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# Liquid organic hydrogen carriers: Process design and economic analysis for manufacturing *N*-ethylcarbazole

**E. M. T. Uijthof**[1] | **B. S. Chavan**[1] | **M. J. Sluijer**[1] | **V. C. Komath**[1] | **A. G. J. van der Ham**[1] | **H. van den Berg**[1] | **J.-P. Lange**[1,2] | **A. Higler**[2] | **S. Wijnans**[2]

[1]Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Enschede, The Netherlands

[2]Shell Global Solutions International B.V., Amsterdam, The Netherlands

**Correspondence**
E. M. T. Uijthof, Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Drienerlolaan 5 7522 NB, Enschede, The Netherlands.
Email: e.m.t.uijthof@outlook.com

## Abstract

This paper revisits the economics of manufacturing *N*-ethylcarbazole (NEC), a strong candidate for large-scale liquid organic hydrogen carrier (LOHC) supply chains, because of its high $H_2$ storage capacity (6 wt%), selective hydrogenation and dehydrogenation reactions, and favorable reaction enthalpy and reaction temperatures compared to other LOHC systems. Two different process routes for producing NEC from industrial chemicals are selected out of 10 possible options: one using aniline and the other using cyclohexanone and nitrobenzene as feedstock. The required capital and operational costs are estimated to determine a NEC break-even cost for a capacity of 225 ktpa. NEC break-even costs of \$3.0 and \$2.6 per kg LOHC are found for the routes. This is significantly less than the \$40/kg cost that has generally been reported in literature for NEC, thus improving the economic viability of using NEC as LOHC. The total fixed capital costs are estimated to be \$200 MM and \$250 MM. Furthermore, the prices of the feedstock show the largest influence (76% and 72%) on the final NEC break-even costs. The overall LOHC price contribution to the levelized $H_2$ cost is estimated to be \$0.77–\$0.90 per kg $H_2$ for a 60-day roundtrip and \$0.09–\$0.10 per kg $H_2$ for a 7-day roundtrip. It is important to note that both routes rely heavily on laboratory scale data and the corresponding assumptions that stem from this limitation. Therefore, this research can serve as a guide to future experimental studies into validating the key assumptions made for this analysis.

**Acronyms:** ABP, 2-Aminobiphenyl; BDA, Benzene-1,4-diamine; CAPEX, Capital expenditure; CEPCI, Chemical Engineering Plant Cost Index; $C_{FC}$, Fixed capital costs; DBT, Dibenzyl toluene; DPA, Diphenylamine; D&E, Design and engineering; IRR, Internal rate of return; ISBL, Inside battery limits; ktpa, Kilo-tonnes per annum; LOHC, Liquid organic hydrogen carrier; NEC, *N*-ethyl carbazole; OPEX, Operating expenditure; OSBL, Outside battery limits; Perhydro-NEC, Perhydro-*N*-ethyl carbazole; PFD, Process flow diagram; TPA, Triphenylamine; tpd, Tonnes per day; *X*, Contingency.

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## 1 | INTRODUCTION

The production of renewable energy is often intermittent and commonly distant from the location of usage.[1] Therefore, it is necessary to find a suitable method to store and transport the generated energy. Hydrogen is a promising energy carrier, because of its high gravimetric energy density.[2] Additionally, the production of hydrogen using renewable solar and wind energy via electrolysis has proven to be versatile and capable of handling high peak powers.[3] This gives hydrogen a great advantage in comparison to other energy storage types. However, currently, $H_2$ is stored and transported either after severe pressurization[1] or cryogenic liquefaction, which consume 20%–40% of the energy stored in $H_2$.[4] Recently, Liquid Organic Hydrogen Carriers (LOHC) have generated interest for $H_2$ transport and storage as milder storage conditions can be achieved by hydrogenating an organic component at the power generation site and subsequently dehydrogenating it at the usage site (see Figure 1).[5]

To ensure efficient $H_2$ transport and storage, LOHC must have certain traits, such as high hydrogen storage capacity, suitable hydrogenation and dehydrogenation reaction conditions and compatibility with current fuel infrastructures.[5,6] *N*-ethylcarbazole (NEC), the compound shown in Figure 1, is considered a promising LOHC candidate due to the following factors[5]:

- High hydrogen storage capacity per amount LOHC ($>56$ kg/m$^3$ or 6 wt%).
- Favorable thermodynamics of dehydrogenation due to its low heat of dehydrogenation ($\Delta H = 53$ kJ/mol $H_2$).
- Compatibility with existing fuel infrastructure, particularly oil pipelines and ships.
- Good safety characteristics, such as ease of handling during production, transportation, and use.

In recent history, multiple publications have reported a manufacturing cost for NEC of \$40/kg[7–10] which makes NEC not economically viable as the carrier in commercial scale $H_2$ supply chains. The cost of inventorizing the supply chain with carrier molecules would then be substantial, leading to prohibitive additions to the delivered cost of hydrogen. A deeper look into the origin of this cost value leads to the suggestion that carbazoles can only be obtained from coal tar distillation.[10] Three things to note on this are: (a) premising LOHC production on a coal-based route seems at odds with advancing the energy transition, (b) carbazoles (in principle) can be synthesized from similar feedstock molecules (i.e. functionalized benzene[11]) as benzyltoluene and dibenzyltoluene, which are LOHC alternatives and for which an order of magnitude lower manufacturing costs were quoted,[10] and (c) Hynertech Co. Ltd. Announced a project to build a dedicated LOHC production facility of 1 ktpa in 2021,[12] which suggests they developed a synthetic manufacturing

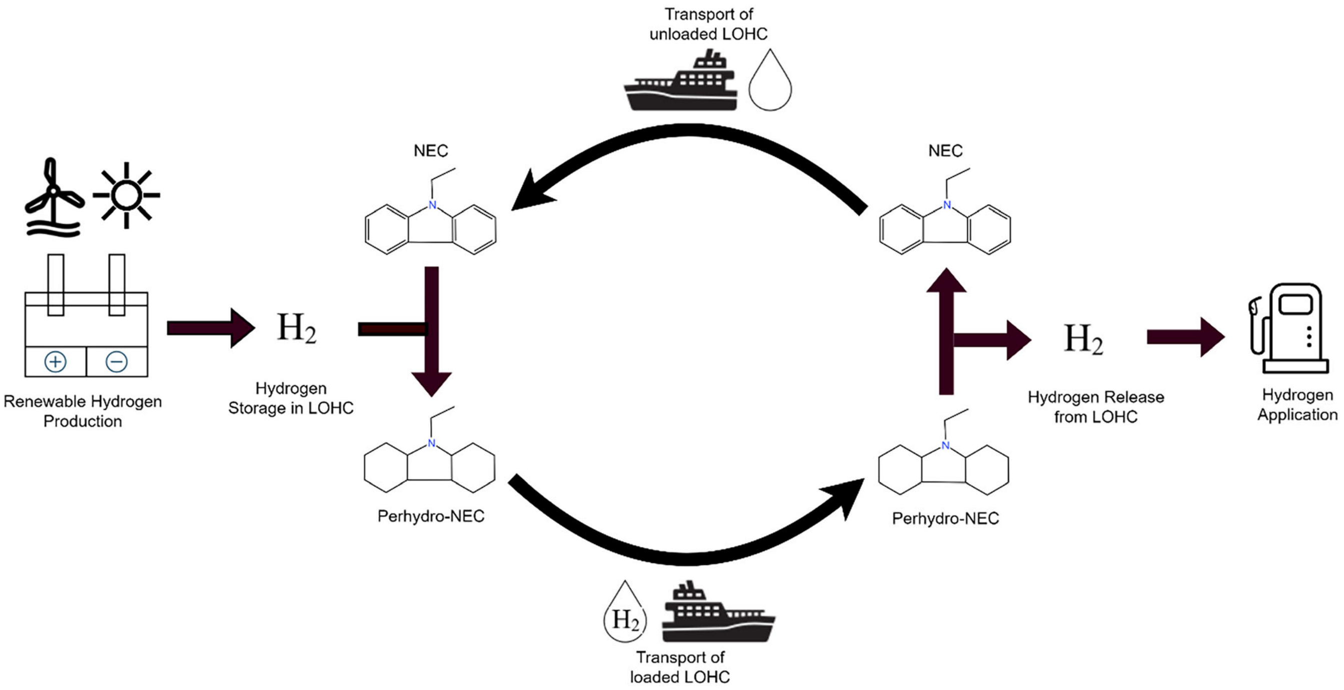

FIGURE 1 Hydrogen supply chain using *N*-ethylcarbazole (NEC) as liquid organic hydrogen carrier (LOHC).

route for carbazole-based LOHC at (modest) scale that is technically and economically viable.

This paper aims to investigate the economic viability of the industrial-scale production of NEC from bulk chemicals. The focus is not on the use of the NEC as an LOHC for $H_2$ transport and storage. Two initial process designs are developed based on two different NEC production methods. Eventually, the NEC break-even costs are estimated and compared to the cost reported in the literature. Both designs will heavily rely on literature information and assumptions. Therefore, the outcome of this research gives a direction to future experimental research to validate the critical assumptions made for this analysis.

## 2 | CHEMISTRY

A detailed literature survey reveals that NEC can be synthesized via various routes. Most literature does not discuss the direct production of NEC, but the production of carbazole instead. Its subsequent ethylation yields NEC as a product.[13] A total of 10 reaction pathways are considered and are summarized in SI Section C. Additionally, a table depicting the molecular structures of compounds are given in SI Section A. Out of these pathways the two most promising options are selected based on the decision tree given in SI Section B. This section will discuss the selected routes (see Figure 2) and mention their corresponding by-products. The reaction pathways are shown in more detail in SI Section D.

The main product of each pathway is NEC; with several by-products formed. Unfortunately, very little information is available on the formed by-products. They are assumed to be molecular isomers and compounds similar to NEC, which have therefore also been considered as LOHC.

### 2.1 | Route 1: Aniline condensation and dehydrocyclization

In the first method, aniline condensation followed by dehydrocyclization of diphenylamine (DPA) is proposed to achieve high purity continuous carbazole production.

In this first step, two aniline molecules undergo a gas-phase acid-catalyzed condensation reaction[14] yielding DPA and ammonia in a well-known industrial synthesis route.[15,16] Further studies find that aniline converts to DPA with a selectivity and conversion of up to 98% and 36%, respectively.[16–18] The reaction proceeds via protonation of the benzene ring resulting in the formation of an anilinium ion. The attack of a second aniline molecule on the anilinium ion results in the formation of a *N*-containing biphenyl cation and ammonia, which further deprotonates to diphenylamine. Since limited information on the by-products is available, 1,4-benzenediamine (BDA) is assumed as the major by-product[16] emerging from the reactions with an assumed selectivity of 2%. The detailed reaction mechanism can be found in SI Section D.

As per the literature, industrial aniline condensation is conducted at temperatures of 320–450°C and pressures of 1–2 bar for a duration of 4–9 h in the presence of γ-alumina or zeolite catalysts.[15,19] The use of a vapor phase is advantageous since the liquid phase aniline condensation occurs in batch operation.[14] Among the catalysts shown in literature for this process, γ-alumina is the least prone to deactivation by basic reactants and products,[17] and therefore is considered for the reaction. This catalyst, however, undergoes coke deposition on its surface at higher temperatures and therefore needs a regeneration step to burn the deposited coke. Further, the reaction temperature and pressure are chosen as 460°C and 1 bar, respectively based on literature[18] and reactor design studies shown in SI Section I.

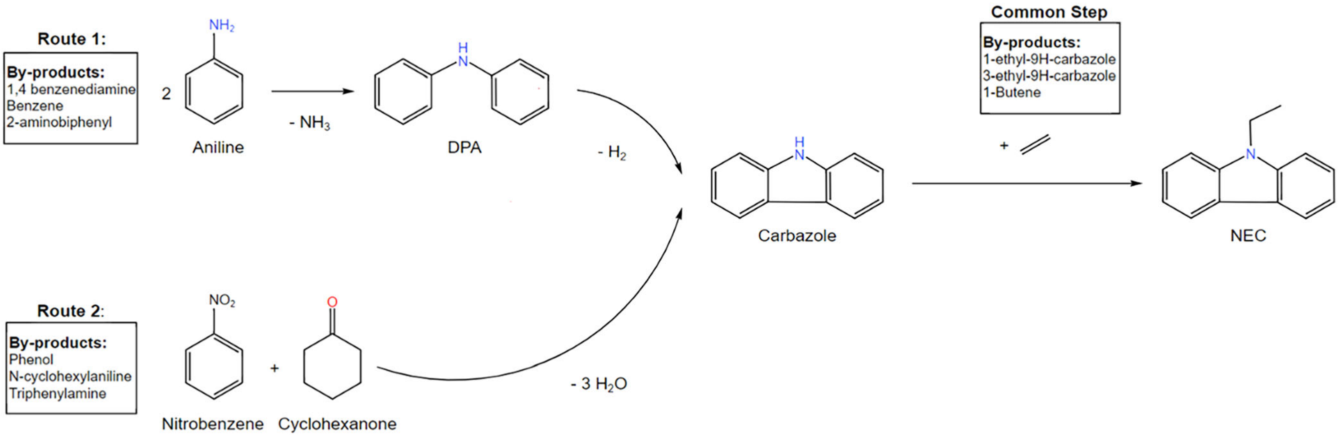

**FIGURE 2** Selected Reaction pathways for synthesis of *N*-ethylcarbazole (NEC).

The second step is the dehydrocyclization of DPA to carbazole. It is an exothermic reaction due to the C—C bond formation with subsequent evolution of hydrogen gas. Among the various d-band metals, Pd[20] and Pt[21] are the most explored metal catalysts. The reaction mechanism is shown in SI Section D. Yamamoto et al.[21] and Vlčko et al.[22] report that the catalyst mechanism of Pd and Pt catalysts occurs via the production of 2-aminobiphenyl (ABP). The by-products reported include benzene, ammonia, and trace amounts of ABP[23,24] with the selectivity towards benzene and ABP of 9% and 1%, respectively. The DPA conversion in the dehydrocyclization step ranges from 96% to 98%. Thus, the yield for carbazole from DPA is close to 88%.

For the dehydrocyclization reaction, an $H_2$-enriched atmosphere is required to continuously regenerate the catalysts. A study by Vlčko et al.[24] shows that the presence of iridium with platinum is useful in removing coke depositions by hydrogenolysis. However, here it is assumed that the $H_2$ produced during the reaction is enough to keep a $H_2$-enriched atmosphere in the reactor. In most of the experimental trials from Vlčko et al. and others, diphenylamine is generally dosed in the form of a solution in aniline or toluene. Furthermore, Vlčko et al. state that the conversion and selectivity can be enhanced by using aniline as a feed solvent.[22] The use of aniline as a solvent is advantageous owing to less separation units and already available aniline. The reaction conditions are set at 560°C and 1 bar pressure. The $Pt/Al_2O_3$ catalyst with aniline as a solvent[22] is chosen for this step since, it gives a conversion and selectivity towards carbazole of 97% and 90%, respectively. A consolidated table of the process conditions is provided in the Table 1. This method is considered as a highly feasible production route due to the easily available and relatively less expensive feedstock aniline and continuous mode of operation.

## 2.2 | Route 2: Dehydrogenative aromatization

A second method proposed to produce carbazole is one single reaction step from nitrobenzene and cyclohexanone. This method, inspired by Zeng et al.,[25] produces DPA by condensation of aniline and cyclohexanone. It produces the aniline in situ by reduction of nitrobenzene, additionally producing carbazole as a minor by-product. As it is necessary to convert the DPA to carbazole, it is assumed that the reaction conditions can be adjusted to push the equilibrium reaction towards carbazole in a single-step route. This assumption needs to be validated experimentally in a more detailed design of the process in the future.

More specifically, the pathway mentioned by Zeng et al.[25] describes a synthesis route for DPA through the dehydrogenative aromatization of a Schiff base (*N*-phenylcyclohexanimine) over a homogeneous palladium catalyst, similar to catalysts described by Chiang et al.,[26] in the presence of nitrobenzene as a $H_2$ acceptor (see SI Section D for full mechanism). This Schiff base is formed through the reaction between the reactants, aniline, and cyclohexanone, with an additional water molecule as by-product. The researchers state that without the presence of a hydrogen acceptor, a substantial amount of the Schiff base remains present. The same figure in SI Section D shows the mechanism proposed by the researchers to explain this behavior. Eventual further dehydrogenation of DPA leads to the formation of carbazole. However, only trace amounts of the component are formed. See Figure 3 for a simplified overview of the reaction.

Interestingly, $H_2$ acceptor nitrobenzene is converted into aniline, which is one of the reactants. One nitrobenzene molecule can facilitate three dehydrogenation steps, while producing two additional water molecules. Carbazole formation requires exactly three dehydrogenation

**TABLE 1** Reaction conditions for the two chosen routes.

| | **Route 1** | | **Route 2** | |
|---|---|---|---|---|
| **Parameter** | **Aniline condensation** | **Oxidative cyclization of DPA** | **Dehydrogenative aromatization** | **Carbazole ethylation** |
| Catalyst | $\gamma$-$Al_2O_3$ | $Pt/Al_2O_3$ | $Pd/(Al_3Ba)O_x$ | NaH |
| Solvent concentration | – | 50 wt% in Aniline | 42 wt% in toluene | 25 wt% in NEC |
| Conditions | 460°C, 1 bar | 560°C, 1 bar | 250°C, 30 bar | 90°C, 45 bar |
| Product | Diphenylamine | Carbazole | Carbazole | NEC |
| Conversion | 31% | 96.6% | 84.2% | 100% |
| Selectivity | 98% | 90% | 36.8% | 98% |
| By-products | 1,4-Benzenediamine | Ammonia, benzene, 2-aminobiphenyl | Phenol, TPA, water | – |

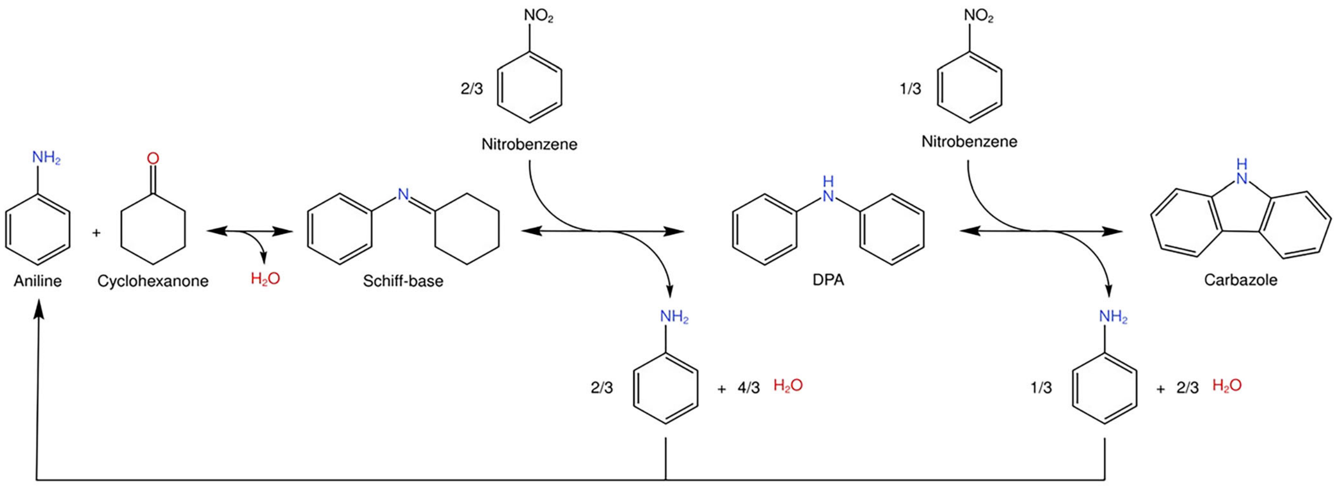

FIGURE 3 Simplified reaction mechanism of Route 2.

steps. Thus, for a continuous carbazole production process, no additional aniline needs to be fed, only nitrobenzene.

Besides DPA and carbazole, other by-products are formed during the reaction. One is phenol which is formed by dehydrogenation of cyclohexanone before the Schiff base can be formed. Another by-product mentioned by Zeng et al.[25] is *N*-cyclohexylaniline which forms through hydrogenation of the Schiff base intermediate. The last important by-product is triphenylamine (TPA) which is formed through condensation of *N*-cyclohexylaniline or DPA with a second cyclohexanone molecule and is subsequently dehydrogenated.

Understanding the mechanism opens the possibility of increasing the production of carbazole, changing it to the main product.[25] It is assumed that the equilibrium of the reaction can be shifted to favor carbazole production through the addition of more nitrobenzene as hydrogen acceptor. It is assumed that a DPA:carbazole ratio of 1:1 can be achieved and that the unconverted DPA can be recycled for dehydrogenation to the desired carbazole. Due to the large amount of unconverted DPA, the recycle stream will be relatively large. As mentioned previously, the assumption of excess nitrobenzene will favor dehydrogenation reactions. By-product *N*-cyclohexylaniline is formed through an opposing hydrogenation reaction. It is therefore assumed that no significant amount of this by-product will be formed under the new proposed conditions. Again, all these assumptions need to be checked experimentally.

Other alterations from the original research are implemented to facilitate small improvements to process operation. These include the use of toluene as the diluent instead of m-xylene and raising the temperature and pressure from 220°C/20 bar to 250°C/30 bar.

### 2.3 | *N*-ethylcarbazole synthesis from carbazole

The final step in both pathways is the reaction of carbazole with ethylene to form *N*-ethylcarbazole (NEC). A reaction proposed by Lei et al.[13] is already shown in Figure 2. The possible mechanism could be the nucleophilic addition of carbazole anion on the ethylene molecule. Na or NaH, being a strong base is capable of deprotonating the 9H-carbazole to an 8H-carbazole anion. The anion subsequently attacks the ethylene group to form *N*-ethylcarbazole.

Since, it is still unclear which functional isomers are formed during this reaction, it is assumed that the formation of by-products depends on the stability of different anions present in NEC. A study reveals that the reactivity of different carbon atoms mainly leads to the formation of ortho- and para-substituted molecules.[27] All the isomers that are formed can also be used as LOHC, and possess the same hydrogen capacity as the primary product shown in SI Section A. To minimize the required number of separation steps and avoid the usage of anhydrous acetonitrile, which is applied by Lei et al.,[13] it is decided to use NEC itself as the solvent in a 1:4 carbazole:solvent ratio. It is assumed that the yield and selectivity of the reaction are not influenced significantly by this change.

## 3 | PROCESS DESIGN

The process design follows the systematic method proposed by James Douglas[28] and discussed in several textbooks. It starts with a simple black box model of the process that defines the incoming and outgoing streams for a plant with a capacity of 700 tonnes/day of NEC. The black box is then specified in terms of process segments with dedicated reactors, separation trains and recycles of unreacted compounds back to the reactors. The separation trains are defined based on the thermo-chemical properties of the components and the separation heuristics of Barnicki and Fair.[29] These separation heuristics involve the selection of separation equipment using a decision tree, which utilize the pure component and mixture properties and product specifications. A flowsheet is modeled in Aspen Plus and fine-tuned by varying the amount of the components sent for purge and comparing the product recovery using additional equipment. Finally, detailed designs of the units are made and heat integration, control, safety, sustainability analyses are conducted for both routes. For both routes, the flowsheets and corresponding stream tables are available in the SI Section H.

## 3.1 | Route 1

The first route to NEC proceeds via aniline condensation followed by dehydrocyclization of DPA. In Figure 4, a simplified process flow diagram (PFD) for carbazole production following this route is shown.

The aniline condensation step is run in a gas phase reactor (R-101) at 460°C and 1 bar, where the reactor is fed with aniline and produces DPA, benzene-1,4-diamine (BDA), $NH_3$, and $H_2$. The reactor kinetics are modeled in MATLAB using Langmuir-Hinshelwood mechanism as given in SI Section I. The thermodynamic property sets in Aspen Plus are selected based on the nature of the properties of interest, the composition of the mixture, the pressure and temperature range and the availability of parameters. The Peng-Robinson Equation of state is used for operating pressure greater than 10 bar, whereas NRTL is used for pressure less than 10 bar. Two key assumptions taken at this level of process design are the neglect of pressure drop across equipment and a clear cut in the phase split. While practically infeasible, these assumptions are made to simplify model the process without significantly impacting the rest of this study. The heavier components aniline, DPA and BDA are separated from the lights by means of a flash column (FL-101) to reduce the duty from further downstream processes. The bottom of column FL-101 is sent to the distillation column D-101, where the unreacted aniline (and BDA byproduct) is sent back to R-101, while the DPA is sent to R102 for the cyclization reaction. The overhead from FL-101 is sent to the flash column FL-102, to separate the lights such as $H_2$ and $NH_3$ from residual aniline and BDA. The residual bottoms of column FL-102 are fed back to the reactor, while the overhead $NH_3$ and $H_2$ undergo further separation in an absorption column to sell the resulting aqueous ammonia as a separate bulk chemical and to send $H_2$ to the furnace (FUR). However, the additional revenues from the sales are not incorporated in the economic evaluation. In

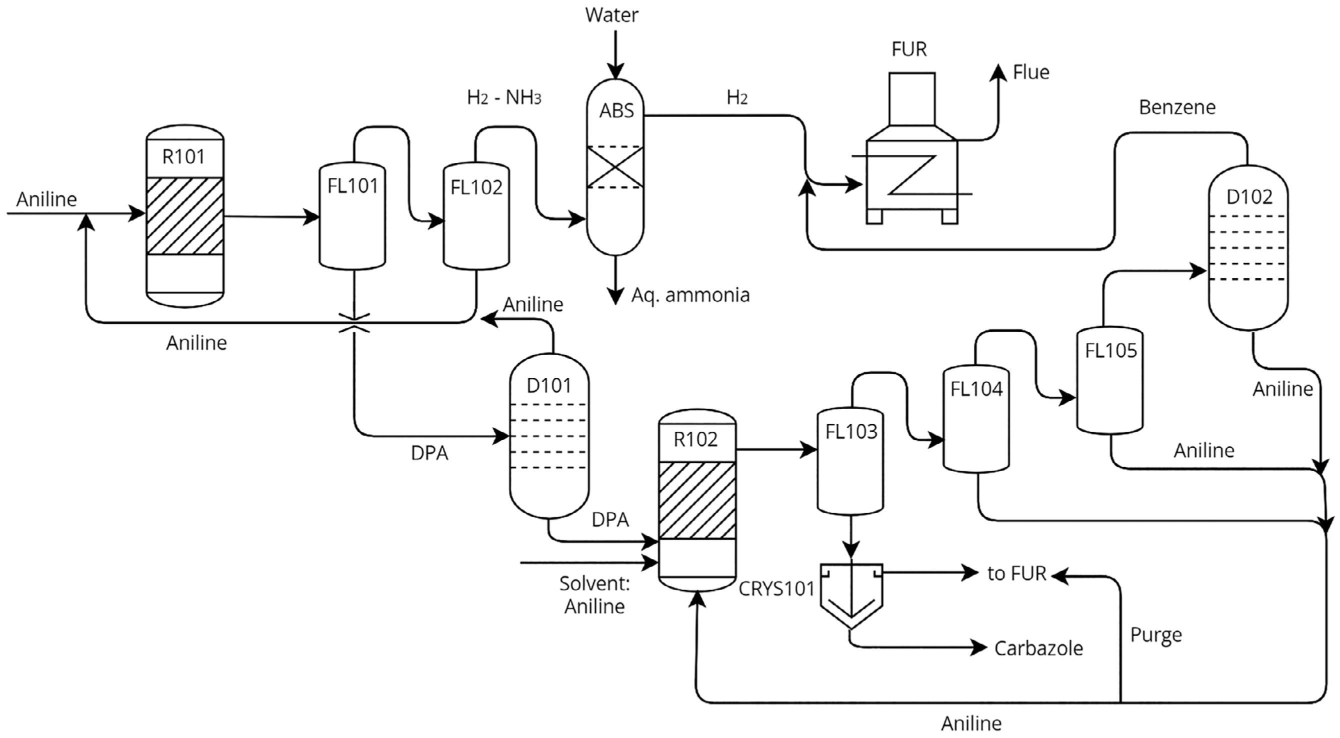

FIGURE 4 Simplified process flow diagram (PFD) of Route 1.

addition, it is assumed that the use of a weakly acidic catalyst and a low $NH_3$ partial pressure within the reactor omits the need for a regeneration step.

For the DPA cyclization stage, the DPA is dissolved in aniline and fed to reactor R-102 where the cyclization occurs at 560°C and 1 bar. The reactor effluent consists of the desired product carbazole, unconverted DPA, the aniline solvent, as well as benzene, 2-aminobiphenyl (ABP), $H_2$ and $NH_3$. Flash vessel FL-103 separates unreacted DPA, carbazole and ABP from aniline, benzene, $NH_3$ and $H_2$. The aniline is separated from the benzene, $NH_3$ and $H_2$ via flash vessels FL-104 and FL-105. Distillation column D-102 is utilized to recover the rest of the aniline from the vapor stream stream, which is then recycled back to the reactor after a certain amount is purged to the furnace to prevent the accumulation of residual benzene in the reactor. The separated benzene, $NH_3$ and $H_2$ are also purged to the furnace. The use of a furnace reduces utility costs.

The main product carbazole is sent to the third reactor to convert it into NEC. The crystallizer CRYS-101 separates the carbazole rich stream from BDA and unreacted DPA. This carbazole stream is then sent for an ethylation step. The stream rich in BDA and DPA post crystallization is purged in the furnace. A separate catalyst regeneration step is assumed not to be necessary since the $H_2$-rich environment is assumed to prevent coke precursors from becoming coke.

## 3.2 | Route 2

The second route to NEC proceeds via a one-step conversion of cyclohexanone and nitrobenzene to carbazole that is followed by ethylation to NEC. See Figure 5 for a simplified PFD of carbazole production following this route.

The first reactor (R-201) operates at 250°C and 30 bar, and yields an effluent comprising of carbazole, unreacted cyclohexanone, solvent toluene and by-products, namely phenol, aniline, DPA, and TPA, as well as a large amount of water. The exact composition of this stream follows from the conversion values mentioned by Zeng et al.[25] and the assumptions mentioned in Section 2.2. This stream is led to a flash drum (FL-201) where a large part of the water is removed. However, this vapor phase also contains several valuable components that are worth recycling. The stream is cooled down to 30°C and the resulting liquid stream is led into a decanter (LLS-201), where the organic phase is separated from the water and recycled back to the reactor.

The heavy components (DPA, carbazole and TPA) from the bottoms of the flash drum (FL-201) are separated using a crystallizer (CRYS-201), melted, and fed into a distillation column (D-203) to remove DPA. The DPA is recycled back into the reactor and the bottom stream of the column, containing carbazole with a relatively large amount of TPA (13 wt%), is introduced into the second reactor for ethylation.

The leftover liquid from the crystallizer (CRYS-201) contains, next to water and some light organics (cyclohexanone, toluene, phenol, and aniline), a small amount of DPA and carbazole due to the non-ideal recovery of the crystallizer. A decanter (LLS-202) is used to remove the water, a distillation column (D-201) recycles the toluene solvent, and a second distillation column (D-202) separates the remaining light organics from the heavy ones. To prevent the build-up of aniline, the top product

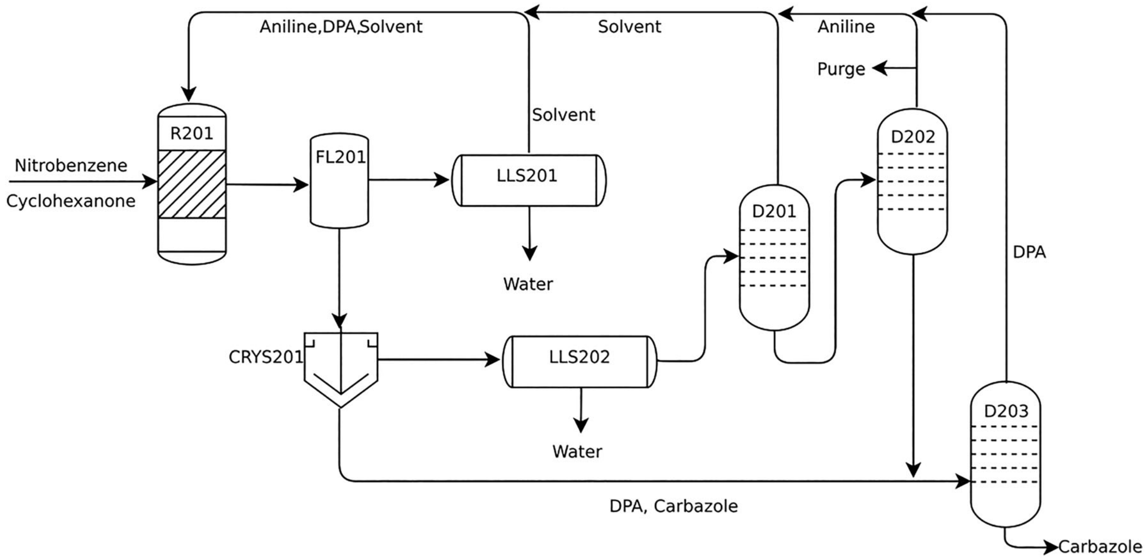

FIGURE 5 Simplified process flow diagram (PFD) of Route 2.

is partly purged and subsequently recycled to the reactor. The bottom stream (DPA and carbazole) is mixed with the melted product of the crystallizer and led into distillation column D-203.

Furthermore, the carbazole product stream leaving distillation column D203 consists of 13 wt% TPA. Wasserscheid et al.[30] state that the presence of NEC derivatives in the LOHC could actually have beneficial consequences by working as LOHC themselves and by lowering the melting point of pure NEC ($T_m = 70°C$), which allows for an easier transport. Therefore, it is assumed that TPA or any isomers of NEC that are produced in the reactor do not have to be removed and can actively take part as LOHC.

### 3.3 | Carbazole ethylation

The last stage of both routes is the direct ethylation of carbazole. A PFD of the carbazole ethylation step is shown in Figure 6. This process is started by feeding carbazole with an excess of ethylene (1.2–1.5:1 molar ratio of ethylene to carbazole) to the reactor (R-301) with NEC as a solvent and NaH as the catalyst (2 wt% compared to carbazole). The catalyst is dispersed in the solvent and fed continuously as no catalyst recycle is present. The reaction occurs at 90°C and 50 bar. The product stream contains NEC, NaH and unconverted ethylene. The outlet stream of the reactor is flashed (FL-301) to remove the unreacted ethylene, which is then recycled back into R-302. The subsequent step is the removal of the catalyst. To do this, water is added to convert the NaH into NaOH, which is then filtered out of the mixture (FILT-301). The catalyst conversion generates hydrogen gas which is removed alongside any left-over ethylene using a second flash separator (FL-302). The resulting NEC stream is then split into two streams of which one is used as the solvent for R-301 and the other is the final product stream.

Although both routes proceed with the ethylation reaction via the same process, there are some differences in the feed, feed ratios, and solvent ratios. As mentioned, there are differences in the stream composition entering reactor R301 due to the presence of TPA in the feed stream of Route 2.[30]It should also be noted that the molar ratios of solvent (NEC) to carbazole varies in both routes, with Route 1 using a ratio of 1:1 while Route 2 uses a 4:1 ratio. The ratio of solvent to carbazole is varied in order to study the effect of the solvent ratio in the sizing of the reactor. The purity of LOHC obtained by both routes is 99%.

## 4 | ECONOMICS

The preliminary process designs enable the estimation of the capital expenditure (CAPEX) and operational costs (OPEX), as well as the break-even cost of LOHC at a production capacity of 225 ktpa. This comprehensive analysis further assists in the identification of the major cost contributors and most critical improvement requirements. Furthermore, as this entails a conceptual design and since some of the assumptions made may have a large influence on the productivity of the plant, a sensitivity analysis is conducted to determine the influence of changes in the CAPEX and OPEX on the break-even cost.

### 4.1 | Calculation methodology

The total fixed capital cost or CAPEX is calculated by determining the purchased costs of the major equipment by utilizing cost curves developed by Sinnott and Towler,[31] shown in Equation 1 below.

$$C_e = a + bS^n. \tag{1}$$

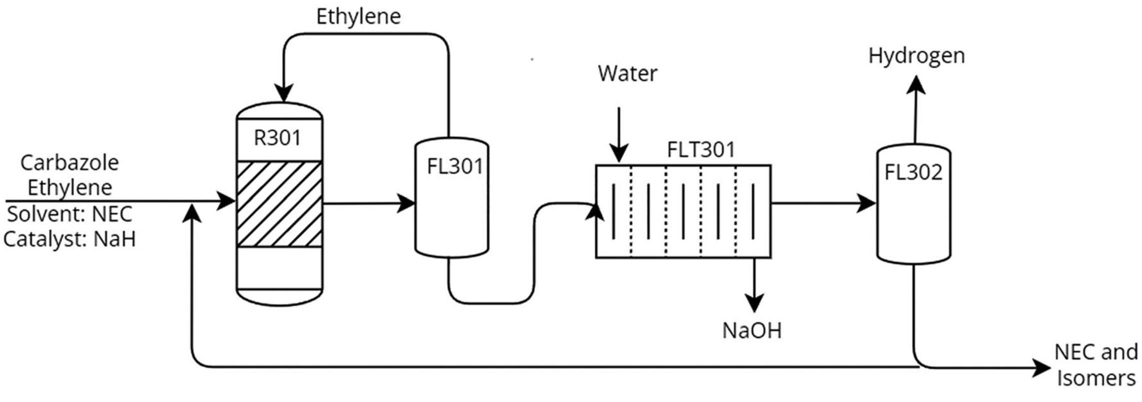

FIGURE 6 Simplified process flow diagram (PFD) of common route.

**TABLE 2** Specific size parameter *S* for several process units.

| Process unit | Size parameter, *S* |
|---|---|
| Compressors | Power (kW) |
| Crystallizers | Length (m) |
| Distillation columns: vessels | Shell mass (kg) |
| Distillation columns: trays | Diameter (m) |
| Filters | Capacity ($m^3$) |
| Flash separators | Shell mass (kg) |
| Furnaces | Duty (MW) |
| Heat exchangers | Area ($m^2$) |
| Liquid–liquid separators | Capacity ($m^3$) |
| Pumps | Flow (L/s) |
| Reactors | Capacity ($m^3$) |

**TABLE 3** Traditional outside battery limits (OSBL), D&E and *X* values.

| Factor | Value |
|---|---|
| Outside battery limits (OSBL) | 0.40 * ISBL |
| Design and engineering (D&E) | 0.25 |
| Contingency (*X*) | 0.10 |

**TABLE 4** Final raw material costs based on 2017–2021 price indices.

| Raw material | Price ($/tonne) | Usage Route 1 (tonne/day) | Usage Route 2 (tonne/day) |
|---|---|---|---|
| Aniline | 1183 | 1078 | 0 |
| Nitrobenzene | 1099 | 0 | 458 |
| Cyclohexanone | 1413 | 0 | 389 |
| Toluene | 649 | 0 | 0.14 |
| Ethylene | 961 | 134 | 94 |

In the equation above, $a$ and $b$ refer to cost constants, $S$ refers to a specific size parameter and $n$ is an exponent factor specific to each type of equipment. The relevant specific size parameters are listed in Table 2 below.[31]

Subsequently, the resulting delivered costs are multiplied by the Lang installation factor of 5.04 to account for the installation costs (Seider et al.[32]) and by a factor of 1.5 to update the 2010 prices to 2022 using the Chemical Engineering Plant Cost Index (CEPCI).[33] This defines the total inside battery limits (ISBL) costs, which are related to the equipment, material, and labour costs of constructing the process plant within the physical boundaries of the plant site. Then, the outside battery limits (OSBL) costs, which pertain to additional site infrastructure and preparation, are calculated as a percentage of 40% of the ISBL costs.[31] Ultimately, the total fixed capital costs ($C_{FC}$) are obtained by combining the ISBL and OSBL in addition to factors accounting for thecosts related to the design and engineering process (D&E) as well as some contingency ($X$). This relation is shown in Equation 2 below.[31] Traditional values for the OSBL, D&E and X factors are summarized in Table 3 below.

$$C_{FC} = (\text{ISBL} + \text{OSBL})\,(1 + D\&E + X). \tag{2}$$

The OPEX are determined based on the required feedstock consumption and prices, utilities and factors accounting for the operations, maintenance, operating overhead, depreciation, interest, and other general expenses.[31] This is visualized in SI Section F. The heat integration analyses show savings of 37.9 and 16.1 MW between the hot and cold streams for Routes 1 and 2, respectively. These energy savings are reflected in the calculated utility costs. The treatment and discharge costs of the output streams are also considered as a part of the utility costs. Further, the yearly depreciation and interest are both considered to be 10% of the CAPEX. Then, by dividing the OPEX by the production capacity of 225 ktpa, the LOHC break-even cost is calculated.

The raw material prices utilized in this estimation, as presented in Table 4 below, are determined through a price index collection known as Business AnalitIQ.[34] Internal consistency for the set of prices is secured by determining the price correlation for each component versus that of benzene over the period 2017–2021 and selecting the prices that correspond to the pre-pandemic 2018 benzene price of 920 $/tonne (see SI Section E for more details). These correlations are based on European prices for all components except for nitrobenzene, for which only Asian market prices can be found.

## 4.2 | Results

Based on the aforementioned methodology, total fixed capital costs, $C_{FC}$, are estimated to be approximately \$200 MM and \$250 MM for Routes 1 and 2, respectively. The $C_{FC}$ is for 30–40% determined by the reactor costs. This correlates to 60%–70% of the primary ISBL costs, as is summarized in the ISBL break-down given in Figure 7 and Table 5 below.

OPEX of \$685 MM and \$590 MM are found for Routes 1 and 2, respectively. Assuming a capacity of 225 ktpa, this correlates to break-even costs of \$3.03 and \$2.61 per kg LOHC. Notably, the analysis reveals that the feedstock costs are the most significant contributor to the OPEX, accounting for 76% and 72% for Routes 1 and 2, respectively, as shown in Figure 8. Feedstock costs, and more specifically, the price difference between aniline and cyclohexanone/nitrobenzene also accounts for most of the break-even cost difference between the routes, as the CAPEX related costs (depreciation, interests, maintenances, taxes, etc.) are similar for both.

## 4.3 | Sensitivity analysis

Several key assumptions are made during the design process, for instance related to the raw material prices, reaction selectivities and yields. Therefore, it is necessary to investigate how changes in these factors would influence the final break-even costs. Accordingly, a 25% increase in the feedstock prices or drop in yields increases the break-even costs by 19% and 17% to $3.61 and $3.07 per kg, for Route 1 and Route 2, respectively. As the yearly feedstock expenses are responsible for the majority of the OPEX, the sensitivity of the break-even cost to the other cost factors is not as large in comparison. Similarly, if the CAPEX of either method increases by 25%, this would have a moderate impact of 3%–4% on the break-even costs. In conclusion, the viability of the project is largely dependent on the raw material cost that is, prices and yields.

Finally, by assuming a required $H_2$ flow of 500 tpd per supply chain, a hydrogenation (and dehydrogenation) efficiency of 95%, and 15 days for the loading, unloading and forwards and backwards transport, resulting in a total round-trip time of 60 days, the contribution of the LOHC price to the transportation cost of $H_2$ and with that to the overall $H_2$ cost can be calculated. Additionally, it is assumed that every year, 2% of the carrier molecules are lost and need to be added to the supply chain again. Finally, a plant lifetime of 20 years and an Initial Rate of Return (IRR) of 5% are chosen, resulting in an annualization factor of 8%. For this analysis, LOHC cost boundaries of $2.61 and $3.03 per kg LOHC are chosen, as calculated in Section 4.2. This results in annualized inventory CAPEX and OPEX values of $107 MM-–$125 MM and $27 MM–$31MM, respectively, causing an LOHC price contribution to the levelized $H_2$ cost of $0.77–$0.90 per kg $H_2$.

If again a required $H_2$ flow of 500 tpd per supply chain is assumed and the LOHC is only employed for short-distance transport and small-scale use, which would result in much shorter round-trip times of 7 days and, thereby, a much smaller inventory, the contribution of the LOHC price to the overall levelized $H_2$ cost is much smaller at $0.09–$0.10 per kg $H_2$. Finally, once the 'first fill' of the

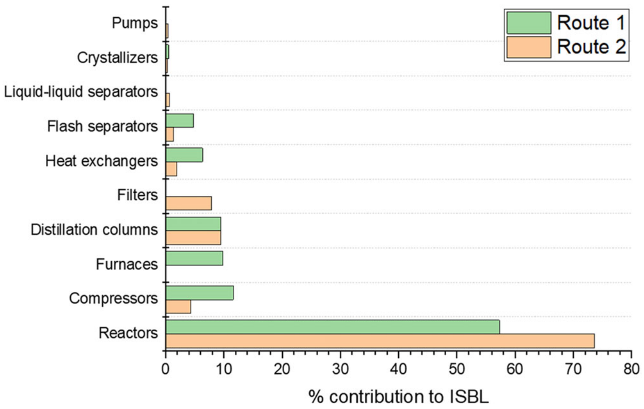

**FIGURE 7** Inside battery limits (ISBL) make-up for Routes 1 and 2.

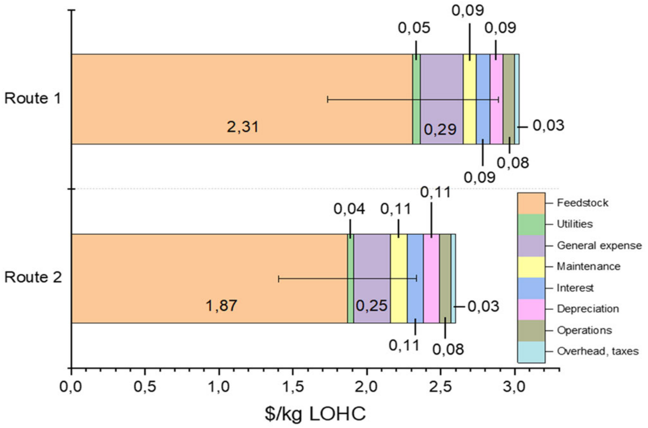

**FIGURE 8** Operational Expenditure (OPEX) make-up for Routes 1 and 2.

**TABLE 5** Costs of the primary installed equipment and their fraction of the total ISBL for Routes 1 and 2.

| Route 1 | | Route 2 | |
|---|---|---|---|
| **Process unit** | **Cost (% of ISBL)** | **Process unit** | **Cost (% of ISBL)** |
| *Distillation Column 1* | $8.5 MM (8.1%) | *Distillation Column 1* | $3.5 MM (2.6%) |
| *Distillation Column 2* | $1.5 MM (1.4%) | *Distillation Column 2* | $5.3 MM (4.0%) |
| *Reactor 1* | $40.3 MM (38.2%) | *Distillation Column 3* | $3.8 MM (2.9%) |
| *Reactor 2* | $11.6 MM (11.0%) | *Reactor 1* | $53.6 MM (40.2%) |
| *Reactor 3* | $8.5 MM (8.1%) | *Reactor 2* | $44.5 MM (33.4%) |
| *Furnace 1* | $10.3 MM (9.8%) | *Filtration 1* | $10.6 MM (8.0%) |

supply chain has been completed, it would also be possible to sell the remaining inventory for around 80% of the original production cost, resulting in a significantly smaller contribution of the LOHC price to the overall $H_2$ cost, as some of the CAPEX can be recovered.

## 5 | CONCLUSION

This paper reports a techno-economic evaluation of NEC production for use as an LOHC. Two reaction routes are examined: the first route involves aniline condensation to DPA, followed by DPA dehydrocyclization forming carbazole. The second route converts nitrobenzene and cyclohexanone to carbazole directly. Both routes produce carbazole, which subsequently undergoes an ethylation reaction to produce NEC.

Process design studies are conducted for both routes and modeled to achieve a production of 700 tpd LOHC. Based on the process design, the total fixed capital costs and OPEX of the production are determined resulting in break-even costs of NEC around \$3.0/kg LOHC and \$2.6/kg LOHC for Routes 1 and 2, respectively. Notably, the feedstock costs are the most significant contributor to the break-even cost, accounting for 76% and 72% of the OPEX. Second, it is found that the ISBL costs are dominated by reactors costs and only have a limited influence on the break-even costs, mitigating the criticality of the assumptions made here. Based on the estimated break-even costs, the LOHC price contribution to the overall $H_2$ cost is estimated to be \$0.77–\$0.90 per kg $H_2$ for a 60-day roundtrip and \$0.09–\$0.10 per kg $H_2$ for a 7-day roundtrip.

This work guides future experimental research, enabling further optimization of the proposed design. While the process design and modeling have been conducted on the backing of theoretically sound assumptions, experimental research should be conducted to validate the assumed selectivities as well as the possibility to integrate the two reaction steps of carbazole formation into a single step as proposed for Route 2. These validation efforts extend to the ethylation step, for which limited reported data is available.

The synthetic production of NEC from aniline or nitrobenzene/cyclohexanone has the potential to reduce the manufacturing costs by an order of magnitude versus previously explored methods such as coal tar distillation. This would aid in the affordable delivery of hydrogen via an LOHC-based supply chain.

## AUTHOR CONTRIBUTIONS

**E. M. T. Uijthof:** Writing – review and editing; visualization; investigation; writing – original draft; methodology; validation; software; formal analysis. **B. S. Chavan:** Investigation; writing – original draft; methodology; validation; visualization; writing – review and editing; software; formal analysis. **M. J. Sluijer:** Formal analysis; software; methodology; visualization; writing – review and editing; validation; writing – original draft; investigation. **V. C. Komath:** Investigation; writing – original draft; writing – review and editing; visualization; methodology; validation; software; formal analysis. **A. G. J. van der Ham:** Conceptualization; supervision; project administration; writing – review and editing; methodology; resources. **H. van den Berg:** Supervision; conceptualization; project administration; writing – review and editing; methodology; resources. **J.-P. Lange:** Supervision; conceptualization; investigation; project administration; writing – review and editing; resources. **A. Higler:** Supervision; conceptualization; investigation; project administration; writing – review and editing; resources. **S. Wijnans:** Supervision; conceptualization; investigation; project administration; writing – review and editing; resources.

## CONFLICT OF INTEREST STATEMENT

For the research paper titled 'Liquid Organic Hydrogen Carriers – Process design and economic analysis for manufacturing *N*-ethylcarbazole'. The authors whose names are listed immediately above certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

JPL, AH, and SW are working for Shell Global Solutions Internal B.V., which is supporting Shell's commercial activities in Hydrogen. [Correction added on February 28, 2024 after first online publication: The Conflict of Interest Statement was updated to include the name of author's who are affiliated with Shell Global Solutions, B.V.]

## DATA AVAILABILITY STATEMENT

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. Should any raw data files be needed in another format, they are available from the corresponding author upon reasonable request.

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## SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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