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Techno-economic and life-cycle analysis of single-step catalytic conversion of bioethanol to fuel blendstocks over Ni-doped HZSM-5 zeolite catalyst

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ABSTRACT

This work presents techno-economic and life-cycle studies focusing on the catalytic conversion of ethanol into hydrocarbon fuel blendstocks. These analyses benefit from recent advancements in catalyst and process development. The consolidated alcohol dehydration and oligomerisation for ethanol-to-hydrocarbon (CADO-ETH) conversion approach, described here, achieves a single-step transformation of wet ethanol vapour into hydrocarbons and H_2O using a Ni-doped HZSM-5 catalyst. Catalyst cost estimation using the CatCost model showed that commercial synthesis of Ni/HZSM-5 incurred significant processing costs, which varied greatly depending on the manufacturing scale. Hence, catalyst production using 100 % and 50 % baseline scale production (BSP) requirements resulted in net catalyst costs of $31.4 and $69.9/kg, respectively. Although current CADO products closely resemble gasoline blendstocks, they can also be blended with gasoline fuel at low levels. There is potential for higher-level blending in the future. The operating and annualised capital costs for converting wet ethanol into fuel blendstocks were predicted to be $0.05/L at present and projected to decrease to $0.03/L in the future. This cost is comparable to the unit energy cost of synthesising anhydrous ethanol from wet ethanol, which is $0.02/L. At an oil price of 100 $/bbl, the expected minimum selling prices for the fuel blendstocks produced by CADO are similar to the prices for conventional gasoline. However, at an oil price of $60/bbl, the estimated minimum selling prices for CADO-derived blendstocks are not competitive with conventional gasoline. Nevertheless, considering existing production incentives, the projected minimum selling price for gasoline blendstock is comparable to the oil price of $60/bbl. The LCA shows that the CO_2 emissions of gasoline produced from crude oil are 90.2 gCO_2 e/MJ, which is 25 %, 53 % and 63 % more than the emissions of gasoline produced from corn starch, sugarcane, and cane cellulose, respectively. The results of this study indicate that the single-step CADO-ETH technology is promising for the production of renewable fuels and offers a potential pathway to reduce the carbon footprint.

1. Introduction

Recently, there has been a surge in the interest in renewable fuels due to the depletion of fossil fuels and growing concerns about climate change and air pollution. Liquid fuels such as petrol and diesel contribute approximately 40 % of global energy consumption [1]. The global transport industry has witnessed a substantial increase in greenhouse gas (GHG) emissions, surpassing emissions from any other sector. The transport sector has now become the primary source of carbon emissions in most countries, overtaking electricity generation. Most industry analysts agree that combining electric vehicles with low-carbon electricity production is the most promising strategy for minimising fossil fuel emissions in the commercial transportation sector. However, incorporating energy storage systems utilising batteries or hydrogen onboard poses significant challenges in non-light-duty transportation sectors (aviation, ocean shipping, etc.) [2]. Hence, energy-

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dense liquid hydrocarbon (HC) fuels are expected to continue being utilised in these areas. Despite aggressive efforts to minimise travel growth, promote mass transport means, enhance efficiency, and promote the commercialisation of electric and H_2-powered automobiles, it is projected that liquid fuels will still be necessary to meet around 50 % of the required transportation fuel by 2075 [3]. Biofuels, fuels produced from biomass, are considered the most advantageous option for generating low-carbon liquid fuels.

To reduce fossil emissions in the transport sector, active efforts are underway to explore various strategies involving biofuels. These strategies include the production of fuel-range HCs other than ethanol from biomass, engine modification to utilise E100, and the conversion of ethanol into hydrocarbon fuels. Among these approaches, the latter shows promise due to the low cost of ethanol and its extensive production capacity. Similar to the methanol-to-gasoline (MTG) technology, which was pioneered by Mobil, the ethanol-to-hydrocarbon/gasoline process offers a viable approach for the ETH conversion. There has been significant interest in the catalytic conversion of ethanol into hydrocarbons (ETH) to produce renewable fuel [4]. The typical approach involves a three-step process that includes ethanol dehydration, ethylene oligomerisation, and hydrogenation to produce a final renewable fuel suitable for blending with conventional fuels. Another approach involves a one-step transformation of ethanol-to-hydrocarbon (ETH) blendstocks, utilising a metal-doped zeolite catalyst. This consolidated alcohol dehydration and oligomerisation (CADO) process, proposed by Narula, et al. [5], aims to achieve dehydration and oligomerisation of alcohols in a single reactor without needing external H_2 addition. Narula, et al. [5] showed complete ETH over ZSM-5 and a single reactor setup in laboratory experiments. The researchers found that the percentage of ethanol in H_2O had no significant effect on the ETH conversion rate or product selectivity. The study also suggested a mechanism for HC formation that bypasses the intermediate production of ethylene, directly transforming ethanol into long-chain HCs and H_2O. The CADO for ethanol-to-hydrocarbon (CADO-ETH) technology has shown compelling findings of greenhouse gas emission reductions by 40–96 %. This innovative approach holds great promise in enabling the development of environmentally friendly and sustainable gasoline production for transportation purposes. The CADO-ETH process offers several advantages over traditional catalytic upgrading methods. It can be conducted in a single step at temperatures ranging from 275 to 350 °C, close to atmospheric pressure, and does not require the addition of external hydrogen. These characteristics make CADO-ETH potentially more cost-effective [2].

According to Van Allsburg, et al. [6], out of a total of 250,643 entries in the dataset from a comprehensive literature review and frequency survey conducted to investigate the cost of catalysts (2010–2020), 5.80 % of the articles were identified as containing the words 'cost' or 'costs' in either the title or abstract. Among these articles, only 0.25 % featured terms in their titles or abstracts that indicated a specific discussion on the cost of catalysts. These terms included "catalyst(s) cost," "manufacturing cost," "synthesis cost," "material(s) cost," "production cost," or "economic cost. This literature review and frequency survey serve as a valuable resource for understanding insufficient information related to the cost aspects of catalysts. However, many researchers in this field lack the necessary information to conduct such assessments [6].

The existing literature shows a variety of studies on techno-economic analyses (TEA) and life cycle analyses (LCA) of biofuel production, including bioethanol, with different results and objectives such as energy costs and consumption, greenhouse gas emissions, land use, economic viability, feedstock cultivation and water footprint. In particular, these studies use different variables tailored to specific research objectives [7–9]. Over the last decade, a plethora of LCA studies have emerged with the aim of evaluating different methods of producing biofuels in comparison to conventional fossil fuels [10–12]. Alexiades, et al. [13] Alexiades et al. (2017) investigated a low-carbon pathway to produce bioethanol from sugar beet. The resulting carbon intensity (CI) for ethanol derived from this simulated pathway was 25.5 g CO_2e/MJEtOH, a remarkable 44 % reduction compared to the average ethanol produced in this state. Importantly, the total pollutant emissions in this simulation were 71 % lower than those of diesel in automobiles [13]. Similarly, Lask, et al. [14] evaluated the use of miscanthus as a feedstock for bioethanol production and found lower impacts on greenhouse gas emissions, fossil resource depletion, natural land conversion and ozone depletion. Another comparative study by Rathnayake, et al. [15] evaluated bioethanol production from cassava, sugarcane molasses and rice husks. Their comprehensive LCA comparison, based on indirect process data from simulations and minimal changes in settings, highlighted that bioethanol production from cassava outperformed the others in terms of net energy ratio (1.34), renewability (5.16) and GHG emission reduction (410 kg CO_2eq/1000 L). In addition, the substitution of fossil natural gas with softwood chips as the primary energy source showed a significant potential (45 %) to reduce the carbon footprint of sugar production [16]. While Santoyo-Castelazo, et al. [17] employed a robust and comprehensive LCA methodology to examine the entire life cycle of bioethanol production, Amezcua-Allieri, et al. [18] conducted both techno-economic and LCA analyses to assess the costs and environmental impacts of providing heat and electricity in the sugar production process. Their comparison between the use of fuel oil and sugarcane bagasse showed that the use of bagasse as a solid fuel is more cost-effective and results in lower energy production costs in the form of steam and electricity.

Recent studies on TEA of biofuel production have focused primarily on biodiesel [19–23] and jet fuel [24–28] from different feedstocks, while little attention has been paid to gasoline production [29–32]. The existing literature on gasoline TEA has investigated various feedstocks, catalysts and processes, such as methanol, hardwood and corn stover, along with Fischer-Tropsch, integrated (hydropyrolysis and hydroconversion) process and pyrolysis using a fluidised bed reactor (Patel et al, 2019; Tan et al, 2014; Yan et al, 2021; Borugadda et al, 2020). The liquid fuel yields obtained so far from these studies have been relatively low, and further development of the catalyst process is needed. However, a notable gap in these studies is the extensive use of commercial catalysts coupled with the lack of a comprehensive life cycle assessment (LCA) for the gasoline production processes. Currently, research efforts are focused on catalyst and process development for CADO-ETH technology, and there are few TEA or LCA for CADO-ETH. The present study attempts to address these limitations by conducting a TEA of gasoline production using the newly developed Ni/HZSM-5 catalyst. The feedstock chosen for this study is ethanol, and the gasoline production process involves the CADO-ETH method. In contrast to previous studies, our research places a special emphasis on evaluating the life cycle analysis of the entire gasoline production process. By incorporating this holistic approach, we aim to provide a more comprehensive understanding of the economics, environmental impact and sustainability aspects associated with the CADO-ETH process for gasoline fuel blendstock production using a novel Ni/HZSM-5 catalyst.

2. Materials and methods

The study employed several chemicals, including sodium silicate solution ($Na_2O{\cdot}SiO_2{\cdot}H_2O$), aluminium sulphate ($Al_2(SO_4)_3{\cdot}18H_2O$), tetrapropyl ammonia bromide ($C_{12}H_{28}BrN$), sodium hydroxide (NaOH, 97 %), sulfuric acid (H_2SO_4, 98 % conc.), and ammonium nitrate (NH_4NO_3). Nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) was used as precursors for transition metals. Sigma-Aldrich provided the ethanol feedstock. To estimate the costs associated with the catalyst and CADO-ETH gasoline production (including biomass to bioethanol and bioethanol to fuel blendstocks), we used the Catcost v1.1.0 model [6] and the 2011 National Renewable Energy Laboratory (NREL) biochemical ethanol model [2,33]. For the life cycle (CO_2) emissions assessment, we employed the Greenhouse Gases, Regulated Emissions, and Energy Use in

Transportation (GREET) model developed by Argonne National Laboratory.

2.1. Laboratory-scale catalyst synthesis and evaluation procedures forming the basis of process designs

Ni-doped HZSM-5 catalyst (Ni/HZSM-5) was synthesised using the novel batch formula: $10Na_2O{:}40SiO_2{:}1.0Al_2O_3{:}10.5TPABr{:}3740.6H_2O$ via hydrothermal method involving several processes (Fig. 1) as reported in our previous study [34]. The synthesised catalyst was denoted NiZ. Following NiZ deactivation after the initial cycle, the catalysts underwent a five-hour regeneration process at 550 °C, with an airflow rate of 80 mL/min. The regenerated catalyst was denoted NiZ/R. The catalyst was characterised using different techniques. The catalyst was tested for CADO-ETH conversion at a temperature of 350 °C and weight hourly space velocities (WHSV) of 7 h^{-1} for 96 h. An HPLC pump introduced the feedstock into the fixed-bed reactor after the catalyst's initial activation at 400 °C. The determination of product selectivity (Si) and conversion (X) was carried out according to the methodology outlined by Sun, et al. [35].

2.2. Ni/HZSM-5 catalyst cost estimation

Laboratory-scale synthesis methods serve as the basis for designing industrial processes. Building upon these laboratory techniques, conceptual catalyst production techniques were established and optimised in the Catcost Excel version. These procedures were designed to be sustainable, aiming to minimise raw material utilisation by recycling unreacted reactants and reducing waste generation in wastewater and air pollutants. Process heat integration was also employed to maximise energy efficiency by reclaiming high-value heat and minimising heat rejection. Material and energy flows derived from the process model were employed for equipment sizing. These process designs were crucial

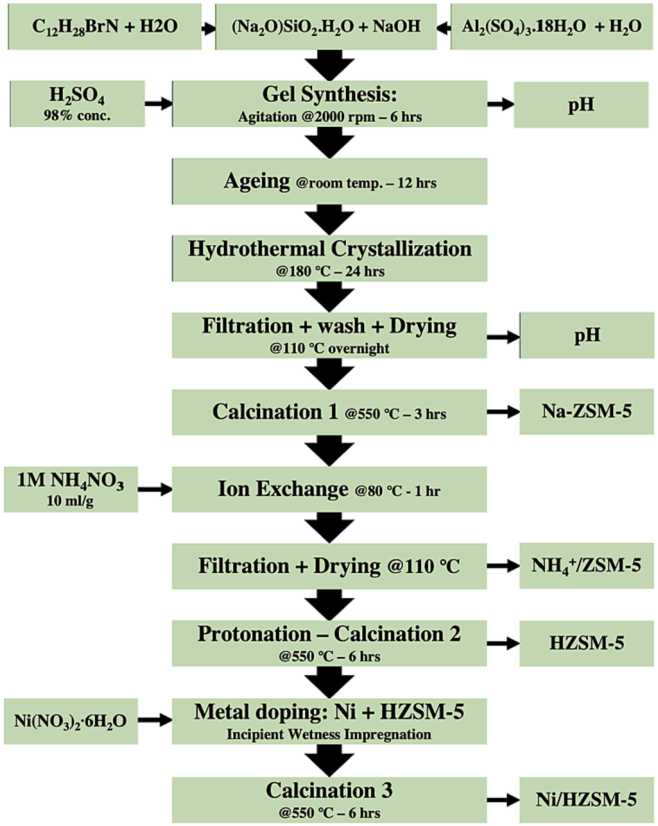

Fig. 1. Schematic diagram of Ni/HZSM-5 catalyst synthesis procedure.

for cost analysis and have been implemented as process templates in CatCost for easier analysis. The catalyst manufacturing scale in a biorefinery was established as the baseline. The consumption rate of catalysts in the biorefinery, measured in grams of catalyst per global gram equivalent (GGE) of product, was determined based on various sources of information according to [6]. For example, the consumption rate for the ZSM-5 catalyst was 18.12 g per GGE, as reported by the National Renewable Energy Laboratory (NREL). On the other hand, the annual catalyst demand in the biorefinery, which processes 2,000 dry tonnes of biomass per day and produces 47.0 million GGE per year, was estimated to be 911 tonnes (baseline scale production [BSP] requirement) for ZSM-5 only during catalyst replacement years.

To estimate the cost of the Ni/HZSM-5 catalysts, the CatCost v1.1.0 spreadsheet tool was utilised, and the cost estimates were compiled in Microsoft Excel and the CatCost web version. The Supplementary Information (SI) comprehensively describes the assumptions, input costs, cost factors, and other variables used in the calculations. All values were converted to US dollars in 2016, using either the Chemical Producer Price Index or the Chemical Engineering Plant Cost Index, depending on the nature of the expenditure. The prices of raw materials were determined using various sources, including vendor quotations, publicly available and proprietary price databases, and insights from industry experts. Multiple sources were considered to calculate an average price and validate the estimates. Two methodologies, the Step technique and the CapEx and OpEx Factors method, were used to estimate the processing costs. For the present study, we employed the CapEx and OpEx Factors methods for cost estimation. For the CapEx and OpEx Factors method, a BSP for a dedicated catalyst synthesis plant was assumed to be the annual biorefinery catalyst demand for ZSM-5. Detailed breakdowns of the calculation steps and equipment lists for the estimation method are provided in Supplementary Information (SI) Section 1.0 and Fig. 1a-k. The capital costs, including installation, piping, instrumentation, and buildings, as well as indirect costs and working capital, were estimated using fixed factors (multipliers) based on the total cost of purchased equipment (Fig. 2). Similar calculations and factors were used to determine operating costs, such as supervisory labour and maintenance supplies, as well as fixed/indirect costs and general expenses. Continuous operation (8,760 h per year) with full staffing levels, including maintenance downtime, was assumed. A worker rate of $48 per hour was used for production, according to [6], which accounted for additional perks.

2.3. CADO-ETH techno-economic analysis (TEA) methodology

The operational costs involved in CADO-ETH technology were estimated according to [2]. This was done by evaluating and considering various factors such as wastewater treatment, catalyst expenses, electricity, waste disposal, insurance and taxes, and labour. It was assumed that the water produced during the process would be treated in a standard wastewater facility, costing $1.85 per 1000 L or $7 per 1000 gallons. For the existing CADO-ETH technology, it was estimated that the reactor catalyst would need replacement every 6 months at $70/kg. As for the future CADO technology, the catalyst replacement was projected to occur every 9 months at a cost of $31.42/kg, corresponding to the net catalyst cost from 100 % BSP estimated from the CatCost model. The electricity unit cost used for calculations, at $0.05/kWh, represented the average in the Midwest, the primary region for ethanol synthesis in the US. The electricity demand in this region mainly powered compressors and pumps. Insurance and municipal taxes were estimated to account for 2.0 % of the total installed capital (TIC), while maintenance and labour were projected to make up 3.0 % and 1.0 % of the TIC, respectively. The NREL's mass and energy balances and unit costs were utilised for the conversion process from wet alcohol to anhydrous ethanol. To estimate the capital costs, equipment sizes were determined based on energy balances and combined with costs from comparable equipment, as stated in NREL TP 47764 [2,33]. The scaling factor of 0.60 was

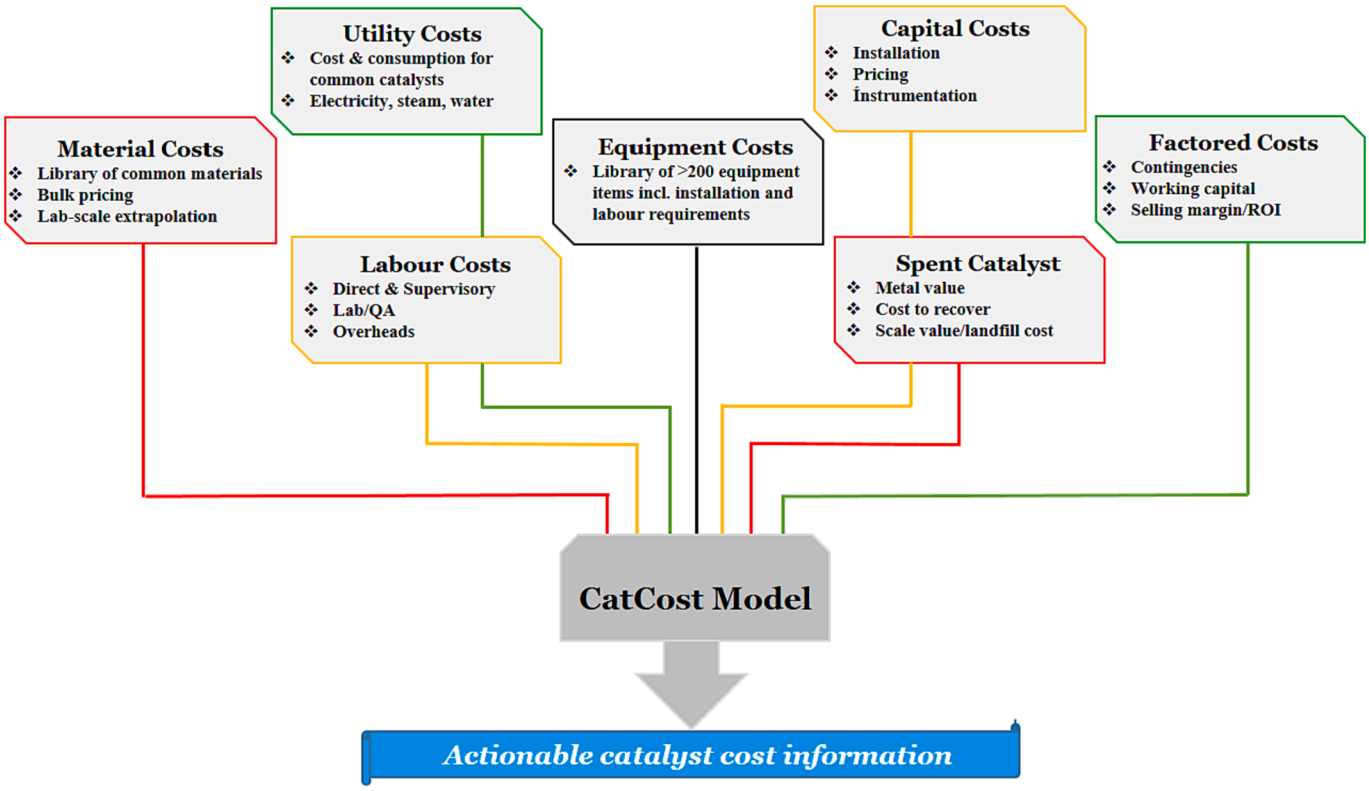

Fig. 2. Catcost Model components for catalyst cost estimation.

employed to evaluate the change in equipment costs when scaling up from the reference sizes provided by NREL [36]. Installation factors similar to NREL TP 47764 were applied. Equipment costs were adjusted for inflation by increasing them by an average of 1.5 % (the average annual inflation rate for equipment over the past ten years) to 2023 values. The installation variables from NREL Technical Paper 47764 were used to calculate the installed capital costs according to [2,36,37].

2.4. LCA methodology

The LCA Methodology involved calculating the life-cycle greenhouse gas (GHG) emissions for producing 1 MJ of hydrocarbons from corn starch and corn stover using current and advanced conversion technologies. The Argonne National Laboratory developed the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model with funding from the Office of Energy Efficiency and Renewable Energy in the US Department of Energy, which was applied for this purpose. The GREET model also provided results for producing conventional gasoline fuel from fossil sources. In addition, the life-cycle GHG emissions of ethanol synthesis from cane juice and cane cellulose in Brazil were evaluated according to [2]. This encompasses various aspects, including farming activities, feedstock collection and transportation, and ethanol manufacturing. The second section of the investigation focused on converting ethanol to hydrocarbons, covering catalytic operations, product recovery, and HC transportation, distribution, and storage. The end-of-life combustion of the CADO product, specifically for gasoline fuel, was also included in the system boundary. More detailed information about the LCA inputs can be found in the supplementary information. LCA input details are shown in SI, Table 5a-d.

3. Results and discussion

3.1. CADO-ETH conversion result

Fig. 3a presents the result for the CADO-ETH, along with the phase selectivity of the catalyst for gaseous and liquid products for the first and second (after catalyst regeneration) cycles. The primary liquid products included aromatics (BTX: benzene, toluene and xylenes), C_5 + hydrocarbons (C_5-C_{12} – gasoline blendstock consisting of gasoline range HCs (GRH) and C_{10}-C_{20} – diesel fuel blendstock consisting of diesel range HCs (DRH)), and their selectivity changed over time. The NiZ catalyst from the first cycle showed appreciable stability but experienced a decrease in ethanol conversion after 48 h on stream. The Ni-doped catalyst (NiZ) recorded a gradual reduction in ETH conversion from its initial value of 100 % to 62.4 % after 40 h on stream. This decrease in conversion can be attributed to increased oligomerisation of ethylene resulting from the early stages of ethanol dehydration reaction [38]. Additionally, the selectivities of the NiZ catalyst towards C_5-C_{12} and BTX declined after 32 and 40 h on stream, respectively, shifting towards selectivity for C_{10}-C_{20}. However, the ETH conversion rate gradually increased and reached approximately 100 % after 56 h on stream, followed by a decrease of 39.5 % after 80 h. After 64 h on stream, the selectivity towards GRH exhibited a significant increase, likely due to the weakening of acid sites during deactivation. Gaseous hydrocarbons (C_1-C_4) decreased with increasing time on stream, particularly after 64 h for the catalyst. The NiZ recorded the highest selectivity for C_5-C_{12} (89.9 %), BTX (10.6 %), and C_{10}-C_{20} (21.8 %) at 72, 88, and 96 h on stream. NiZ demonstrated significant average selectivity towards C_5-C_{12} (79.2 %) and C_{10}-C_{20} (7.4 %), BTX (4.5 %).

Following NiZ deactivation after the initial cycle, the catalysts underwent a five-hour regeneration process at 550 °C, with an airflow rate of 80 mL/min. The regenerated catalyst is denoted NiZ/R. The results of the regeneration procedure indicated an improvement in the catalytic performance of the used and deactivated catalysts. After regeneration

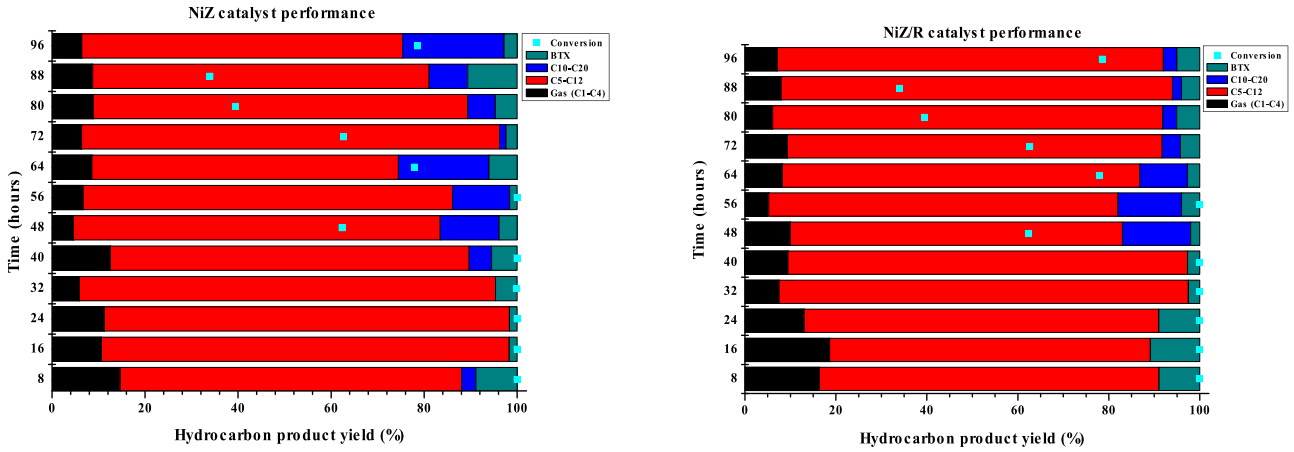

Fig. 3. a & b. Product distribution (GRH, DRH, & BTX) of NiZ and regenerated catalyst (NiZ/R).

following deactivation, the NiZ/R catalyst exhibited enhanced catalytic activity, like the behaviour observed with the deactivated catalyst. These findings align with previous studies by Yung, et al. [39]. The NiZ/R catalyst, like the fresh catalyst, maintained a consistent CADO-ETH conversion of around 100 % up to 48 h on stream. However, after that point, a drop to 60.6 % was observed, followed by a progressive decline after 56 h on stream (Fig. 3b). In contrast to the pure catalyst, the NiZ/R catalyst showed an increase in the synthesis of GRH, resulting in a decrease in selectivity towards DRH fractions. With an increase in time on stream (TOS), the selectivity of the regenerated catalyst exhibited a significant decrease in their ability to favour gaseous HCs. The regeneration and application of regenerated catalysts demonstrated that they retained their catalytic activity after the regeneration cycle. This indicates that the catalyst did not undergo irreversible dealumination during the extended TOS required for the CADO-ETH process [40,41]. The product distribution analysis of the second cycle CADO-ETH conversion demonstrated that the regenerated catalyst displayed comparable catalytic performance to NiZ, exhibiting a significant preference for GRH (80.7 %) over DRH (4.3 %) and BTX (5.1 %). This discovery aligns with the product distribution observed in the first cycle. Table 1 shows the average distribution of products (major and minor products) from the CADO-ETH conversion, while the reaction pathway of the processes involved in the CADO-ETH conversion is shown in Fig. 4.

3.2. Cost estimation of catalyst using CatCost

The cost estimation of catalysts was efficiently carried out using CatCost, available as a spreadsheet or web-based application that can be easily launched in any modern web browser. Both versions of CatCost can be downloaded from the website https://catcost.chemcatbio.org. The tool is designed with modular components encompassing the essential aspects of catalyst cost analysis. The web-based software and the spreadsheet version of CatCost follow a similar workflow, ensuring consistency in the estimation process. In CatCost, various inputs are considered, including the pricing year, the unit for mass calculations (e.g., US$ per kilogram of catalyst), raw material costs, processing costs, the value of the spent catalyst, and desired outputs. The module in CatCost dedicated to managing raw material expenses plays a crucial role as they typically constitute a significant portion of the total catalyst cost. This module allows easy and quick entry of synthesis recipes from laboratory notebooks or publications. It features automated unit conversions, synthesis yield calculations, and the ability to query libraries for relevant information. Additionally, CatCost enables manual entry of raw material prices and provides guidance on obtaining appropriate pricing information for bulk quantities (above 1,000 kg). It provides access to various price databases, including free options (e.g., Alibaba), proprietary resources (e.g., IHS Process Economics Programme), vendor websites, and quotes. CatCost employs log–log extrapolation techniques, as described by [42], for smaller purchasing sizes based on laboratory chemical suppliers' prices. Furthermore, CatCost incorporates a built-in library with freely available data on price trends for different items. Lastly, the tool includes a component to account for inevitable losses of raw materials during production due to spoilage and waste. With its comprehensive functionality, CatCost simplifies and streamlines the estimation of catalyst costs, making it a valuable resource for cost analysis in research and development endeavours.

3.2.1. Effects of scale on the cost of the catalyst

The cost of (Ni/HZSM-5) catalyst in a process plant is significantly influenced by the amount of catalyst purchased. It is expected that an increase in production scale (using the baseline catalyst requirement) and purchasing will result in cost savings due to economies of scale and

Table 1
Average yield of ethanol conversion to gasoline blendstock and other products over NiZ & NiZ/R catalysts (operating conditions: WHSV – 7 h^{-1} and T – 350 °C).

TOS	Gas (%)	Gasoline blendstock (%)	Diesel blendstock (%)	Aromatics (BTX) (%)	Conversion (%)	Liquid HCs (%)
8	15.5	74.0	1.5	8.9	100	84.5
16	14.6	79.1	0	6.3	100	85.4
24	12.2	82.5	0	5.3	100	87.8
32	6.7	89.7	0	3.6	99.9	93.3
40	11.0	82.5	2.4	4.1	100	89.0
48	7.3	75.9	13.8	2.9	62.4	92.7
56	6.0	78.1	13.1	2.8	100	94.0
64	8.4	72.3	15.0	4.4	77.9	91,6
72	7.8	86.2	2.7	3.3	62.6	92,2
80	7.5	83.1	4.5	4.9	39.5	92,5
88	8.3	79.2	5.2	7.3	34.0	91,6
96	6.8	76.9	12.4	3.9	78.6	93,2

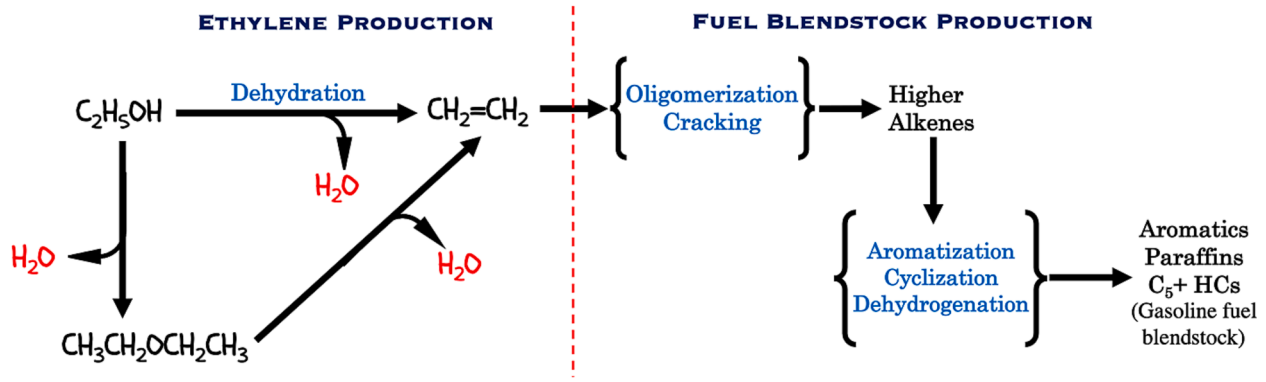

Fig. 4. Reaction pathway showing the various processes involved in CADO-ETH conversion.

volume purchasing. Although this is a well-known assumption, there are few tools available to researchers to measure the impact of scale on catalyst costs. CatCost addresses this using its built-in scaling logic, which adjusts catalyst cost estimates based on the entered production scale. This automatic adjustment includes modifying equipment sizes and quantities to ensure they remain within the valid range for each cost estimate function. Equipment with unit sizes below the lower limit is priced based on its minimum size, while equipment with unit sizes above the upper limit has its quantity increased until the unit size falls within the range. ZSM-5 may be relatively expensive per GGE (gallon of gasoline equivalent) due to its higher utilisation rate than next-generation catalysts. The costs displayed in Fig. 5a represent the net costs

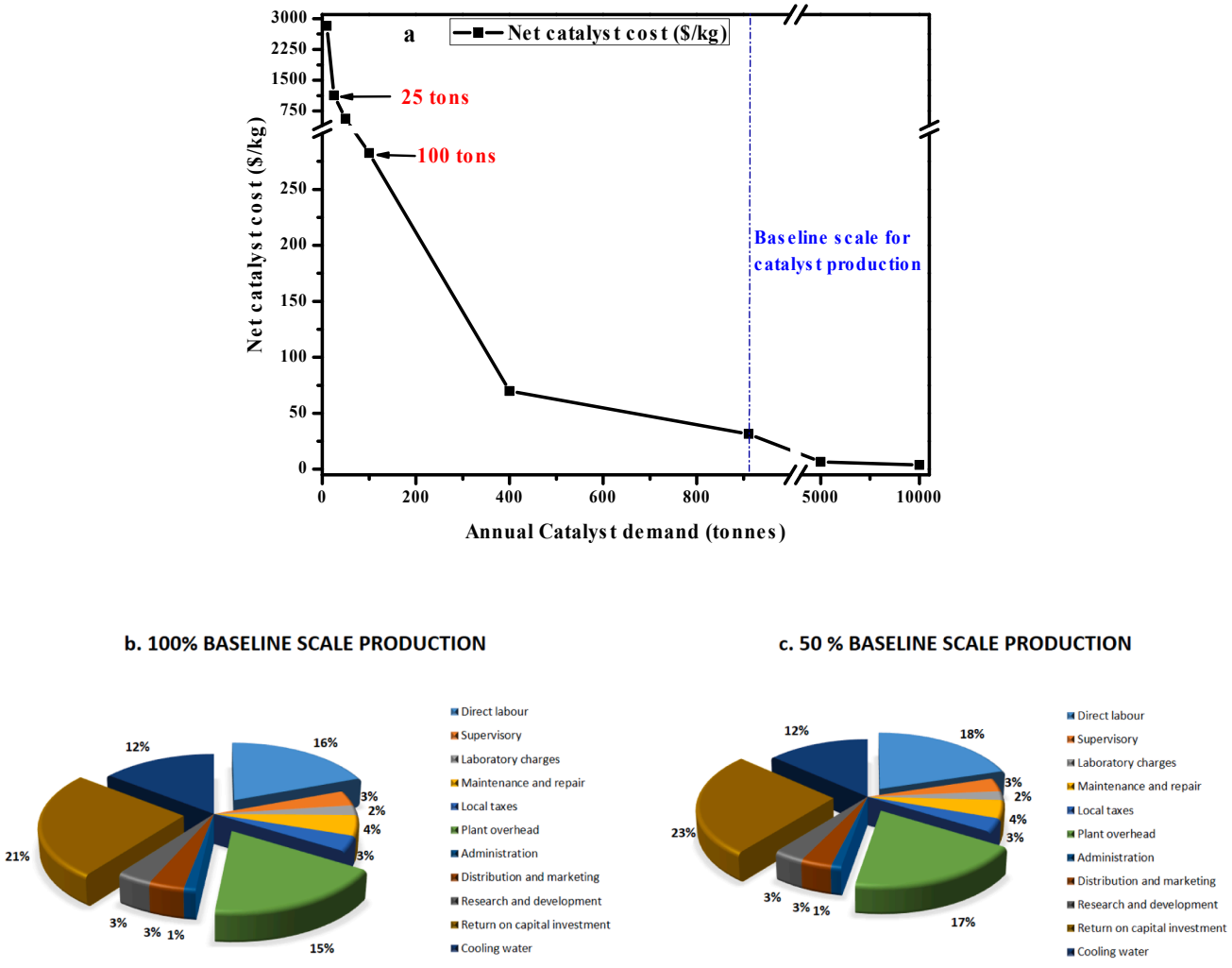

Fig. 5. (a) Effect of scale on net cost of catalyst. Cost estimated from the CatCost model, (b & c). Catalyst purchase cost breakdown for 100 and 50 % BSP using CapEx and OpEx method.

associated with the catalyst, including the projected SCVs (scaleup costs) for the Ni/HZSM-5 catalyst. Discrepancies in price may be observed when compared to reducing the scale of production (for instance, 50 % of baseline scale production (BSP) requirement) showed an increase in net catalyst cost from $31.42/kg to $69.96/kg ($31.31/kg and $69.85/kg after deducting the projected SCVs) (SI, Figs. 1j & k) which can also be attributed to jumps between synthesis scales, primarily due to contract manufacturers having equipment at predetermined scales. In practice, these discrepancies would likely be smoothed out by mixing equipment with varying scales and making discretionary adjustments to the selling margin. According to the data presented in Table 2, the cost of catalysts obtained from the current study is comparable to that of commercial vendors for large-volume production. This finding demonstrates the efficiency of purchasing from a contract manufacturer when catalysts are required in smaller quantities, i.e., less than a few kilotons per year. In this case, the contract manufacturer is responsible for procuring the necessary raw materials and managing all aspects of capital and operating costs, waste disposal, and related activities according to the buyer's requirements. A study conducted by Baddour, et al. [43] found that estimating the cost of catalysts synthesised by a contract manufacturer using an all-in hourly cost method for specific equipment yielded results that were within 20 % of market prices for various catalyst materials. On the other hand, catalysts that are produced in large quantities, such as fluid catalytic cracking catalysts (with a global production volume of 650 kilotons) [6], and those that must meet standardised specifications, are typically produced in dedicated facilities. A comparison of catalyst costs with commercial vendors is presented in Table 2. Fig. 5b & c illustrates how the components of catalyst purchase cost, including direct labour, overhead, maintenance, and repair, change as materials progress through two distinct purchasing scales. This is consistent with the study by [6]. The tabular representation of this information can be found in the SI, Table 1.

When investigating the influence of scale on CADO catalysts using CatCost, significant discrepancies are observed among different material types. The intricate and resource-intensive synthesis process of the Ni/HZSM-5 catalyst means that its net cost depends to a considerable extent on the purchasing scale, as shown in Fig. 5a. The scale-dependent cost breakdown shown in Fig. 5b & c reveals that processing costs dominate at 50 % BSP due to their proportionality with the amount of Ni/HZSM-5 produced compared to 100 % BSP. This aligns with the high-consumption, low-cost approach to catalysts in recirculating bed applications, where Ni/HZSM-5 has a relatively lower contribution from raw materials cost. It is evident that in the case of 100 % BSP of catalyst, processing and overhead costs decrease proportionally with increasing scale (compared to 50 % BSP), making raw materials the primary targets for additional cost reduction at larger production scales. This is further explained by the Donut chart in SI, Fig. 2a $ b. The findings of this study showed that the cost of the catalyst and its components are significantly influenced by the operation's magnitude, material type and application. By examining cost and impact, catalyst developers can identify the primary cost factors that offer the most significant opportunities for targeted research and development. CatCost web-based application provides interactive visualisations of catalyst cost to facilitate the decision-making process in R&D. These visualisations offer more detailed breakdowns than shown in Fig. 5b & c. As demonstrated in Fig. 6 using CatCost-generated Sankey diagrams, the cost breakdowns for Ni/ZSM-5 catalysts exhibit a balanced composition, unlike other catalysts in that a single material may dominate cost contributor (*SI, Fig. 3* presents the Sankey plot for the 50 % BSP). The well-balanced cost breakdown for Ni/HZSM-5 reflects its status as an established, commercially available material that has undergone optimisation throughout the scaleup process to minimise costs. Consequently, Ni-doped HZSM-5 may exhibit a lower total cost compared to other materials. Overall, understanding the effects of scale on catalyst costs and identifying the significant cost factors contribute to informed decision-making and optimisation in catalyst development and purchasing.

Table 2
Price comparison (present study and commercial vendors).

Catalysts	Price ($/kg)	Vendor	Source
Ni/HZSM-5 (1000 tons)	28.7	Present study	Present study
Ni/HZSM-5 (100 % BSP)	31.4		
Ni/HZSM-5 (50 % BSP)	69.9		
Ni/HZSM-5 (25 % BSP)	121.5		
ZSM-5	40	Made in China	https://pingxiangnaike.en.made-in-china.com/product/zdCTiOXGrLRK/China-Zeolite-Zsm-5-Used-for-Hydrocarbon-Interconversion.html
ZSM-5	25–30	Alibaba	https://www.alibaba.com/product-detail/Hot-Sale-Synthetic-Zeolite-ZSM-5_1600449192511.html?spm=a2700.7724857.0.0.4ac97f55SF3Iq4
ZSM-5	50–200	Alibaba	https://www.alibaba.com/product-detail/ZSM-5-zeolite-for-FCC-catalyst_62208192183.html?spm=a2700.7724857.0.0.4ac97f55SF3Iq4

3.2.2. Sensitivity analysis

Sensitivity analysis is crucial in evaluating the ambiguity associated with catalyst costs. It goes beyond simple cost analysis and provides valuable insights into the risks and rewards involved for catalyst researchers. CatCost offers a quantitative approach for analysing the impact of various input variables, providing developers with valuable information. In Fig. 7, a tornado plot visually depicts the influence of different cost inputs on the net cost of producing Ni/HZSM-5 in a dedicated factory. A combination of literature resources and price surveys was utilised to determine the high and low inputs for each category. This approach ensured accurate identification of the upper and lower bounds of the inputs. As previously demonstrated (Fig. 6), the production scale and raw material prices have the greatest impact on cost uncertainty, which is unsurprising given that the precursor cost contributes significantly to the total catalyst purchasing cost at this scale. Figure 7 further highlights some intermediate contributors to the uncertainty. These include the utilisation and pricing of process gas, the number of direct labour operators in the production facility (indicating the potential for process intensification), the capacity factor (accounting for planned vs actual productivity discrepancies), and the factor for distribution and marketing charges. Additionally, several minor factors have a smaller impact on catalyst cost, each affecting it by <$3/kg. These factors include synthesis yield, metal losses during catalyst use and refining, utility expenses, and various capital and operational expenditures components. SI, Fig. S4 and S5a-c present a Tornado plot for 50 % BSP and a detailed breakdown of the Tornado plot for 100 % BSP. CatCost, as a web-based application, incorporates sensitivity analysis to assist researchers in identifying the areas of the manufacturing process, materials, and market factors that provide the greatest potential for future advancement. Sensitivity analysis plays a crucial role in evaluating cost ambiguity associated with catalysts. CatCost provides researchers and catalyst manufacturers with a comprehensive tool to quantitatively assess the impact of different inputs, facilitate informed decision making and identify areas for cost optimisation and process improvement in large-scale production.

However, the transition from laboratory to industrial catalyst production is crucial but complex. The physicochemical properties of a catalyst, such as surface area and porosity, can vary during scaling, affecting performance and requiring recalibrations. Heat and mass transfer issues, such as hotspots and mixing problems, are common at industrial scale due to differences in transport phenomena. Economic

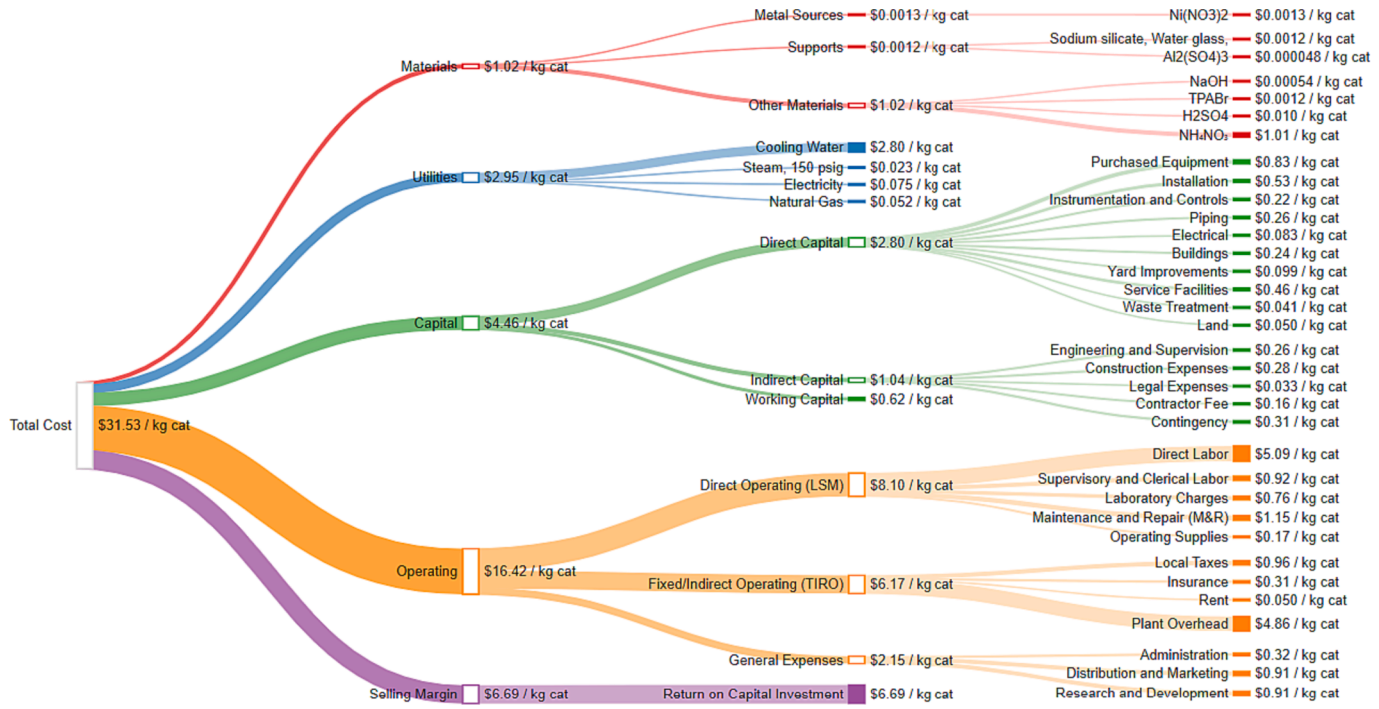

Fig. 6. Sankey diagram for catalyst cost showing a detailed breakdown of contributors to the net catalyst cost (purchase cost) for Ni/HZSM-5 catalyst Lines and width correlate to the cost contribution. The Sankey diagram is an example of visualisation in the Catcost web-based software version. LSM – Laboratory supplies and maintenance; TIRO – Taxes insurance, rent and overhead.

and environmental concerns, including rising costs, emissions management and the challenge of maintaining efficiency on a larger scale, present significant hurdles. Reproducing laboratory results on an industrial scale is a major challenge, as introduced variables can affect the behaviour of catalysts in unpredictable ways. Overcoming the challenges of scaling up catalysts requires a comprehensive strategy that integrates technology, expertise and innovation. Proven tactics include pilot-scale testing that provides insights and minimises errors during full-scale production. Advanced simulation and modeling predict challenges and reduce the trial-and-error approach. Continuous monitoring and feedback loops ensure efficiency and product quality. The implementation of safety and environmental protocols mitigates the risks associated with handling larger quantities of materials [44].

3.3. CADO-ETH – conversion of wet ethanol to anhydrous ethanol and fuel blendstocks

In an industrial facility that produces ethanol, a beer column separates the ethanol-containing broth from fermentation into wet ethanol vapour, water, and any solid residues (Fig. 8). For this analysis, we assume a second-generation ethanol production process (wet vapour concentration of 40 wt%, equivalent to a liquid feed concentration of 6.4 wt%, i.e. 8.1 vol% by volume). The sensitivity of cost estimates varies for the two processes being examined. For the conversion of wet ethanol vapour to anhydrous ethanol (referred to as CADO), the impact on capital costs (CapEx) is expected to be low, while to produce anhydrous ethanol from 40 % ethanol vapour, both operating costs (OpEx) and capital costs (CapEx), especially for distillation steam, are affected. Both processes involve ethanol, and we will analyse the costs associated with each conversion pathway. The comparison is based on the process configurations shown in Fig. 8. It assumes an annual ethanol production rate of 61 million gallons (231 million litres), typical for small ethanol plants in the US and Brazil [2]. This production rate was used in the TEA conducted by the NREL for cellulosic ethanol production. In producing anhydrous ethanol, the wet ethanol vapour undergoes rectification in a column, followed by molecular sieve dehydration. On the other hand, the CADO process involves introducing moist ethanol vapour into a catalytic reactor, where it is converted into liquid hydrocarbons, light gases (excluding ethylene), and water. This mixture is then cooled to the ambient temperature and passed through a three-phase separator. Water is separated from the bottom, less dense liquid HCs are extracted from the middle, and incompressible gases are collected from the top. Most of the gas, approximately 73 % by mass, is burned to reduce the demand for natural gas in the process heat, while the remaining gas is recycled back into the reactor to be converted into liquid fuels [2].

3.3.1. Economics of CADO-ETH process

The estimation of manufacturing fuel-grade hydrocarbons from moist ethanol vapour is based on the NREL model from 2011 [36]. Given that stoichiometric yields, market prices, and price supports are comparable for gasoline, aviation fuel, and diesel (as shown in SI, Table S2), this analysis is presented in relation to HC fuel blendstocks. Costs associated with the operation of the process can be found in the SI. The current and future catalyst purchase prices for converting wet ethanol into fuel blendstocks are estimated at $70/kg and $31.42/kg, respectively (SI, Table S3*a* & *b*). These prices were determined using the NREL catalyst cost estimator, CatCost, and compared and verified through consultation with a commercial catalyst manufacturer [45]. The lifespan of the catalysts is expected to be 6 months for laboratory powder and pilot pellets catalysts, and this is extended to 9 months for present commercial catalysts and future catalysts, based on extrapolation estimates from 200-hour ageing investigations, according to [2]. Conducting studies on ageing over longer periods would enhance these estimates' reliability. The electricity cost was $0.05/kWh, which is a typical rate for the midwestern region of the US [2]. Approximately 60 % of the operating expenses can be attributed to replacing catalysts and energy consumption. Additionally, the use of chemical wastewater treatment additives for removing dissolved hydrocarbons results in an additional cost of $1.85 per 1,000 L of treated water, which is considered. The cost of returning used catalysts to the provider is factored into the overall cost of catalyst disposal, with a unit cost of $2,000 per tonne of catalyst. For consistency with the NREL anhydrous ethanol model

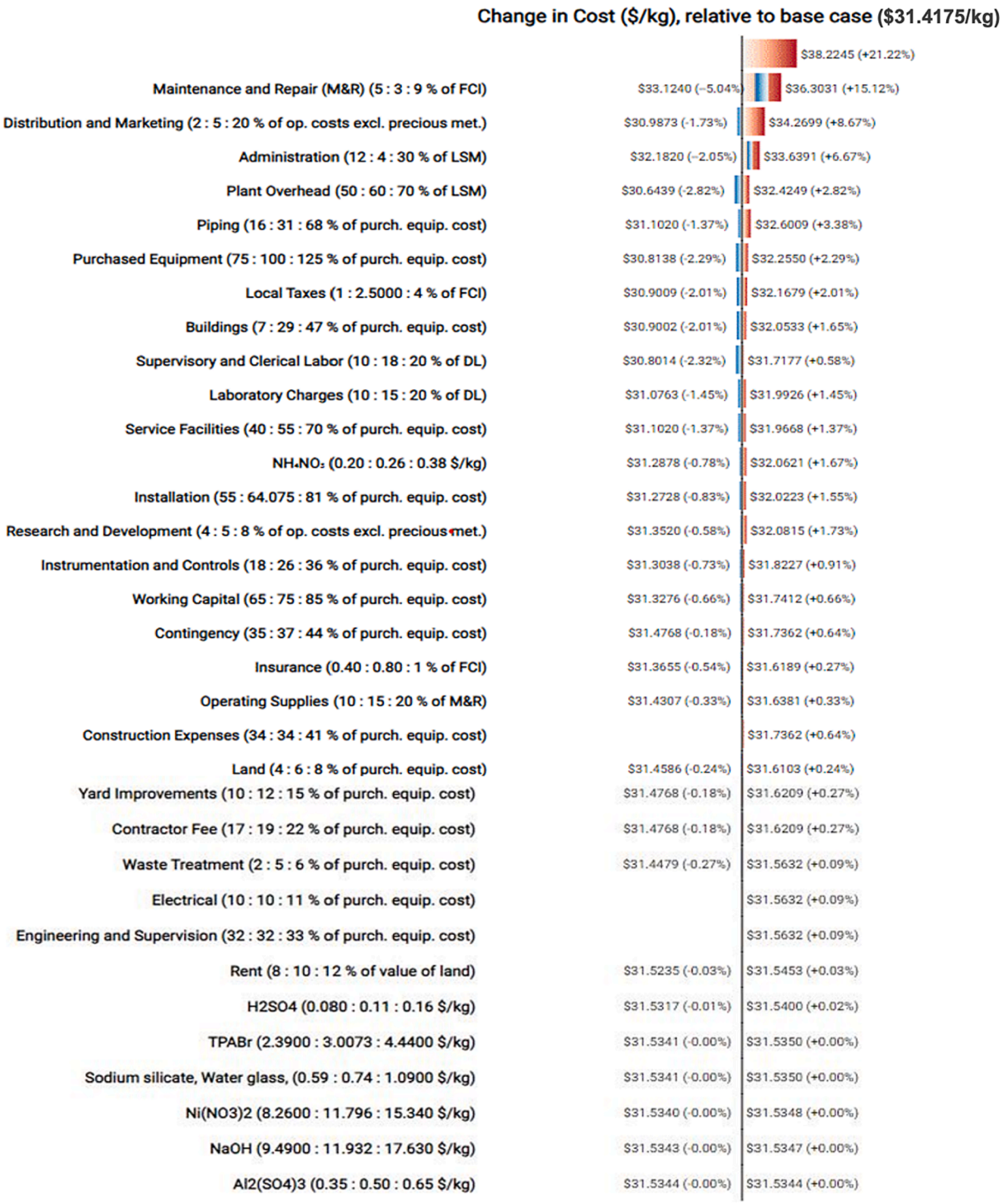

Fig. 7. Sensitivity analysis results are illustrated in a tornado plot, depicting the impact of crucial input variables on the net catalyst cost for Ni/HZSM-5 in a dedicated plant operating at an annual production scale of 911 tons (100% BSP). This scale aligns with the biorefinery baseline of processing 2,000 dry tonnes of biomass per day. SI, Fig. 4 presents the tornado plot for 50 % BSP.

[36], insurance, taxes, and maintenance costs are included. It is anticipated that the labour requirements for converting blendstocks to ethanol will be similar to those for ethanol dehydration, as the unit operations involved are of similar complexity. Despite the unlikely need for additional personnel, the labour cost is accounted for, and the labour costs are comparable in SI, Table S3b & c. The capital costs are presented in SI, Table S3d. The NREL model is converted to 2023 dollars, according to [2], resulting in an estimated capital expenditure of $25.14 million for manufacturing anhydrous ethanol from wet ethanol vapour. To annualise the expenses related to capital expenditures, they are multiplied by 0.18 (average inflation rate for the past 10 years), adjusted value for inflation (0.03 increase from 2019 [2]), representing a 10-year amortisation period with a 12 % interest rate. Following this approach, the annualised cost of capital contributes $0.037/L of anhydrous ethanol, equivalent to a reduction of $1.74 per gigajoule (GJ) lower heating value (LHV).

The key equipment required to produce fuel blendstocks from wet ethanol vapour in the CADO process includes two catalytic reactors to

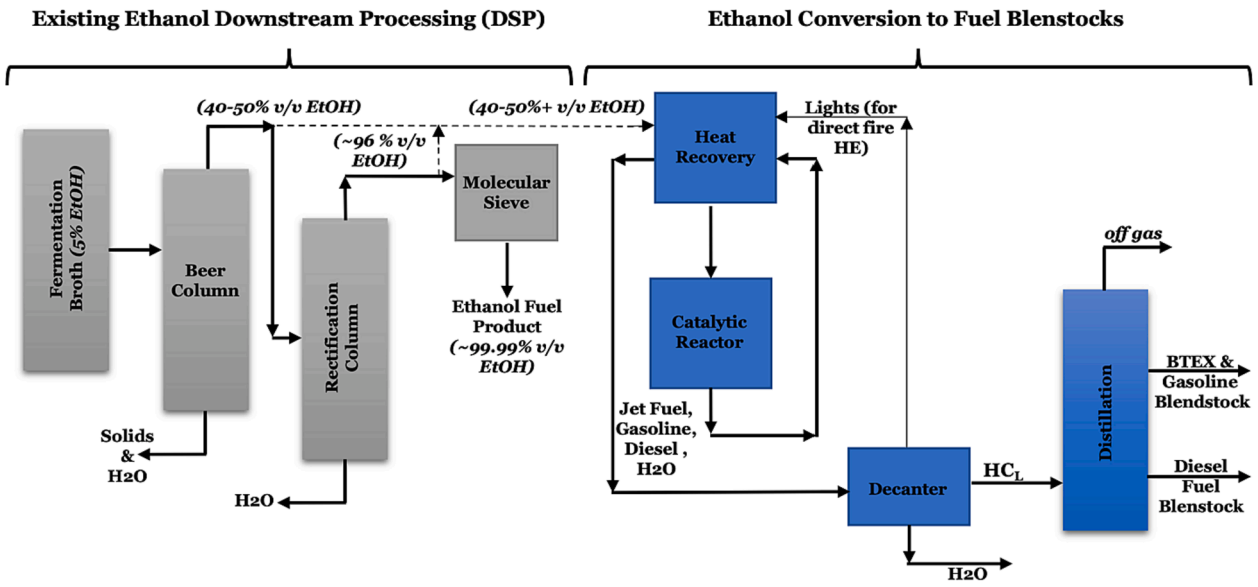

Fig. 8. Catalytic conversion of bioethanol to fuel blendstocks via CADO-ETH.

allow for catalyst regeneration, a three-phase decanter, four heat exchangers, pumps, and load-out systems. It is assumed that the storage tank requirements for fuel blendstock and H_2O-product are the same as those for ethanol. The dissolved hydrocarbons remaining in the H_2O after decanting are typically between 600 and 1,500 ppm and are removed and transferred to wastewater treatment [2]. A compressor is installed to generate the required pressure of 0.417 MPa for moving wet ethanol through the reactor, and another compressor is used for gas recycling. It should be noted that compressors may not be necessary if distillation is performed under pressure. Although including a compressor in the design is precautionary, a back pressure-controlled flash system may be used in practice for a Greenfield facility. The anticipated total installed capital expenditure is approximately $18.1 million ($15.3 million in 2019), equivalent to $0.079 per litre of ethanol feed or $0.143 per litre of fuel blendstocks (~15.5 % increase compared to the cost in 2019 attributed to the 0.03 % increase in average inflation for the past 10 years). It is assumed that the CADO processing capital expenditures will remain consistent regardless of the underlying technology. Applying the same capital recovery factor of 0.18 to anhydrous ethanol, the annualised cost contribution for ethanol transformation to fuel blendstocks via CADO is estimated at $0.022 per litre ($1.03/GJ LHV). With expected advancements in the future, the overall expenses associated with producing fuel blendstock from wet ethanol vapour using CADO technology are expected to be ~3 % away from the costs involved in ethanol distillation and dehydration to meet fuel grade standards [2,5].

3.3.2. *Comparative Evaluation of CADO-ETH using feedstock from different sources*

We conducted a comprehensive economic analysis to evaluate the competitiveness of producing fuel blendstocks using both current and projected CADO-ETH technologies. These technologies utilise ethanol derived from corn (from the US) and sugar cane juice (from Brazil) through present and future cellulose conversion techniques, including the combined conversion of sugar cane juice and cellulosic feedstocks like bagasse and leaves. Fig. 9a showed global ethanol production from 2007 to 2023 (projected) from different sources: corn (US), sugarcane (Brazil) and sugar beet (EU), while Fig. 9b showed a comparison of costs between ethanol (corn and sugarcane), and gasoline, covering the period from 2007 to 2023. With a significant global production, it is evident that there is a readily available and sustainable supply of ethanol feedstock for CADO-ETH, indicating the feasibility of producing ethanol from these feedstocks. To determine the projected costs of ethanol production, we considered estimates of operating expenses obtained from reliable sources and an annualised capital cost derived by multiplying the total capital by 0.18, as mentioned earlier. Although most corn ethanol plants in the US have fully amortised their investments, we used average feedstock prices and treated the processes as new facilities. This approach was necessary due to the unpredictable nature of biomass feedstock pricing, particularly in the case of corn. The

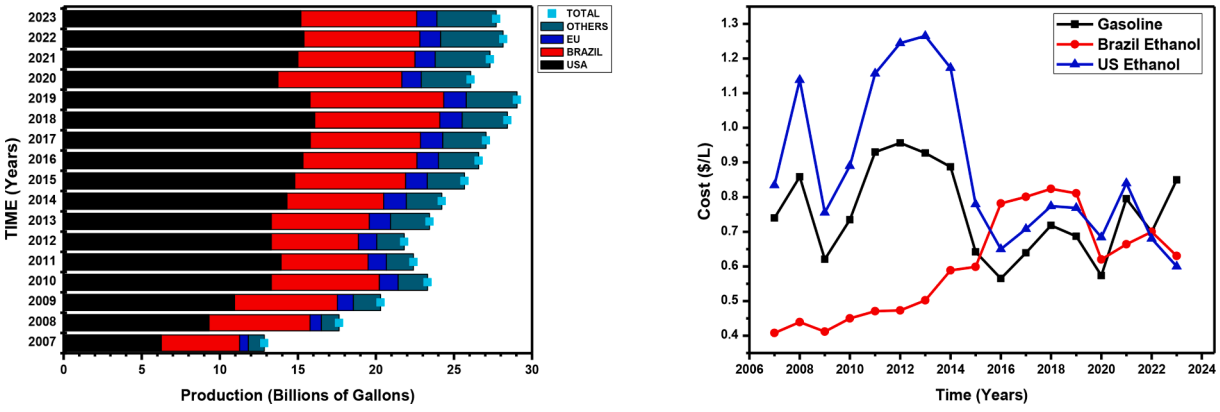

Fig. 9. (a). Global EtOH production (2007–2023), (b). Cost comparison between (corn and sugarcane) EtOH and gasoline (2007–Jan 2023).

costs associated with producing 40 % ethanol vapour, as outlined in SI, Table 3*c*, were calculated by subtracting the costs of distillation and dehydration from the overall cost of producing fuel-grade ethanol, according to [2]. The cost of ethanol, the mass yield of blendstock fuel per unit of ethanol, and the conversion cost from ethanol to fuel blendstocks were considered in determining the minimum blendstock product selling price (MBSP). The MBSP was compared to the historical wholesale pricing of gasoline fuel when the price of petroleum ranged from $60 to $100/bbl. Our analysis revealed that the price of gasoline fuel from CADO-ETH is higher than that of petroleum on a volumetric basis. For instance, when the wholesale oil price was $75 per barrel, the wholesale gasoline fuel price was $2.64/gal, representing a ~10.3 % lower than the price of gasoline fuel ($2.95/gal). This finding is consistent with the research conducted by [2], which reveals that the cost of hydrocarbon fuel derived from ethanol is higher (~19 %) compared to that obtained from petroleum. At a crude oil price of $100/bbl, the conversion of ethanol to gasoline (ETG) can be competitive across various ethanol production platforms, including current cane sugar (Table 3). However, without some form of price support and government subsidy, it is not economically viable at lower oil prices.

3.4. Life Cycle Analysis (LCA) of CADO-ETH technology

Figure 10a provide a comprehensive breakdown of GHG emissions throughout the entire life cycle, from well-to-wheel, for the synthesis of ethanol using CADO from different feedstocks such as corn, cane sugar, corn stover, and cane cellulosic material, while Fig. 10b represents the life cycle analysis for the conversion of petroleum to gasoline. The CO_2 emission, well-to-wheel, WTW (which comprises of wheel-to-pump, WTP and pump-to-wheel, PTW) result from these processes in Figs. 10a & b is presented in Table 4. When ethanol is generated using "first-generation" techniques that employ easily fermentable feedstocks and established technology, overall GHG emissions for gasoline fuel production (used as a reference) are reduced by 25 % for corn starch ethanol and 53 % for sugarcane juice ethanol. These reductions highlight the environmental benefits of ethanol produced through "first-generation" technologies. The combined conversion of sugarcane juice and cellulosic material, utilising current or future CADO technologies, leads to appreciable emissions reductions of approximately 63 %. Compared to ethanol produced through "second-generation" processes involving lignocellulosic conversion using emerging technologies, these numbers show a favourable outcome. It is worth noting that applying CADO to corn starch ethanol results in slightly higher greenhouse gas emissions compared to sugar cane ethanol. This discrepancy arises from the lower emissions associated with farming sugar cane and the ability to utilise lignin for steam and electricity generation in CADO. On the other hand, CADO applied to corn starch ethanol depends on fossil energy. The credit included in Table 4 (specifically 73 gCO_2 e/MJ for HC fuel in this scenario) to account for the CO_2 recaptured through the growth of new plants (biogenic carbon) had a notable effect on maintaining low life cycle GHG emissions for fuels derived from biomass, in contrast to fuels produced from fossil sources. The ethanol conversion values presented in Table 4 were computed using the default information from the Greenhouse gases, Regulated Emissions, and Energy usage in Transportation (GREET) model for corn-based scenarios [49] and the Virtual Sugarcane Biorefinery for sugarcane-based scenarios [50–52]. However, adjustments were made to account for the energy savings from using 40 % ethanol as the feedstock for CADO instead of anhydrous ethanol. Specifically, credits were given for eliminating the energy required for distillation when producing anhydrous ethanol from 40 % ethanol. This elimination of energy corresponds to 25 GJ/h (23.5 MMBtu/h, 0.0016 GJ/L) of natural gas and 2.6 GJ/h (710 kW, 0.00017 GJ/L) of electricity [2].

According to Hannon, et al. [2], biomass conversion into ethanol through fermentation and the subsequent catalytic conversion into hydrocarbon blendstocks using a dehydration mechanism (CADO) achieve considerable energy efficiencies. Combined, the overall energy efficiency exceeds 93 % when these two steps are combined. The potential for high energy efficiency has been demonstrated in practice [2]. However, the primary challenge lies in addressing the cost aspect. Previous studies estimated that a three-step process would increase the cost of ethanol by $3.38 to $7.98 per gigajoule [47,56]. In contrast, in its current state of development, the CADO technology described in this article is projected to increase the cost of ethanol. It is expected to incur no additional cost compared to anhydrous ethanol in the future. When comparing the selling prices of ethanol produced by existing and expected techniques, including both 1G and 2G biomass feedstocks, to the selling price of petroleum-derived gasoline fuel, the prices are approximately equal to or greater than gasoline fuel on a USD/GJ basis. This holds regardless of whether 1G or 2G feedstocks are used. Therefore, even with high efficiency and low conversion costs, the selling price of gasoline or diesel fuel derived from ethanol will at most be equal to or slightly higher than conventional gasoline fuel due to varying operating costs demonstrated by these two processes. The production of fuel

Table 3
Approximate operating and annualised capital costs associated with fuel blendstocks produced by CADO-ETH using ethanol derived from various sources.

Biomass Feedstocks	Technological Maturity		Ethanol Selling price ($/L)	Ethanol to Gasoline (ETG) conversion			MBSL ($/L)		
							From ethanol: Market[¤]	From petroleum[§]	
	Ethanol Production	Ethanol to Blendstock	5 y: 2018–2023 & (Current: (MESP))	Yield (L blend/ L ethanol)	Cost ($/L blend) 2019	Cost ($/L blend) current[*]	5y and Current price	5y ($64/bbl): 2018–2023 & (Current ($75/bbl))	$100/bbl
Corn starch (1G) [‡]	Current	Current	0.55 (0.37)	0.487	0.065	0.077	1.17 (0.78)	0.54 (0.70)	1.28
		Projected	0.55 (0.37)				1.17 (0.78)		
Sugar cane (1G) [‡]	Current	Current	0.60 (0.48)	0.548	0.065	0.077	1.25 (1.00)		
		Projected	0.60 (0.48)	0.487					
SCB (2G)[†]	Current	Current	–	0.487		0.077			
	Projected	Projected		0.548		0.055			

https://www.macrotrends.net/1369/crude-oil-price-history-charthttps://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=pet&s=f000000_3&f=m.

[‡] 1G: First-generation corn starch and sugarcane prices are based on average market values over the past 5 y [46]. MESP EtOH price based on [2] (inflated by 1.8 % average inflation to obtain 2023$).

[†] 2G: Second-generation sugarcane bagasse (SCB) (estimate of MESP from respective sources updated to 2023$ [2,47]. OpEx includes feedstock and co-products. Sugarcane (current and projected) [2,36].

[*] Conversion costs from SI, Table S3a & b, plus annualized capital costs.

[§] HC price from fossil fuel based on oil cost/L. Adapted from Energy Information Administration (EIA) [48].

[¤] HC price from EtOH based on MESP/yield + conversion cost.

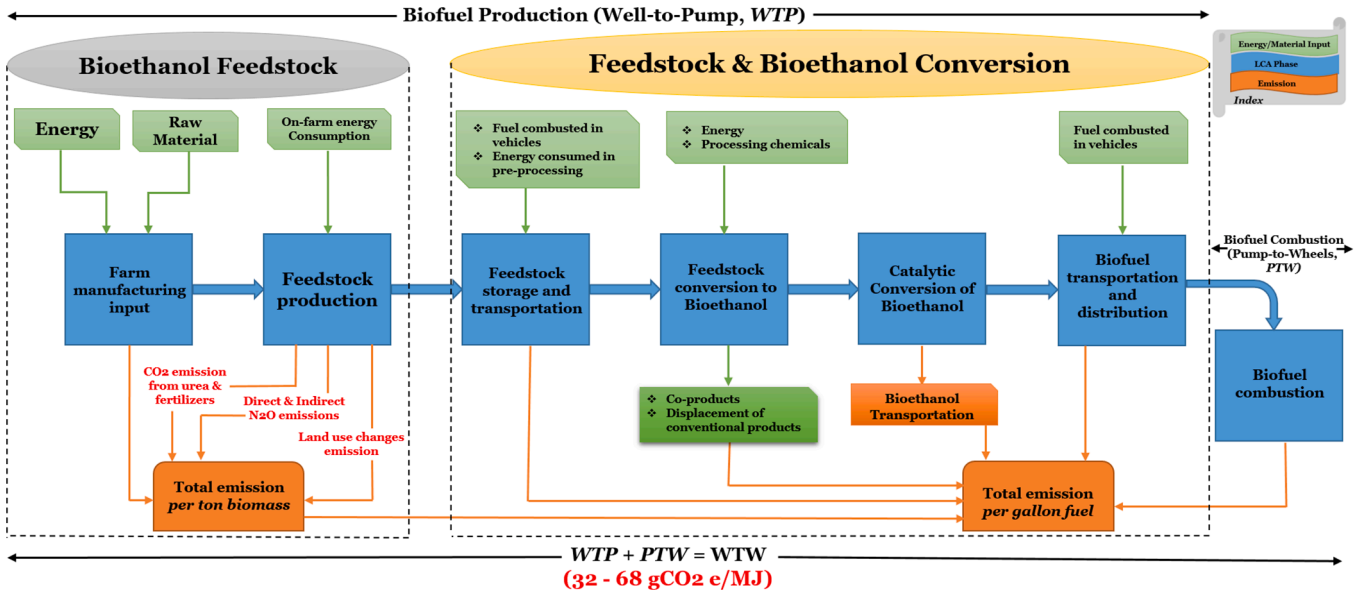

Fig. 10a. Life cycle analysis: Bioethanol to gasoline *(Well-to-Wheel)*.

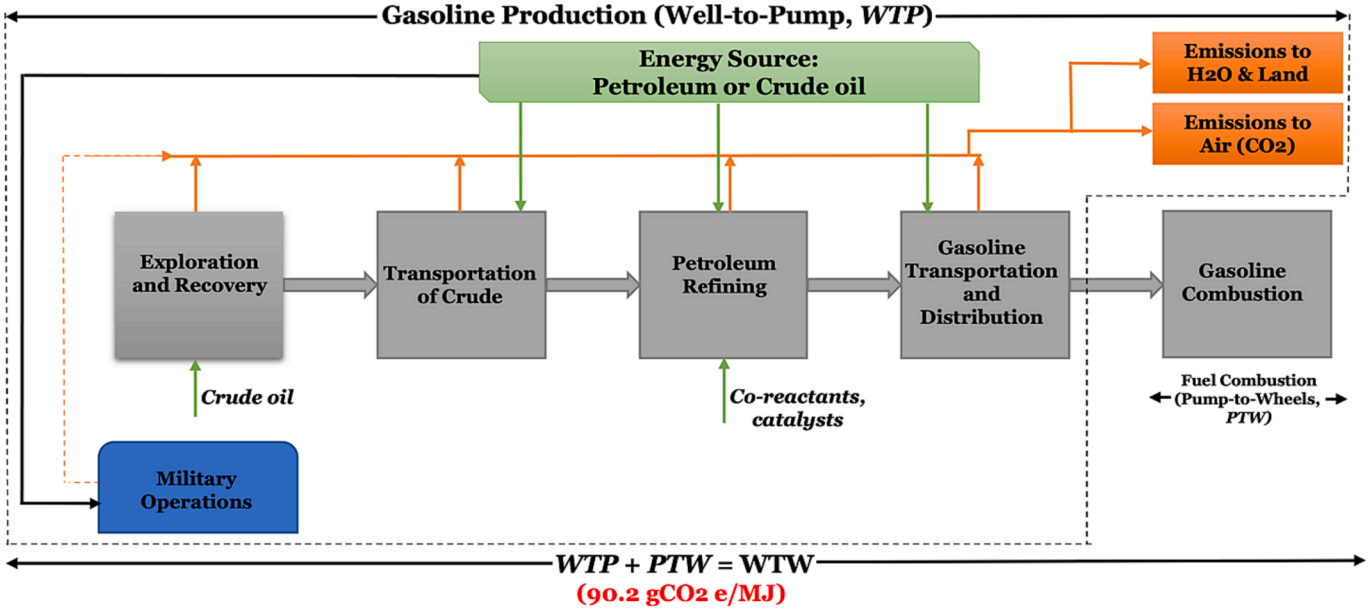

Fig. 10b. Life cycle analysis: Petroleum to gasoline *(Well-to-Wheel)*.

blendstocks using CADO from various biomass feedstocks and processes can be cost-competitive due to existing production incentives. Some regions have a strong market demand for low-carbon blendstocks, and this demand is expected to increase over time, driven by the transportation industries' goals of reducing greenhouse gas emissions.

The study by Hannon, et al. [2] reported that the operational results of CADO cover a scale of up to 0.12 L of ethanol processed per hour, with a potential scaling up to 2.0 L/h currently underway. These scales fall within the validated range for commercialising processes based on gas-phase heterogeneous catalysis [57–59]. To support commercial application in the next stage, further scaling up by a factor of around 1,000 is necessary to process 15×10^6 L per year of ethanol [2]. The distribution of products derived from CADO resembles gasoline blendstocks. Still, modifying the catalyst or developing additional methods to achieve ranges more typical of other fuels, including aviation fuel and diesel, is possible. These modifications and developments also have the potential to decrease the aromatics content, which is important for accessing alternative fuel and engine types. In its present stage of development and considering the limits on aromatic content, CADO-derived blendstocks could be blended at 20–40 % with petroleum-derived gasoline fuel. However, verification and certification are still required. Further utilisation or blending of low-carbon, biomass-derived HCs at higher levels could be enabled by advancing CADO catalysts and technologies, blending with fuels from other processes with lower aromatic content, separating CADO-derived products into fractions suitable for various applications, or a combination of these approaches.

The economics of adding CADO as a bolt-on to current ethanol production facilities are slightly less favourable compared to adding CADO as part of an integrated Greenfield plant that produces partially purified ethanol as an intermediary for further transformation to fuel blendstocks. This is due to the additional cost of producing anhydrous ethanol in existing facilities. However, CADO has a low capital cost,

Table 4
Comparative evaluation of greenhouse gas (GHG) emissions generated during the production of gasoline fuel using two approaches: utilising the CADO process with ethanol obtained from various sources and the conventional petroleum-based production method.

	Bioethanol Source					Petroleum Source	
		Emission (gCO_2 e/MJ of fuel blendstock)					
Bioethanol Biomass	Technology	Feedstock Synthesis and Ethanol Conversion	CADO-ETH	Gasoline use (PTW_{gb})	WTW_{gb} [β] (GHG reduction, %)	PTW_{gp}	WTW_{gp}
[#]Corn starch	Current	45.46	6.67	15.5	67.7(-25 %)		
[*]Sugar cane	Current	23.75	3.15	15.5	42.5(-53 %)	73.4	90.2
[¤]Cane cellulosic	Current	14.46	3.15	15.5	33.2(-63 %)		
[*,¤]Cane cellulosic	Projected	13.87	3.15	15.5	32.6(-64 %)		

PTW (gb, gp) - fuel utilisation in a gasoline system (gb: gasoline from ethanol & gp: gasoline from petroleum).
WTW — full supply, production, and use chain. CO_2 emission of gasoline (derived from ethanol [53] and fossil fuel [54]).
The calculation of catalytic conversion values incorporates emissions resulting from the transportation and distribution of EtOH, with an estimated value of 0.85 gCO_2 e/MJ [2].
[*] Provided by [52].
[β] When expressed as negative percentages, the values indicate the reduction in greenhouse gas (GHG) emissions in contrast to petroleum gasoline fuel.
[#] Provided by Argonne National Laboratory for corn starch ethanol case [2] & [55].
[¤] Cane cellulosic [2].

making adding CADO-mediated fuel blendstock production to existing ethanol plants feasible. This allows for the rapid establishment of low-carbon gasoline fuel production capacity, attractive investment returns, and increased product diversity for biofuel producers. The anticipated cost reduction for future CADO-derived fuel blendstocks is projected to be over 30 %, bringing the estimated cost down to $0.03/L compared to the current process ($0.05/L). However, this reduction is comparatively lower than the historical cost reductions observed for industrial processes, particularly those based on gas-phase heterogeneous catalysis [60,61]. It should be noted that the projected cost reduction for future CADO-derived fuel blendstocks falls short of the post-commercialisation cost reductions typically seen in industrial processes. It is important to recognise that the actual costs of CADO may differ from expected costs due to various factors such as location, time and equipment costs. Therefore, cost estimates are always subject to possible fluctuations. Should it be possible to produce HC blendstocks at a comparable cost to anhydrous ethanol, this would be a significant improvement and an opportunity to direct biofuel synthesis towards applications that are critical to stabilising the climate.

As previously mentioned, the amortisation of investments in corn ethanol plants in the United States can be partially due to government subsidies, which could contribute to the future competitiveness of corn ethanol. The production of corn ethanol in the US receives significant government subsidies. According to Shapouri, et al. [62], the federal excise tax exemption for ethanol blends amounts to $0.53/gal. This tax exemption brings the prices of conventional gasoline and ethanol to a comparable level, promoting the use of ethanol as an alternative to gasoline. However, in Brazil, ethanol producers have been eligible for financial support since the program's initiation, and the government sets the prices consumers pay at the pump. However, as of 1999, prices were allowed to become more competitive, rendering this support unnecessary [63].

4. Conclusion

The potential of biofuels in addressing carbon emissions in the transport sector is significant. With biofuels derived from biomass, there is an opportunity to reduce the reliance on fossil carbon and transition to a more sustainable and environmentally friendly transportation system. However, it is crucial to continue advancing technologies and processes to optimise biofuel production, improve their properties to closely resemble traditional fossil fuels, and explore their compatibility with various engines and transport modes. The catalyst (Ni/HZSM-5) cost was estimated to be $31.4 and $69.9/kg for 100 and 50 % baseline scale production using the CatCost model. The quantity of catalyst purchased by a process plant significantly impacts its cost. Increasing the scale of production and purchasing can lead to cost savings due to economies of scale and volume buying. Discrepancies in price arise from jumps between synthesis scales, which can be addressed by mixing equipment of varying scales and making discretionary adjustments to the selling margin. The cost breakdown of catalyst purchases, including materials, processing, overhead, and margin, varies with different purchasing scales. When analysing the influence of scale on CADO catalysts, significant discrepancies are observed among different material types, with the Ni/HZSM-5 showing a notable reliance on purchase scale due to its intricate synthesis process. Processing and overhead costs decrease proportionally with increasing scale, making raw materials the primary focus for cost reduction at larger production scales.

The production of biofuels from renewable biomass sources is gaining increased attention to address the depletion of crude oil reserves and mitigate the environmental impact of traditional fuels. Ethanol, as the predominant biofuel, has limitations for use as a standalone transportation fuel, but research is underway to improve its properties and explore alternative biofuel molecules. The transport sector requires further advancements in biofuel technologies to reduce carbon emissions. Catalysts such as HZSM-5 zeolite promise to convert alcohols and oxygenates into hydrocarbon fuels. Continued research, development, and investment in biofuel production are necessary to unlock the full potential of biofuels in achieving a sustainable and low-carbon transportation system. The current estimated cost of converting wet ethanol to fuel blends includes operating and annual capital expenditures of $0.05 per litre. These costs are expected to decrease to $0.03/L in future periods. This cost is comparable to the unit energy production cost of producing anhydrous ethanol from wet ethanol, which is $0.02/L. The cost of producing biofuel from CADO was more competitive with the crude oil price of $100/bbl, while at the current oil price, the selling price of CADO gasoline is not competitive with gasoline from petroleum. The single-step catalytic conversion of ethanol into hydrocarbons is a promising avenue for renewable fuel production. Both the traditional three-step processes and the innovative CADO strategy offer potential solutions. However, the CADO technology showed potential in GHG emission reduction (by > 25 %) and carbon balance. Continued research and development are crucial for optimising these processes, improving liquid fuel yields, and conducting comprehensive assessments of their economic viability and environmental sustainability. These analyses and methodologies offer valuable insights into cost estimation, manufacturing processes of catalysts and biofuels, and life cycle assessment (LCA), thereby facilitating decision-making and optimisation within the industry. Despite the potential advances in biofuel technologies, the economic competitiveness of CADO gasoline,

especially compared to petroleum-derived gasoline at current oil prices, remains a constraint. This underscores the ongoing challenge of achieving cost parity with conventional fuels and the need for continued research and development efforts to improve economic viability.

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CRediT authorship contribution statement

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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.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecmx.2024.100529.

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