating section. The

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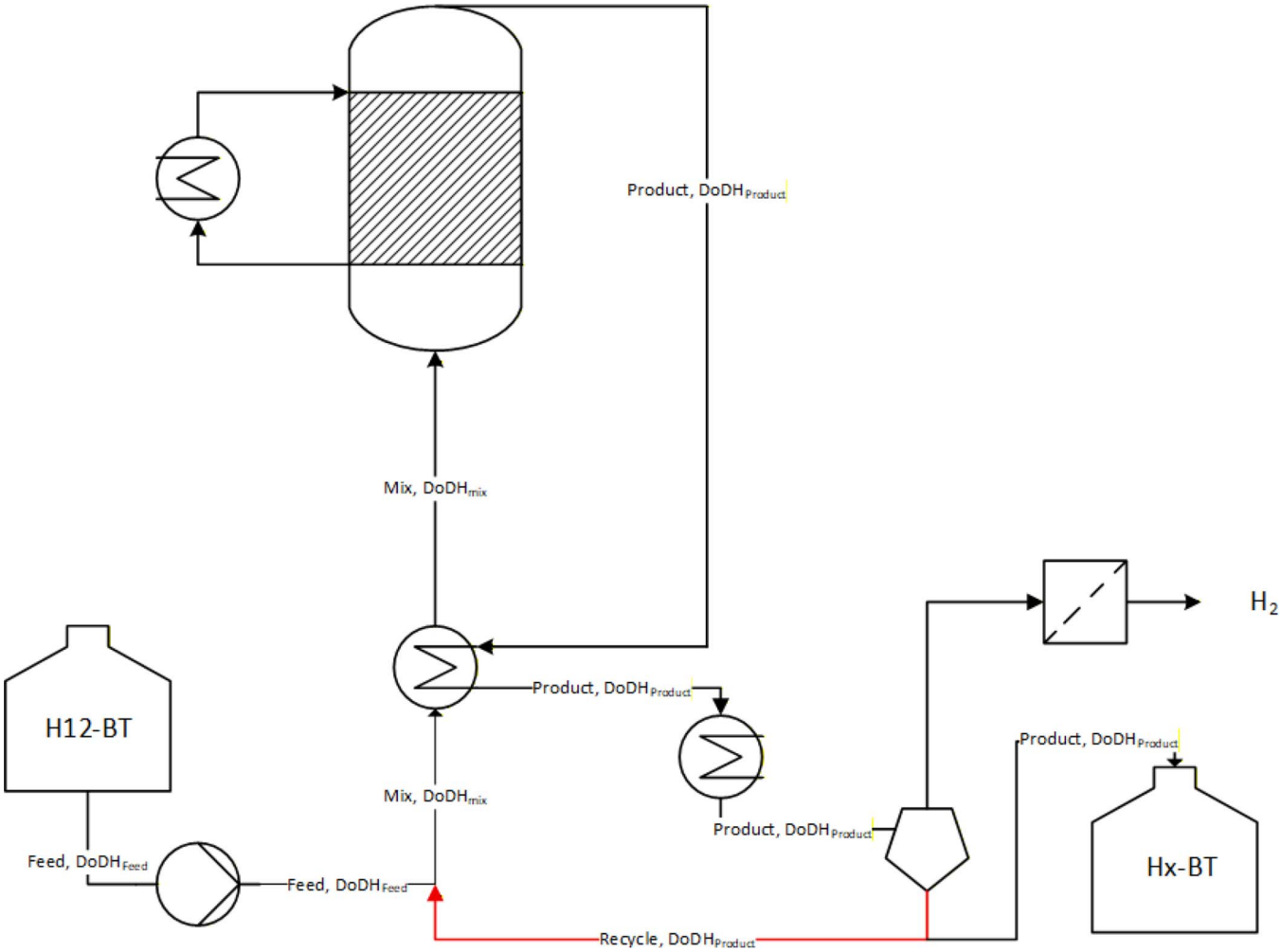

Figure 2. Flow diagram of a classical hydrogen release unit. The necessary additions to realize the recycling concept introduced in this work are highlighted in red in the flow diagram.

resulting mixture is then heated in the feed−product heat exchanger and passed to the dehydrogenation reactor. Because the concentration of H12-BT in the mixed feed is lower, a substantially higher total volumetric feed flow is required to achieve a similar hydrogen release rate for an identical product DoDH. This increases the LOHC-to-hydrogen ratio within the reactor and thereby suppresses full evaporation of Hx-BT. The downstream process remains largely analogous to the classical once-through concept, with the exception that-after gas−liquid separation-a defined fraction of the liquid Hx-BT stream is recycled to the reactor inlet.

2.2. Experimental Setup and Procedure

The experimental setup used to compare the classical reactor concept with the recycling concept is based on the configuration reported by Willer et al.,[6] with minor modifications. Five type-K thermocouples were inserted axially into the reactor to record the axial temperature profile with high spatial resolution. The lower part of the reactor was filled with inert glass beads to provide an additional preheating section, ensuring that the LOHC feed entered the catalytic reaction zone at the desired temperature. The catalyst bed extended from 420 to 770 mm reactor height and contained 156.65 g of a commercially available sulfur-doped Pt/Al_2O_3 catalyst (0.3 wt % Pt, EleMax D012, Clariant, material number 309080).

The recycling concept was evaluated using the same setup. Experimental simulation of internal recycling was achieved by premixing fresh H12-BT with Hx-BT from previous experiments to adjust the feed to the desired degree of dehydrogenation (DoDH). Gas chromatography was employed to determine the DoDH of Hx-BT and the MF concentration using an Agilent 8890 GC equipped with an Rxi-17Sil MS column (30 m × 250 μm).[4] MF concentration must remain below the internal threshold of 0.5 wt % to use the Hx-BT for preparation of the feed. The resulting synthetic Hx-BT blend was transferred to the feed tank, and the volumetric feed rate was adjusted accordingly.

To ensure reproducible operating conditions, a strict startup, reactivation, and shutdown protocol was implemented. For startup, the reactor was heated to the target operating temperature using thermal oil circulating through the reactor shell. During heating, a hydrogen flow of 2 NL min^{-1} was passed through the catalyst bed at atmospheric pressure. Once the catalyst reached the desired temperature, the reactor pressure was increased to the selected operating pressure. Subsequently, the hydrogen flow was stopped and replaced by the LOHC feed of a predefined benchmark experiment used for monitoring potential catalyst deactivation. The benchmark experiment was conducted at a thermal-oil temperature of 320 °C, a pressure of 4 bar, and a feed flow of 50 mL min^{-1} for the recycling experiments and 15 mL min^{-1} for the classical reference experiments. These benchmark experiments showed a standard deviation of less than 5% indicating good reproducibility of the experiments. Steady-state operation was defined as the condition in which both the hydrogen release rate and the catalyst-bed temperature remained constant for at least 15 min.

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For shutdown, the LOHC feed rate was increased to 50 mL min^{-1}, the thermal oil temperature was lowered to 300 °C, and the reactor pressure was raised to 5 bar. This flushing step ensured efficient removal of coke precursors by maintaining liquid-phase conditions over the entire catalyst bed. After 15 min, the LOHC flow was stopped, and the catalyst bed was dried under a hydrogen flow of 5 NL min^{-1} at 300 °C while gradually reducing the pressure to ambient. Following 30 min of drying, the system was allowed to cool under a hydrogen flow of 2 NL min^{-1}. Once the reactor temperature dropped below 50 °C, the thermal oil circulation was stopped, and the pressure was increased to 6 bar to store the catalyst under hydrogen atmosphere. This rigorous shutdown procedure prevented measurable catalyst deactivation for the variation of the operating conditions across several weeks of operation and enabled highly reproducible comparisons of different process conditions.

The DoDH is an important metric to characterize the hydrogen content of the LOHC and represents the ratio of reversibly stored hydrogen that has been released to the maximum amount of reversibly storable hydrogen. Equation 1 can be used to estimate the DoDH.

$$DoDH = \frac{n_{H2,released}}{n_{H2,max}} = \frac{\frac{n_{H6-BT}}{2} + n_{H0-BT}}{n_{H0-BT} + n_{H6-BT} + n_{H12-BT}} \quad (1)$$

The degree of hydrogenation (DoH) is complementary to the DoDH and is defined as the amount of reversibly stored hydrogen to the maximum amount of storable hydrogen. The DoH is linked to the DoDH according to eq 2.

$$DoH = 1 - DoDH \quad (2)$$

The productivity, defined by eq 3, was used as the primary performance metric to evaluate dehydrogenation performance.

$$P = \frac{\dot{m}_{H2,released}}{m_{precious\ metal}} \quad (3)$$

The mass flow of the released hydrogen ($\dot{m}_{H2,\ released}$) was determined using a mass flow meter and to the amount of precious metal of the used catalyst ($m_{precious\ metal}$) was determined by the used catalyst mass and by the Pt content of the catalyst given by the manufacturer.

3. RESULTS AND DISCUSSION

3.1. Introduction of Important Parameters

The nomenclature of all relevant flows is provided in Figure 2. The DoDH of the mixed flow entering the reactor ($DoDH_{mix}$) can be estimated based on a mass balance and is influenced by the DoDH of the feed ($DoDH_{Feed}$) and by the DoDH of the recycling flow ($DoDH_{recycling}$), which equals the DoDH of the product flow ($DoDH_{Product}$) as no hydrogen is released after splitting between product and recycling flow. Accordingly, $DoDH_{mix}$ is determined by the ratio of feed to recycling flow and the corresponding DoDH of each flows as described by eq 4.

$$DoDH_{mix} = \frac{\dot{n}_{Feed} \cdot DoDH_{Feed} + \dot{n}_{Recycle} \cdot DoDH_{Product}}{\dot{n}_{Feed} + \dot{n}_{Recycle}} \quad (4)$$

The recycling ratio (RR) is introduced as molar ratio of recycled and fed flow rate. Consequently, steady-state operation is only achieved when the RR and the change in DoDH across the reactor (ΔDoDH) are fully consistent with one another. Physically, this means that the amount of hydrogen released per reactor pass must exactly match the degree of dilution introduced by the recycled hydrogen-lean LOHC stream. Therefore, not every arbitrary combination of RR and ΔDoDH represents a feasible steady-state operating point. The recycling ratio RR can be expressed as a function of $DoDH_{Feed}$, $DoDH_{Product}$, and the resulting $DoDH_{mix}$, as shown in eq 5.

$$RR = \frac{\dot{n}_{Recycle}}{\dot{n}_{Feed}} = \frac{DoDH_{mix} - DoDH_{Feed}}{DoDH_{Product} - DoDH_{mix}} = \frac{DoDH_{mix} - DoDH_{Feed}}{\Delta DoDH} \quad (5)$$

In this study, a RR between 2 and 16 has been investigated experimentally.

Another key parameter is the evaporation ratio (ER), which defines the fraction of the LOHC feed that evaporates within the reactor. The extent of Hx-BT evaporation can be estimated using the simplified vapor−liquid equilibrium (VLE, eq 6) and by extending the methodology introduced by Kadar et al. (eqs 7 and 8).[14] Equation 9 illustrates that the ER is dependent on temperature, pressure, and ΔDoDH.

$$x_i \cdot P_{0,i}^{LV} = y_i \cdot P \quad (6)$$

$$P_{0,Hx-BT}^{LV} = \frac{\dot{n}_{evap,Hx-BT}}{\dot{n}_{evap,Hx-BT} + \dot{n}_2} \cdot P \quad (7)$$

$$\dot{n}_2 = 6 \cdot \dot{n}_{mix,Hx-BT} \cdot \Delta DoDH \quad (8)$$

$$ER = \frac{\dot{n}_{evap,Hx-BT}}{\dot{n}_{mix,Hx-BT}} = \frac{\frac{P_{o,Hx-BT}^{LV}}{P} \cdot 6 \cdot \Delta DoDH}{1 - \frac{P_{o,Hx-BT}^{LV}}{P}} \quad (9)$$

Here, $P_{0,\ Hx\ -\ BT}^{\ LV}$ denotes the temperature-dependent vapor pressure of Hx-BT, and P represents the total system pressure.

3.2. Enthalpy Balance

To compare the heat demand for H12-BT dehydrogenation in the recycling concept with the classical once-through operation, the enthalpy flows of both configurations were evaluated. A hydrogen release rate of 4.17 g s^{-1} was selected, corresponding to an energy output of 500 kW based on the lower heating value of the released hydrogen. The product flow was assumed to reach a DoDH of 0.85. An isothermal catalyst temperature of 320 °C and an operating pressure of 5 bar were chosen for both setups. Three major heat consumers were considered in the enthalpy balance: the reaction enthalpy, the evaporation enthalpy, and the sensible heat required to raise the LOHC feed from its preheated state to reaction temperature. A feed temperature of 310 °C after the feed−product heat exchanger was assumed, which is a realistic characteristic temperature difference for a technical heat exchanger. All relevant thermophysical parameters are summarized in Table 1.

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Table 1. Parameters for Estimating the Heat Demand of H12-BT Dehydrogenation Using the Classical Once-Through Operation vs Operation Using the Recycling Concept[a]

parameter	H12-BT	H0-BT	reference
$\Delta^{g,l}H_m$/kJ mol^{-1}	42.0	45.0	33
$P^{LV}{}_0$/bar	2.6	2.2	12
c_p/J g^{-1} K^{-1}	2.7	2.2	34

[a]All parameters are given at 320 °C. Whereas $\Delta^{g,l}H_m$ is the evaporation enthalpy at 320 °C, $P^{LV}{}_0$ is the vapor pressure at 320 °C and c_p the specific heat capacity at 320 °C.

The heat demand for the dehydrogenation reaction depends solely on the amount of hydrogen released and can be estimated using the reaction enthalpy reported by Müller et al.[34] For the selected hydrogen flow rate, the reaction heat demand is 139.4 kW for both reactor concepts.

The enthalpy required for LOHC evaporation depends on the fraction of Hx-BT that evaporates inside the reactor. In the classical once-through configuration, the H12-BT feed corresponds to 0.41 mol s^{-1}, and under the chosen process conditions, complete evaporation of Hx-BT occurs.[14] Since a detailed reactor model would be needed to resolve the evolving composition of the vapor phase, an approximate split of 50% H12-BT and 50% H0-BT in the evaporated fraction was assumed. The resulting heat demand for evaporation is 17.8 kW.

For the recycling concept, a target ΔDoDH of 0.1 was selected, resulting in a mixed Hx-BT feed of 3.47 mol s^{-1} and an evaporation ratio (ER) of 0.47. Because the mixed feed contains a higher proportion of hydrogen-lean LOHC, it was assumed that 25% of the evaporated LOHC corresponds to H12-BT and 75% to H0-BT. Under these conditions, the evaporation enthalpy increases significantly to 72.2 kW.

The third heat contribution considered is the sensible heat required to raise the LOHC feed from the outlet temperature of the feed−product heat exchanger (310 °C) to the reaction temperature (320 °C). In the classical once-through concept, the much smaller feed flow results in a heat demand of only 2.1 kW. In contrast, the considerably larger feed flow in the recycling concept increases this requirement to 14.6 kW. This value represents a conservative upper estimate, since the product stream leaving the reactor is partially in the liquid phase. Incorporating an additional gas−liquid separator operating at reaction temperature would allow recycling of the hot liquid LOHC directly back to the reactor inlet. Given an ER of 0.47 for the selected case, such a measure could reduce the sensible heat demand by approximately 53%. The heat demands of both concepts are compared in Table 2.

Table 2. Comparison of the Heat Demand between the Classical Once-Through Operation and the Recycling Concept to Release 4.17 g s^{-1} of Hydrogen[a]

	once-through operation		recycling	
heat consumer	kW	kW kW$^{-1}{}_{H2}$	kW	kW kW$^{-1}{}_{H2}$
reaction	139.4	0.279	139.4	0.279
evaporation	17.8	0.036	72.2	0.144
feed preheating	2.1	0.004	14.6	0.029
total heat demand	159.3	0.319	226.2	0.452

[a]A constant catalyst temperature of 320 °C and a pressure of 5 bar are assumed for the estimations in both cases.

The resulting overall energetic efficiency is 0.681 for the classical once-through configuration and 0.548 for the recycling concept. For the classical reactor, this efficiency remains nearly independent on process conditions. In the recycling concept, however, the efficiency can be improved through the choice of operating parameters and the recycling ratio. Nevertheless, the energetic efficiency of the recycling concept is inherently lower, meaning that this alternative operation concept must outperform the classical configuration in other performance indicators—such as power density or catalyst stability—to compensate for the higher heat demand. Furthermore, reduced efficiency may be less critical if external high-temperature waste heat sources, such as the waste heat of a solid oxide fuel cells or of a hydrogen combustion engines, are available to supply part of the required heat demand.[35,36]

3.3. Heat Transfer

Dehydrogenation is a strongly endothermic reaction. Efficient heat transfer into the catalyst bed is therefore essential for achieving high hydrogen release rates. In fixed-bed dehydrogenation reactors, the heat transfer coefficient is typically highest at the reactor inlet and decreases axially until a plateau is reached.[11,14] This decline is directly linked to the reduction in liquid holdup along the reactor. In the recycling concept, the increased liquid holdup resulting from suppressed Hx-BT evaporation is expected to enhance the heat transfer coefficient and thereby increase the average catalyst temperature. To verify this hypothesis, the axial temperature profiles of the classical once-through reactor and the recycling reactor were experimentally measured at comparable hydrogen release rates (≈0.8 L min^{-1}) ensuring that the heat demand of the chemical reaction remained similar. The resulting axial temperature distributions are shown in Figure 3.

The first half of the reactor (0−420 mm) contains inert glass beads and serves as a preheating zone. Towards the end of this section, the temperature in both reactor configurations approaches the thermal-oil temperature, confirming comparable inlet temperatures to the catalytic section. The minor temperature drop observed between 120 and 280 mm

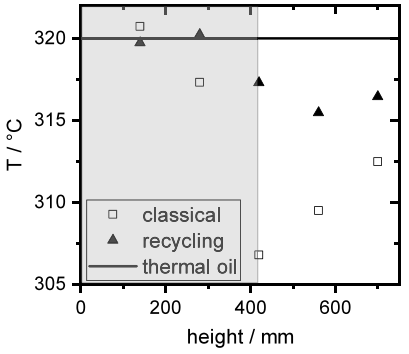

Figure 3. Comparison of the axial temperature profile in a dehydrogenation reactor for the classical once-through operation and the operation with liquid recycling. The gray area indicates the catalytically inactive part of the reactor ($T_{thermal\ oil}$ = 320 °C, p = 4 bara, 0.3 wt % Pt/Al_2O_3, $m_{catalyst}$ = 156.65 g, $\dot{V}_{H2\ released}$ = 0.8 L min^{-1}; classical: $\dot{m}_{Feed}$ = 2 g min^{-1}, $DoDH_{feed}$ = 0.02; recycling: $\dot{m}_{mix}$ = 21 g min^{-1}, $DoDH_{mix}$ = 0.80).

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in the classical reactor may be attributed to back-mixing phenomena.

At the entrance to the catalyst bed, the classical configuration exhibits a pronounced temperature drop caused by the simultaneous heat consumption of the endothermic reaction and significant Hx-BT evaporation. The lowest catalyst-bed temperature occurs directly at the catalyst-bed inlet, where the temperature difference between thermal oil and catalyst bed reaches approximately 13 K. Further up in the reactor, the catalyst temperature gradually rises again as reaction rates decline, and evaporation becomes less significant. The large temperature difference between the heat-transfer medium and catalyst bed clearly indicates a heat-transfer limitation under classical operation.

In contrast, the recycling concept shows only a slight temperature decrease at the catalyst-bed entrance. As anticipated, the average catalyst temperature is markedly higher, with a maximum temperature difference between thermal oil and catalyst bed of only 5 K. Since both concepts release nearly the same amount of hydrogen, the reaction-related heat demand is comparable. Moreover, despite the suppression of complete evaporation, the evaporation enthalpy demand is higher in the recycling reactor (Section 3.2). Therefore, the higher catalyst temperatures observed in the recycling concept demonstrate that heat transfer must be significantly intensified. This enhancement is attributed to the substantially increased liquid holdup resulting from the higher LOHC-to-hydrogen ratio in the reactor. The smoother axial temperature gradient further suggests a more uniform axial hydrogen-release profile.

Overall, the recycling concept clearly improves heat transfer, as evidenced by the higher average catalyst temperature. Since higher temperatures promote dehydrogenation kinetics, this enhancement is expected to positively affect the volumetric reactor productivity, which is evaluated in the next step.

3.4. Productivity

For a fair comparison of the productivity of the two reactor concepts, operating conditions with identical product DoDH, thermal-oil temperature, and pressure were selected, since productivity is strongly influenced by these parameters.[10] A constant thermal-oil temperature was used instead of a constant catalyst temperature, because in technical operation only the former can be directly controlled, while the catalyst temperature results from the prevailing heat-transfer conditions inside the reactor.

In the first step, the feed volume flow was varied for a different $DoDH_{mix}$. In this parameter study, compliance with the RR was not enforced. Consequently, some operating points would not be feasible in a real steady-state recycling reactor, as the resulting product DoDH would differ from that dictated by the RR. However, evaluating a wide range of feed flow rates allows identification of steady-state-compatible operating windows for given process conditions. The corresponding productivity comparison between the two reactor concepts is shown in Figure 4 for thermal oil temperatures between 320 and 340 °C at a reaction pressure of 4 bar.

Productivity decreases with a higher product DoDH but increases with higher thermal-oil temperature. For all investigated conditions, productivity in the recycling concept exceeds

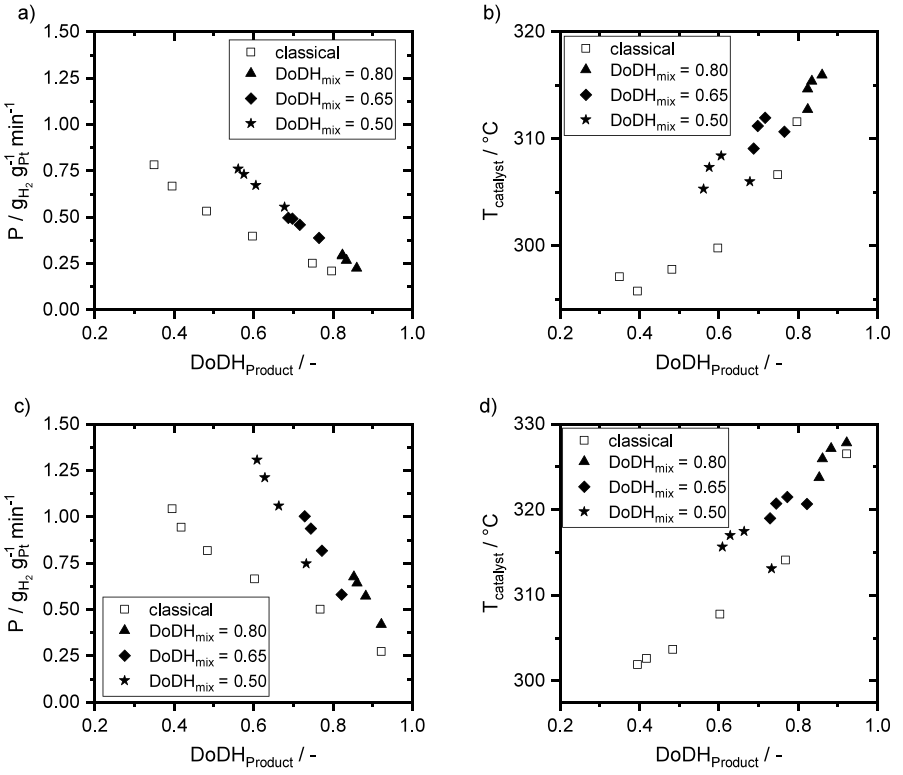

Figure 4. Productivity and catalyst temperature depending on DoDH in the classical once-through and in the recycling reactor (a, b: $T_{thermal\ oil}$ = 320 °C, p = 4 bara, 0.3 wt % Pt/Al_2O_3, $m_{catalyst}$ = 156.65 g, $DoDH_{feed,classical}$ = 0.02, $\dot{V}_{Feed,\ classical}$ = 2–20 mL min^{-1}, $\dot{V}_{mix,\ recycling}$ = 25–100 mL min^{-1}; c,d: $T_{thermal\ oil}$ = 340 °C, p = 4 bara, 0.3 wt % Pt/Al_2O_3, $m_{catalyst}$ = 156.65 g, $DoDH_{feed,classical}$ = 0.02, $\dot{V}_{Feed,\ classical}$ = 2.5–25 mL min^{-1}, $\dot{V}_{mix,\ recycling}$ = 25–100 mL min^{-1}).

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that of the classical once-through reactor, despite the higher average DoDH within the reactor volume due to product recycling. Thus, the increased liquid holdup and the enhanced heat-transfer resulting from the suppression of complete evaporation clearly overcompensates the kinetic disadvantage of operating at a lower average H12-BT concentration.

For a product DoDH of 0.80 at a thermal-oil temperature of 340 °C, a productivity of 0.44 g_{H2} min^{-1} $g_{Pt}{}^{-1}$ is extrapolated from the experimental data obtained in the classical once-through reactor. Under the corresponding steady-state condition in the recycling concept (using a mixed-feed DoDH of 0.65), a productivity of 0.69 g_{H2} min^{-1} $g_{Pt}{}^{-1}$ is obtained. This experiment complies with the RR constraint and would be possible in real steady-state operation. The 50% increase in productivity indicates that reactor volume— and thus catalyst mass— could be reduced by approximately 33% when applying the recycling configuration, which is directly related to a corresponding increase in the power density of the respective hydrogen-release unit.

Notably, the productivity enhancement at a thermal oil temperature of 320 °C is comparable. Moreover, the productivity ratio between recycling and classical concept remains nearly constant when targeting a product DoDH of 0.92 at 340 °C with a mixed-feed DoDH of 0.80, demonstrating that the beneficial effect of internal recycling on productivity is robust across a broad range of operating conditions.

3.5. By-Product Formation

Since the LOHC carrier material must remain stable over many hydrogenation−dehydrogenation cycles, low by-product formation is essential. The formation of coke precursors is particularly relevant in this context as these compounds alter the physicochemical properties of the LOHC material and promote catalyst deactivation.[26] In the recycling concept, each LOHC molecule passes the catalyst bed multiple times, resulting in a higher effective residence time of the material on the catalyst surface. This could, in principle, increase the formation of undesired by-products. MF side products are known to represent reliable indicators of coke precursor formation[26] therefore, Figure 5 compares the MF concentrations in the product flow of the classical once-through and the recycling reactor operation. Note that the fresh H12-BT feed is free of MF, whereas the premixed LOHC feed used in the recycling experiments already contains small amounts of MF originating from previous experiments. Such accumulation would also occur in a real recycling reactor and can therefore be considered representative for practical operation.

MF formation strongly depends on the DoDH of the product flow. At low $DoDH_{product}$, MF is scarcely detectable, while its concentration increases sharply at a DoDH above 0.7. MF forms via deep dehydrogenation of H0-BT, meaning that a sufficiently high H0-BT concentration is required for its formation.[37] MF formation appears largely independent on reaction temperature as a function of the catalyst material and $DoDH_{product}$.

Given that the concentration of H0-BT is higher in the recycling concept, an increased MF formation could be expected. However, no significant increase in MF concentration is observed. The slightly elevated MF levels at 340 °C in the $DoDH_{product}$ range of 0.6−0.8 are likely due to accumulated MF in the premixed feed rather than due to enhanced in-situ formation. At a high $DoDH_{product}$, MF formation is even lower in the recycling concept. We explain this initially unexpected behavior by the fact that, under the conditions applied, the classical once-through reactor operates with completely evaporated Hx-BT at DoDHs above 0.2, and most of the hydrogen is released from evaporated H12-BT or H6-BT species. Under these conditions, the aromatic H0-BT product exhibits a significantly stronger adsorption on the catalyst surface[38] than all hydrogenated or partially hydrogenated LOHC compounds in the reaction mixture. Thus, in pure gas-phase operation, desorption and removal of H0-BT are slow, promoting the formation of the deep dehydrogenation product MF and subsequently coke formation.

In contrast, the recycling concept suppresses full Hx-BT evaporation, ensuring that part of the LOHC remains in the liquid phase. The presence of liquid Hx-BT facilitates the removal of strongly adsorbed H0-BT from the catalyst surface by solvation in the surrounding liquid phase providing essentially an intrinsic "hot wash" procedure for continuous catalyst cleaning.[28] This enhanced removal of H0-BT appears to compensate for its higher concentration in the reactor, resulting in MF levels comparable to, or even lower than, those observed in the classical concept.

3.6. Catalyst Stability

Finally, the stability of the catalyst was evaluated. For both reactor concepts, the operating conditions were adjusted to achieve a comparable $DoDH_{product}$ of approximately 0.75. This DoDH has been chosen to ensure relevant byproduct formation as the

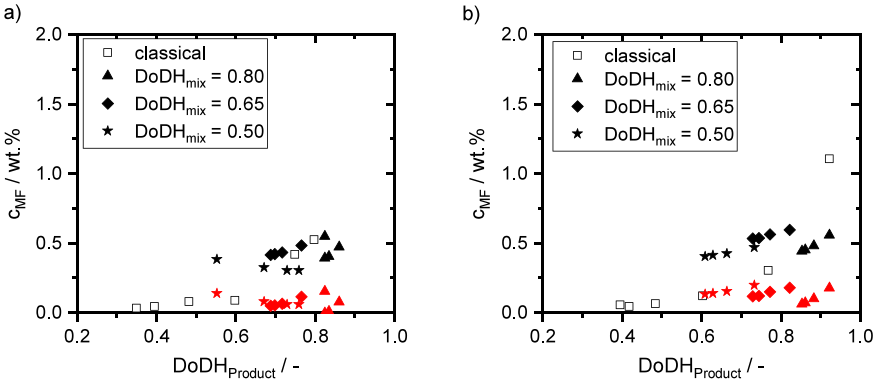

Figure 5. Comparison of methyl fluorene formation between classical once-through and recycling reactor operation. The black symbols give the total MF content of the product flow. The red symbols give the difference between MF content of the feed and the product flow. (a: $T_{thermal\ oil}$ = 320 °C, p = 4 bara, 0.3 wt % Pt/Al_2O_3, $m_{catalyst}$ = 156.65 g, $DoDH_{feed,classical}$ = 0.02, $\dot{V}_{Feed,\ classical}$ = 2−20 mL min^{-1}, $\dot{V}_{mix,\ recycling}$ = 25−100 mL min^{-1}; b: $T_{thermal\ oil}$ = 340 °C, p = 4 bara, 0.3 wt % Pt/Al_2O_3, $m_{catalyst}$ = 156.65 g, $DoDH_{feed,classical}$ = 0.02, $\dot{V}_{Feed,\ classical}$ = 2.5−25 mL min^{-1}, $\dot{V}_{mix,\ recycling}$ = 25−100 mL min^{-1}).

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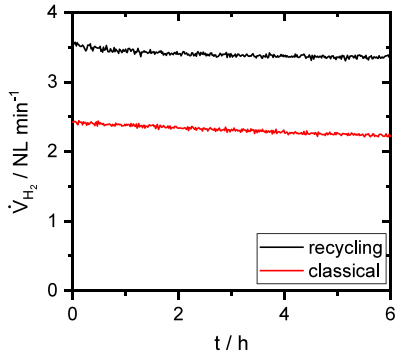

Figure 6. Comparison of the catalyst stability over 6 h operation time in classical once-through operation and in operation using the recycling reactor concept ($T_{thermal\ oil}$ = 340 °C, p = 4 bara, 0.3 wt % Pt/Al_2O_3, $m_{catalyst}$ = 156.65 g, classical: $\dot{V}_{Feed}$ = 5 mL min^{-1}, $DoDH_{feed}$ = 0.02; recycling: $\dot{V}_{mix}$ = 50 mL min^{-1}, $DoDH_{mix}$ = 0.65).

byproducts are potential coking precursors. Figure 6 shows the temporal evolution of the released hydrogen flow for both configurations.

In the recycling concept, the hydrogen flow decreases only slightly during the first three hours TOS, from 3.5 to 3.4 NL min^{-1} A linear fit yields a deactivation slope of −45 10^{-3} NL min^{-1} h^{-1}. Thereafter, the hydrogen flow remains nearly constant over the subsequent three hours, as indicated by a substantially lower slope of −9 10^{-3} NL min^{-1} h^{-1} between 3 and 6 h TOS. In contrast, the hydrogen flow in the classical once-through concept declines from 2.4 to 2.3 NL min^{-1} during the first three hours, corresponding to a slope of −32 10^{-3} NL min^{-1} h^{-1}. The hydrogen flow continues to decrease in the following three hours (3−6 h TOS), exhibiting a similar slope of −27 10^{-3} NL min^{-1} h^{-1}. The pronounced reduction in the deactivation rate observed in the recycling concept between 3 and 6 h TOS, in contrast to the nearly constant deactivation rate in the classical reactor, indicates enhanced catalyst stability. This behavior is attributed to the continuous intrinsic hot washing of the catalyst enabled by the presence of liquid LOHC under recycling reactor operating conditions.

Catalyst deactivation in LOHC dehydrogenation is typically attributed to coking caused by the accumulation of coke precursors on the catalyst surface.[26] As discussed in Section 3.5, the higher liquid holdup in the recycling concept facilitates more effective removal of strongly adsorbed heavy species such as H0-BT or MF from the catalyst surface. This enhanced hot wash suppresses the accumulation of coke precursors and thereby reduces coke formation. Consequently, the increased liquid-phase hold-up in the recycling reactor contributes directly to the superior catalyst stability observed.

3.7. Preliminary Technoeconomic Analysis

The results presented above reveal a fundamental trade-off between the classical once-through reactor and the recycling reactor concept, which extends beyond purely technical performance and directly impacts dehydrogenation costs. To assess these implications, a preliminary and qualitative economic analysis was conducted. The objective is not to provide an absolute cost evaluation, but rather to elucidate the relative economic differences between both reactor concepts based on the process scenario introduced in Section 3.2.

Dehydrogenation costs are defined as the sum of capital expenditure (CAPEX) and operating expenditure (OPEX). Based on the study of Lim et al., approximately 30% of total costs are attributed to CAPEX and 70% to OPEX, highlighting the dominant role of OPEX on dehydrogenation costs.[7]

From a CAPEX perspective, the recycling concept benefits from a significantly higher productivity, enabling a reduction in reactor size. However, this advantage is partially offset by increased requirements for peripheral equipment (e.g., pumps, piping, heat exchangers, and gas−liquid separators) due to the substantially higher LOHC circulation rate. Consequently, CAPEX is assumed to be comparable for both concepts.

OPEX comprises costs associated with heat supply, electricity demand, catalyst consumption, catalyst regeneration, and fixed operational costs. The latter are assumed to be identical for both configurations, as they scale with CAPEX.

The difference in electricity demand between both reactor concepts is primarily determined by the required feed flow. In the classical reactor concept, a feed flow of 69 mL s^{-1} must be compressed from 1 to 5 bar, resulting in a pumping power of 40 W (η = 0.7). Assuming 8000 operating hours per year, this corresponds to an annual electricity demand of 319 kWh and costs of 38 $ a^{-1} assuming electricity costs of 0.12 $ kWh^{-1}.[7] In contrast, the recycling concept requires a significantly higher feed flow rate of 590 mL s^{-1}, increasing the electricity demand to 2700 kWh and resulting in costs of 325 $ a^{-1}.

The heat demand, as discussed in Section 3.2, represents the dominant contribution to OPEX. For the purpose of comparability, heat is assumed to be supplied via electricity, representing a conservative, worst-case scenario. The classical reactor concept requires 159.3 kW, corresponding to an annual electricity demand of 1.28 10^6 kWh and heating costs of 153,358 $ a^{-1}. The recycling concept exhibits a higher heat demand of 226.2 kW, resulting in 1.81 10^6 kWh and costs of 216,362 $ a^{-1}. It should be noted that the availability of low-cost or waste heat would significantly reduce this cost contribution and alter the relative importance of heat demand.

Catalyst-related costs were estimated based on the productivity values shown in Figure 4. For the classical reactor concept, a productivity of 0.377 g_{H2} min^{-1} $g_{Pt}$$^{-1}$results in a catalyst demand of 221.2 kg, corresponding to annualized costs of 3318 $ (assuming 300 $ kg^{-1} catalyst costs and a lifetime of 20 years[7]). The higher productivity of the recycling concept (0.600 g_{H2} min^{-1} $g_{Pt}$$^{-1}$) reduces the catalyst demand to 139 kg and annual costs to 2085 $.

Catalyst regeneration costs are strongly influenced by deactivation behavior. Based on the findings of Lim et al., three regeneration cycles per year are assumed for the classical reactor concept for a similar deactivation behavior as reported in Figure 6.[7] This results in regeneration costs of 119,490 $ a^{-1} assuming catalyst regeneration costs of 180 $ kg^{-1}.[7] In contrast, the recycling concept exhibits a substantially reduced deactivation rate (~33% of

Table 3. Comparison of the OPEX between the Classical Once-Through Operation and the Recycling Concept

	once-through operation$ a^{-1}	recycling$ a^{-1}
electricity costs for pumping	38	325
costs for heat supply	153,358	216,362
catalyst costs	3318	2085
catalyst regeneration costs	119,490	25,020
total OPEX	276,204	243,792

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the classical case), allowing for a reduction to a single regeneration cycle per year and corresponding costs of 25,020 $ a^{-1}.

A summary of the OPEX contributions is provided in Table 3. Overall, the recycling concept achieves an approximately 10% reduction in operating costs despite its higher heat demand. This improvement is primarily driven by enhanced catalyst productivity and stability, which outweigh the penalty associated with increased heat demand.

Green hydrogen represents a central building block for the defossilization of the energy system. However, its large-scale implementation remains limited by the high costs associated with production, storage, and distribution. Within LOHC-based systems, the dehydrogenation step constitutes a key cost driver. Consequently, the reduction of dehydrogenation costs represents a critical lever for enabling industrial implementation of LOHC technology. Thus, reductions in dehydrogenation costs decrease the cost of hydrogen release and thereby strengthen the competitiveness of LOHC technology as a storage and distribution pathway for renewable hydrogen. This facilitates the substitution of fossil-based energy carriers and contributes to the reduction of CO_2 emissions.

The data from the results section of this publication are also available via Zenodo.[39]

4. CONCLUSIONS

In this study, a new reactor concept for the dehydrogenation of H12-BT was developed and evaluated. Under technically relevant operating conditions, Hx-BT evaporates rapidly in a classical fixed-bed reactor, resulting in predominantly gas-phase dehydrogenation despite feeding H12-BT as a liquid. In contrast, multiphase dehydrogenation of H12-BT offers several advantages, including improved heat transfer, enhanced catalyst stability, and higher catalytic activity. Although lowering reaction temperature or increasing pressure can suppress Hx-BT evaporation, both strategies negatively impact the thermodynamics and kinetics of the dehydrogenation reaction. To overcome these limitations, we developed a concept of internal LOHC recycling to increase the ratio of LOHC to hydrogen and the liquid hold-up in the dehydrogenation reactor and thereby suppress complete evaporation of Hx-BT.

This new recycling concept for hydrogen release from LOHC systems was first evaluated in terms of energetic efficiency. Due to the higher total amount of LOHC that evaporates, the energetic efficiency of the recycling concept is inherently lower than that of the classical once-through operation. An enthalpy balance for a dehydrogenation reactor shows an approximately 40% increase in heat demand for the recycling concept, which can, however, be reduced to some extent by adjusting the operating parameters. Subsequently, heat transfer within the catalyst bed was compared between the two concepts, revealing a clear intensification of heat transfer in the recycling reactor. As a direct result of improved heat transfer and increased liquid holdup, the recycling concept achieved a productivity enhancement of up to 50%, while maintaining similarly low by-product formation. Finally, a clear improvement in catalyst stability was demonstrated due to the more efficient removal of coke precursors under conditions that ensure sufficient liquid hold-up.

Overall, the combination of intensified heat transfer, increased productivity, and enhanced catalyst stability shows that internal LOHC recycling provides a simple yet highly effective strategy to increase the power density and operational robustness of dehydrogenation units for LOHC-based hydrogen storage systems. A preliminary economic evaluation revealed a 10% reduction of OPEX for the recycling concept. The new recycle reactor dehydrogenation concept is expected to be of particular interest for application cases, in which waste heat from the energetic use of the released hydrogen is available at sufficient quantity and temperature level (e.g., from the energetic use of the released hydrogen in an SOFC system), as in such scenarios OPEX can be decreased even more by the recycling concept. We furthermore anticipate that our findings are of general interest beyond the topic of chemical energy storage using the LOHC concept. Similar trade-offs of heating demands, and intensified heat provision may also be relevant in other technical applications where endothermal reactions are conducted in multiphase reactors, such as e.g. in some liquid phase reforming reactions.

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Notes

During the preparation of this work the authors used ChatGPT in order to edit the language. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

The authors declare the following competing financial interest(s): PW is co-founder and minority shareholder of Hydrogenious LOHC Technologies GmbH, Erlangen, a company that has commercialized equipment for hydrogen storage using the LOHC technology. There is no conflict of interest to declare with regard to the specific scientific results reported in this paper.

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