

## Article

# Alternative Integrated Ethanol, Urea, and Acetic Acid Processing Routes Employing CCU: A Prospective Study through a Life Cycle Perspective

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**Abstract:** Despite the importance of inputs such as urea, ethanol, and acetic acid for the global production of food, energy, and chemical bases, manufacturing these substances depends on non-renewable resources, generating significant environmental impacts. One alternative to reducing these effects is to integrate production processes. This study compares the cumulative environmental performance of individual production routes for ethanol, urea, and acetic acid with that of an integrated complex designed based on Industrial Ecology precepts. Life Cycle Assessment was used as a metric for the impact categories of Global Warming Potential (GWP) and Primary Energy Demand (PED). The comparison occurred between the reference scenario, which considers individual processes, and six alternative integrated arrangements that vary in the treatment given to a stream concentrated in fuels generated in the Carbon Capture and Usage system that serves the processing of acetic acid. The study showed that process integration is recommended in terms of PED, whose contributions were reduced by 46–63% compared to stand-alone processes. The impacts of GWP are associated with treating the fuel stream. If it is treated as a co-product and environmental loads are allocated in terms of energy content, gains of up to 44% can be expected. On the other hand, if the stream is a waste, the complex's GWP becomes more aggressive than the baseline scenario by 66%.

**Keywords:** life cycle assessment; carbon capture usage; process integration; industrial ecology; environmental performance



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## 1. Introduction

Urea [ $\text{CO}(\text{NH}_2)_2$ ] is essential for food production in agribusiness. Its high nitrogen content (46% *w/w*) makes this compound the dominant n-fertilizer among its class. As a result, around 40% of the food grown on the planet is fertilized with urea, demonstrating its influence on economies strongly linked to the agricultural sector [1]. On the other hand, urea production is highly dependent on the petrochemical sector, and its unbalanced and uncritical use by the farming sector can cause severe damage to the global N cycle, whose consequences only now begin to be known due to the proposition of robust and accurate determination methods [2]. This picture makes urea an expensive asset, not only from an economic perspective, but also, perhaps more importantly, from an environmental point of view. Therefore, developing alternative routes to producing urea more cheaply and with less impact has become a strategic challenge [3].

In the particular case of Brazil, this problem could be addressed by integrating urea synthesis with the processing of first-generation ethanol (1G). The connection between these routes occurs from using sugarcane and straw bagasse surpluses as raw materials for obtaining synthesis gas (syngas) that serves as an input for ammonia ( $\text{NH}_3$ ) manufacturing,

from which the urea would be processed. Although they have profitable markets, these types of biomass proceed from the sugar and alcohol sectors, which, for being consolidated in the country, avoid (or at least absorb) supply fluctuations and allow for more competitive prices. In addition, the choice of fibrous sources reduces the ancestry of the petrochemical segment on  $\text{CO}(\text{NH}_2)_2$  processing, leading to potential impact reductions in Global Warming Potential (GWP) and Primary Energy Demand (PED) [4].

The path to environmental sustainability must invariably involve reducing anthropogenic contributions to GWP. To this end, practices based on reducing remuneration, compensation, and capturing greenhouse gas (GHG) emissions, or, more specifically, carbon dioxide, are currently available. Carbon Capture and Usage (CCU) techniques stand out from other mechanisms because they convert  $\text{CO}_2$  into short-chain chemical intermediates with a high added value [5–7].

The successive steps involved in the conversion of biomass in  $\text{CO}(\text{NH}_2)_2$  operate under extreme temperature and pressure conditions; therefore, it becomes inevitable to consume fossil assets to meet the demands of the integrated plant. Regarding PED, the adverse effects of this circumstance can be mitigated by choosing a fuel with a high energy content, such as natural gas. On the other hand, the consequences of GWP can be mitigated by coupling a CCU technology to the agreement, which, in addition to environmental gain, would also allow for the manufacture of another good consumption: acetic acid ( $\text{CH}_3\text{COOH}$ ).

The technical literature that describes process integration experiences is vast and varied. However, most of these studies are dedicated to elaborating proposals for technologically consistent arrangements or to verify their technical and economic validity [8–11]. Few publications have investigated the environmental behavior of integrated plants [12–14], and no cases were identified in which this kind of analysis was performed under a broad perspective, considering environmental impacts generated externally to the unit's boundaries. This study proposes contributing to the theme by verifying the environmental viability of processing ethanol, urea, and acetic acid in the same productive complex.

The analysis was conducted by comparing the environmental performance of the integrated plant with the sum of the results obtained individually using the same productive cycles. The verification's systemic character was provided by applying the Life Cycle Assessment (LCA) technique in the attributional modality and with a scope 'from cradle-to-gate' [15] for the Global Warming Potential and Primary Energy Demand impact categories. LCA is a well-established approach in the academy, generating information on environmental performance for the most diverse and varied sectors, from integrated bio electrochemical-constructed wetland systems (ECW) [16] to the marketing and supply of coffee [17]. The consumptions and emissions that originated from integrating the systems were determined using computational modeling, considering the regular operating conditions for each manufacturing. The study also discusses the effects of methodological decisions inherent to LCA on the diagnoses that result from its application.

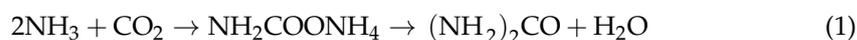
Although the selection of chemical commodities considered in the study was influenced by the technical viability of designing an arrangement that bound its productions, the need to obtain ethanol, urea, and acetic acid with low environmental impacts was also a criterion for determining these options. For this reason, more than producing detailed environmental diagnoses, this research is expected to provide technical-scientific arguments that support the conception of more environmentally favorable synthesis routes for the same assets.

## 2. Background

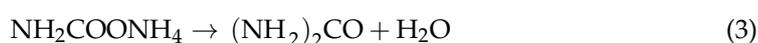
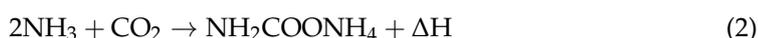
### 2.1. Urea

Urea [ $\text{CO}(\text{NH}_2)_2$ ] is a nitrogen organic compound established via the chemical binding between a carbonyl group and two amine groups [1]. Its conventional production route, called Total-Recycle, has paved the way for large-scale technical and economic viability for this input. A simplified flowchart of this process is represented in Figure 1 [18,19]. Total-Recycle comprises four steps: (i) obtaining ammonium carbamate [ $(\text{NH}_4)\text{NH}_2\text{CO}_2$ ]; (ii) dehydrating carbamate in an aqueous solution at  $100\text{ }^\circ\text{C}$  and under controlled pressure;

(iii) the continuous recycling of  $[(\text{NH}_4)\text{NH}_2\text{CO}_2]$  to increase the yield rate of the urea production reaction; and (iv) urea pearling (i.e., concentration and granulation), for preparing it for commercialization and use [20]. Even if subjected to all these interventions and care, the process reaches global discrete conversion rates ( $\eta \sim 35\%$ ). The sequencing depicted in Equation (1) summarizes the transformations in the Total-Recycle process.



Later, Total-Recycle was improved, becoming the major process for urea synthesis. The transformation, which is still commercially practiced on a large scale, can be simplified for a mechanism composed of two elementary steps (Equations (2) and (3)) [18].



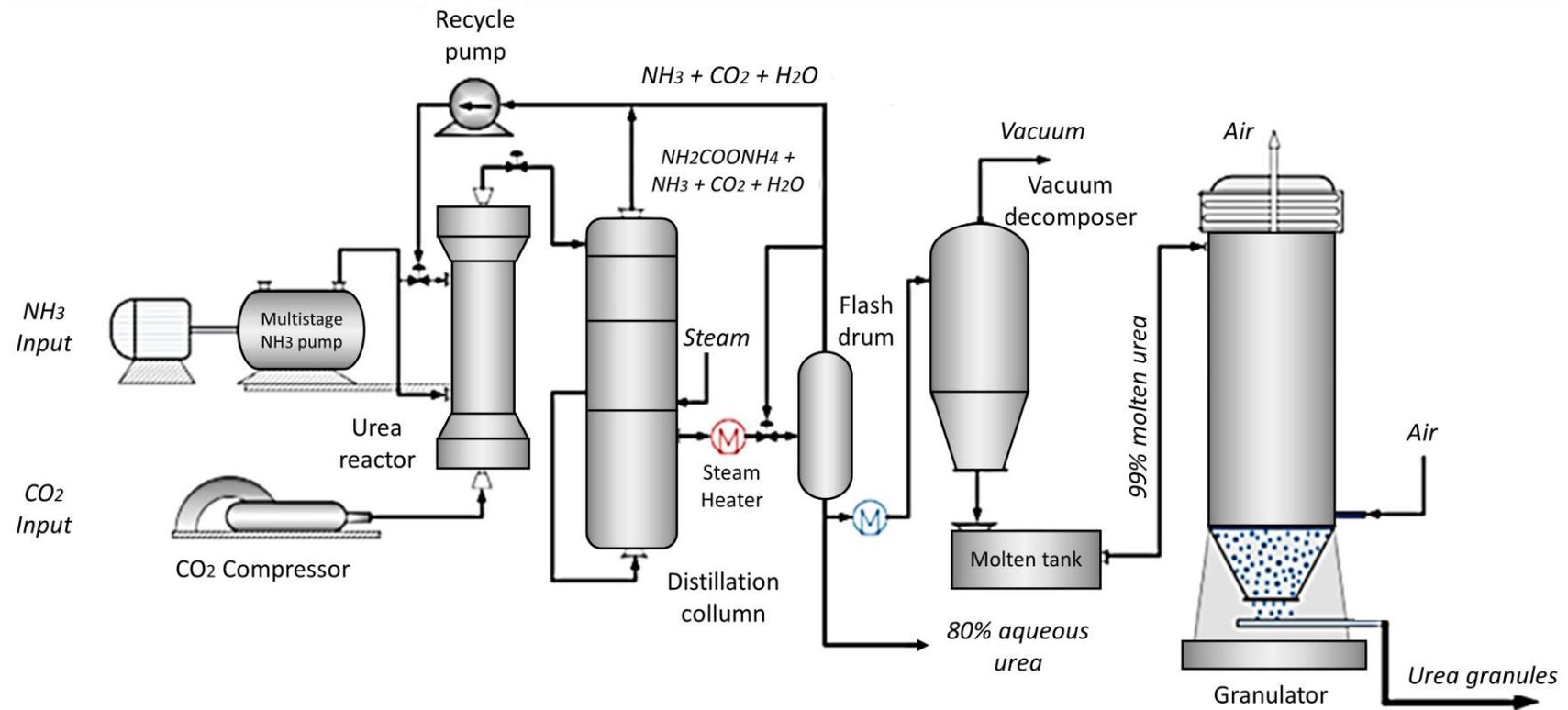
Equation (2) depicts obtaining  $(\text{NH}_4)\text{NH}_2\text{CO}_2$  through a fast and exothermic reaction, while Equation (3) comprises the dehydration of ammonium carbamate, forming urea and water, from a slow and slightly endothermic reaction, whose yield is limited by thermodynamics. The overall urea formation reaction from  $\text{NH}_3$  and  $\text{CO}_2$  is exothermic. Therefore, it is assumed that high temperatures are required to accelerate the ammonium carbamate dehydration reaction rate, which occurs in the liquid phase. In addition, side reactions that may disrupt the process are favored by conditions such as structural similarity among intermediates. These transformations reduce the selectivity of the process when generating by-products like biuret and isocyanic acid [18].

The slow reaction (Equation (3)) occurs in the Urea Reactor, resulting in a  $\text{CO}(\text{NH}_2)_2$ , water, unconverted  $(\text{NH}_4)\text{NH}_2\text{CO}_2$ , excess  $\text{NH}_3$ , and a small amount of  $\text{CO}_2$  mixture. Under typical conditions, it is expected to maintain excess ammonia in the reactor, with a ratio from  $4 < (\text{NH}_3/\text{CO}_2) \text{ mol/mol} < 6$  at the beginning of the mixture. The remaining unconverted  $(\text{NH}_4)\text{NH}_2\text{CO}_2$  decomposes into ammonia and carbon dioxide in the Vacuum decomposer. Under reduced pressure, the  $\text{NH}_3$  and  $\text{CO}_2$  evaporate from the solution as vapor. The exhaust gases from this decomposer are then sent to a distillation column, in which the top stream consists of pure ammonia gas and the bottom stream, a liquid ammonium carbamate solution. This is made possible by using pure ammonia liquid as the reflux fluid at the top of the column [18,19].

In addition to the  $\text{NH}_3$  reflux, the ammonium carbamate solution reflux, a product obtained at the Distillation column, is continuously recycled to the Urea Reactor due to low process yield rates. Following the recirculation section, the urea solution is again subjected to decomposing any remaining ammonium carbamate at a low pressure.

The urea solution that leaves this low-pressure section will likely be considered to be ammonium carbamate-free. It then undergoes evaporation, where all water vapor is removed. Finally, the Granulator transforms the melted urea into solid aggregate particles [18].

Despite its virtues and limitations, urea synthesis still faces the challenge of achieving a successful design and operation that combines a technologically mature process with scalability, high conversion rates, low environmental impacts, economic viability, operational reliability, and a good product quality [18]. As previously described, commercial urea production proceeds from the dehydration of ammonium carbamate synthesized from ammonia and carbon dioxide. As  $\text{CO}_2$  is an  $\text{NH}_3$  production by-product, urea plants used to be adjacent to an  $\text{NH}_3$  plant. In most cases, both factories share the same property [1].

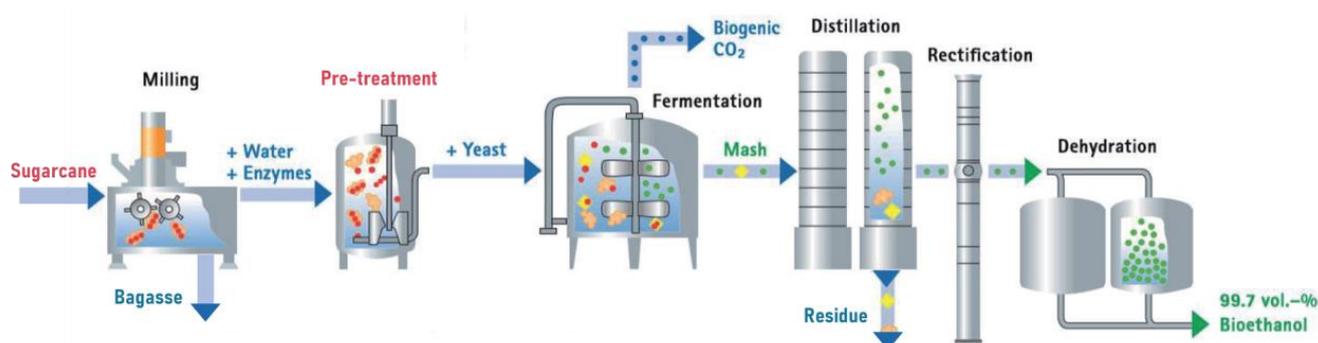


**Figure 1.** Simplified Urea Synthesis Plant comprising the stages of the urea reactor, distillation column, vacuum decomposer, and granulator. Adapted from [19].

## 2.2. Ethanol

Due to its high octane number (RON~109), ethanol ( $C_2H_5OH$ ) is classified as an excellent liquid fuel. In addition, although its anhydrous form has low energy levels available per unit volume, it is also an additive to gasoline itself, considerably reducing the gas emissions from automotive vehicles operating via the Otto cycle [21]. The United States and Brazil are the largest global ethanol producers, accounting for around 70% of its global production [21].

The ethanol manufacturing process can occur via synthetic production or, mainly, through the fermentation of carbohydrates from different raw materials [22]. The ethanol production cycle is directly associated with the type of substrate, depending on raw material availability versus location, reflecting regional climate and cultivation conditions, production costs, and energy efficiency [23]. In cases where the raw material contains sucrose, the process is simplified, and ethanol is produced via the biochemical route based on fermentation. The most widespread sucrose-rich contents are sugarcane and sugar beet [24]. A simplified ethanol production diagram is depicted in Figure 2.



**Figure 2.** A simplified ethanol production diagram, adapted from [25].

The extraction of the sucrose-rich juice contained in sugarcane stems via grinding produces bagasse, a fibrous biomass originating from the Brazilian agroindustry, mainly employed as an energy source, fuel, and in generating electricity in self-sufficient ethanol plants [26,27].

In this context, energy integration aiming at increased productivity and using by-products is targeted by virtually all sugar energy production units. Bioelectricity is generated from biomasses such as bagasse and straw and used in production plants. At the same time, the surplus is marketed. In the last decade, energy due to biomass burning had a variable contribution between 8.0 and 9.1% of the total Brazilian electricity supply. However, in 2022, there was a drop in this contribution (to 4.7%) because of the relative growth of other sources (i.e., wind and even hydroelectricity), and because most plants and distilleries employ it for other purposes [28].

## 2.3. Acetic Acid

The two main applications of acetic acid ( $CH_3COOH$ ) comprise the production of vinyl acetate monomer (VAM) and purified terephthalic acid (PTA), which are also responsible for boosting a wide value chain, such as the polyester, polyvinyl acetate, and polyvinyl alcohol industries. Their end applications include the production of acetic anhydride, monochloroacetic acid (MCAA), and ethyl acetate [29].

$CH_3COOH$  can be manufactured through different processes, but catalytic methanol carbonylation is the most practiced, comprising about 85% of the global installed capacity [29]. Initially, the route used a cobalt iodide catalyst, and although the process operated under extreme temperature and pressure (250 °C; 700 bar) conditions, it was attractive economically [30]. Some years later, a rhodium-based system under mild conditions was conceived [31]. This alternative rapidly replaced cobalt-catalyzed technology due to its

higher selectivity (for CO and CH<sub>3</sub>OH), less severe conditions, and faster reaction. In this case, CH<sub>3</sub>OH is carbonylated under 1.0–3.0 MPa pressures, yielding 99% and 90% concerning methanol and carbon monoxide, respectively [31].

Recently, Qian et al. [32] proposed the methanol, carbon dioxide, and hydrogen reaction using a bimetallic Ru-Rh homogeneous catalyst. The transformation also requires imidazole as a ligand, lithium iodide (LiI) as a promoter, and 1,3 di-methyl-2-imidazolone as a solvent. This concept brings about a new approach to the production of acetic acid and the transformation of CO<sub>2</sub>, which involves advances from synthetic chemistry. The process shows significant potential due to its use of available and economically affordable raw materials, a high conversion efficiency ( $\eta \sim 77\%$ ), and an expressive Turnover Number (TON > 1000). Its complete mechanism is detailed in [32]. An investigation conducted by Cardenas-Gonzales et al. (2023) [33] followed in the same direction. It employed two catalysts, Rh (Rh/TiNT) and Ru nanoparticles (Ru/TiNT), to synthesize CH<sub>3</sub>COOH. Both catalysts exhibited activity in the gas-phase hydrocarboxylation of methanol, utilizing carbon dioxide and hydrogen as reactants, with methyl iodide serving as a promoter to yield methyl acetate. One of the merits of this development is to value CO<sub>2</sub> fixation.

Concerning environmental aspects, LCA studies have demonstrated that acetic acid production results in a cradle-to-gate Global Warming Potential (GWP) of 1.0 kg CO<sub>2eq</sub>/kg of CH<sub>3</sub>COOH, indicating that the manufacture of this product contributes, in terms of Global Warming Potential, 13 Mt CO<sub>2eq</sub> annually [34]. With such a high relevance in the primary chemical industry, reducing GWP contributions would be a big step towards mitigating fossil-based productive processes under a climate change scenario.

#### 2.4. Industrial Ecology

Conceptually, Industrial Ecology is a multidisciplinary approach that examines complex integrated anthropic systems from diverse points of view (e.g., technical, social, economic, and environmental) and makes proposals based on the behavior of natural systems to (re)design them according to an integrated and sustainable perspective [35]. The model establishes the transition between the Linear Economy, based on the trinomial extraction–use–disposal, and the Circular Economy, which reduces pressure on natural resources, recycles consumer goods whose original services have been exhausted, and thus restricts losses and waste [36]. An example of an industrial complex operating on an Industrial Ecology approach is the Kalundborg Industrial Park in Denmark. In this case, the waste heat produced by a coal-fired power plant is used by a fish farm, whose solid waste is processed and sold as fertilizer by another manufacturer. The nearby households can also absorb the waste heat from the industrial complex [12].

El-Halwagi et al. (2011) [13] showed that using residual heat in integrated fuel production complexes brings environmental advantages for different production conditions. The same happened with Singh et al. (2007) [14], who, after evaluating the environmental impacts of an industrial complex implanted in the Mississippi River basin (US), proposed that the thirteen agrochemical units installed in the zone there were integrated according to Industrial Ecology procedures. According to the authors, this intervention could reduce the accumulated GWP of those enterprises by up to 66%.

As mentioned in the Introduction section, records were not found in the literature on actions involving the integration of ethanol, urea, and acetic acid processing plants. However, obtaining ethanol from a renewable resource such as sugar cane, combined with the availability of residual energy sources from this and other plants, and with the capture of fossil CO<sub>2</sub> from the same processes to synthesize acetic acid from, for example, Carbon Capture and Utilization (CCU) technology, are promising indications of the environmental gains from such a scheme. Therefore, these circumstances lead us to believe that adopting an Industrial-Ecology-based approach may also be promising, thus justifying this investigation.

### 3. Methodology

This study was structured according to the following methodological steps: (a) review of the literature focused on identifying the technological and procedural aspects of the syntheses of the products under analysis; (b) the formulation and specification of technological arrangements based on alternatives collected from the literature; (c) the conception and modeling of an integrated plant based on the precepts of Industrial Ecology; (d) the construction of scenarios involving the arrangement, taking into account different perspectives, (e) the application of the Life Cycle Assessment technique for the elaboration of environmental performance diagnoses of each scenario; and, (f) the results analysis and formulation of considerations on the theme.

#### 3.1. Literature Review

The study's first phase included a literature review aimed at characterizing ethanol, urea, and acetic acid production routes from technological and technical-operational points of view, as well as concerning resource consumption and emissions. Based on consistent and referenceable sources, this step was applied to identify the technological gap in urea production from biomass coupled to an ethanol plant with the generation of inputs for acetic acid production. The search for technologies was followed by identifying the technical aspects, operating conditions associated with the processes investigated, and consumption and emissions related to the same transformations.

Searches were carried out in the Scopus, Web of Science, and Google Scholar Scientific databases, using individual or associated keywords such as *bioethanol production*, *sugarcane bagasse and straw*, *biomass gasification*, *syngas production*, *urea production*, *ammonia synthesis*, *acetic acid production*, *Carbon Capture and Usage*, *CCU*, *energy efficiency*, *energy conservation*, *biorefinery*, *Life Cycle Assessment*, *environmental aspects*, and *Industrial Ecology*. The temporal coverage for the data collection comprised 2009–2021. Still, long-lived information from original or renowned productions was added when no data were found within that collection interval. The search identified 160 documents, including technical articles (89), books or book chapters (41), and technical manuals and official documents (30).

#### 3.2. Technological Arrangement Formulation and Specification

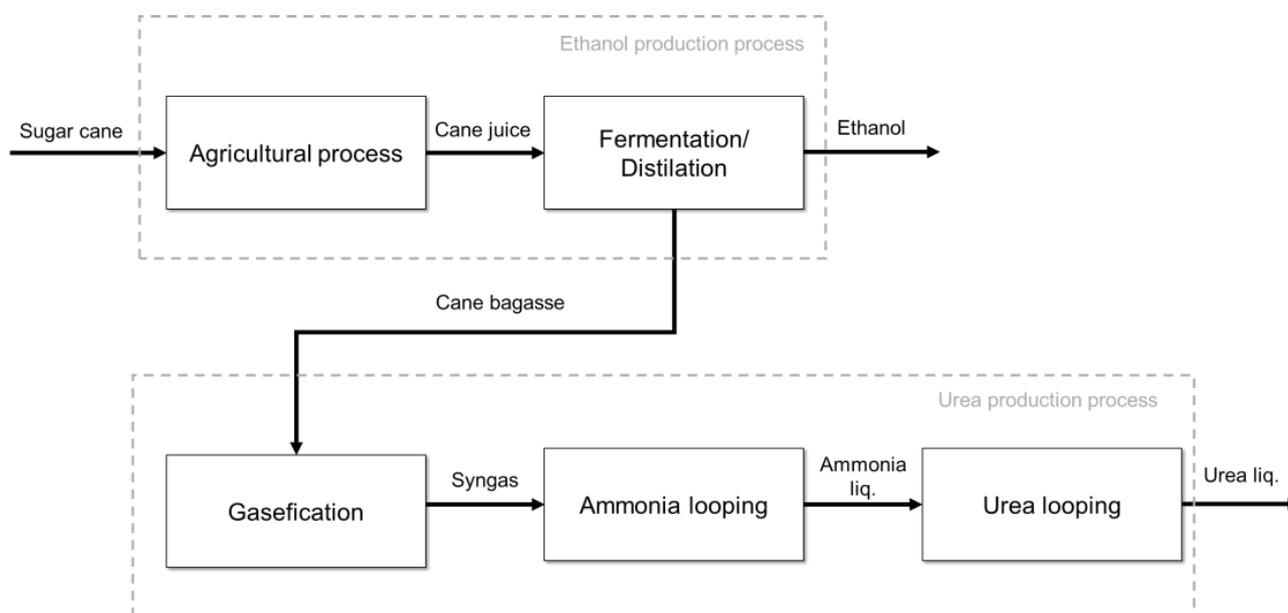
Objective criteria were applied to select the technological arrangements that describe the processing of each chemical involved in the analysis. These requirements comprised (i) process integration potential, (ii) the possibility of implementing industrial ecology practices, (iii) the degree of technology maturity, and (iv) the data availability on the process (e.g., operating parameters, types of raw materials, and auxiliary materials, degrees of conversion, and selectivity), utilities (electricity and heat generation sources, and water and effluent treatments), and environmental performance (consumption and emissions).

The result of applying these criteria converged on a proposal for an integrated plant, in which an autonomous distillery producing anhydrous ethanol (99.5% *w/w*), whose Rankine-cycle of cogeneration operates at  $P = 21$  bar and without electricity export, would be coupled to a unit for producing synthesis gas (syngas). Surplus sugarcane bagasse is converted into syngas in an entering flow gasifier reactor, using air as the gasifying fluid. The product obtained has a ratio  $[H_2/CO]$  mol/mol~1.40, which makes it suitable as an input for obtaining ammonia. The selection of the gasifier geometry was based on environmental and energy performance analyses [8]. The same happened with the choice of atmospheric air as the gasification fluid, for which the low associated costs and ability to produce synthesis gas with an  $H_2$  content compatible with its use in the process added to those arguments.

To obtain  $NH_3$ , we opted for looping synthesis technology because it was less wasteful of energy. Purified syngas is compressed in successive stages before being introduced into the reactor. The cooling temperatures after each stage are 40, 70, and 150 °C, respectively, while the discharge pressure reaches 250 bar. The compressed feed gas is mixed adiabatically with the recycled gas stream, containing unreacted inert  $H_2$  and  $N_2$ , and ammonia to

a lesser extent. A reactor, isothermal and in thermodynamic equilibrium, operates at 550 °C and 250 bar to favor the release of heat (exothermic reaction). Cooled products are fed to a flash drum operating at 20 °C and a high pressure, conditions that allow for NH<sub>3</sub> to be separated from other gases present in the mixture. In this way, pure liquid ammonia is obtained as the plant's main product.

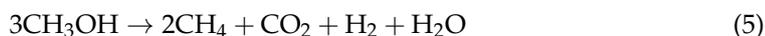
The modeling of urea synthesis combined NH<sub>3</sub> and CO<sub>2</sub> according to Total-Recycle upgraded technology. The specifics and process conditions adopted in this case correspond to those described in Section 2.1. Figure 3 depicts, without detailing the by-products, the urea manufacturing process integrated into an ethanol plant through sugarcane biomass considering the principles of Industrial Ecology. The technologies were reproduced via computational modeling using the AspenPlus v.10 software (Aspentech<sup>®</sup>, Bedford, MA, USA). These constructions considered the typical operating conditions of each processing.



**Figure 3.** Simplified diagram of integrating the ethanol production process from sugarcane and urea.

The main requirements for defining the acetic acid production scheme consisted of (i) the route's ability to be coupled to CCU technology of the Carbon-Lithium (Ca-Li) type and (ii) the selected arrangement proving to be effective in terms of converting reagents into CH<sub>3</sub>COOH. Only synthetic routes were subjected to these requirements, since those based on bacterial fermentation were not considered for the analysis.

Conventional technologies, such as Methanol carbonylation—responsible for around three quarters of global CH<sub>3</sub>COOH production through chemical transformation—Acetaldehyde oxidation, and Ethylene oxidation, were checked. Nevertheless, all of them made the coupling of Ca-Li unfeasible. Therefore, we explored alternative production routes using CO<sub>2</sub> as a reagent, such as CO<sub>2</sub> hydrogenation, CO<sub>2</sub>/CH<sub>4</sub> reforming, and methanol hydrocarboxylation. Among these possibilities, methanol hydrocarboxylation was chosen due to its lower energy demand than the others and the potential for integration with the urea production plant. The arrangement employed a homogeneous Ru-based catalyst using specific ligands and solvents for CH<sub>3</sub>OH, CO<sub>2</sub>, and H<sub>2</sub> reactions. These transformations exhibit restrictions due to changes in closed-system compositions, but may be illustrated by the set of linear Equations (4)–(8). One of the system's restrictions is that CO<sub>2</sub> and H<sub>2</sub> react equally.



One crucial system development condition was using the RStoic module reactor in the Aspen Plus, which operated at 180 °C and 100 bar. The solvent included in the simulation was 1,3-dimethyl-2-imidazolidinone (DMI). The DMI present in the reactor outlet stream was collected and separated from the other components of the reaction mixture so that it could be reused in successive reactions. The model also considered recycling the Ru-based catalyst and unreacted gases. Considering these conditions, the CH<sub>3</sub>COOH production process showed an overall CH<sub>3</sub>OH conversion of approximately 77% [37]. Figure 4 depicts the reactor system, the liquid and gas separation systems (adjacent subsystems), and the feeding and recompression system for the acetic acid production system. The recycle streams aim to recover CO<sub>2</sub> and H<sub>2</sub> in the gas separation subsystem [37].

### 3.3. Model Integration from a CCU Perspective

Figure 5 shows a general schematic of the integrated production plan for ethanol, urea, and acetic acid. The diagram also depicts the connection between the CO(NH<sub>2</sub>)<sub>2</sub> production unit, the CCU technology, and the CH<sub>3</sub>COOH synthesis unit. The CO<sub>2</sub> emission sources available in the arrangement that could be used to produce CH<sub>3</sub>COOH were evaluated for their degree of CO<sub>2</sub> purity, since the output stream from the mixer that supplies the 'Feeding and re-compressing' unit of the acetic acid synthesis process (Figure 4) must contain at least 98% v/v of that component.

As this is a crucial parameter in the model, the amount of CO<sub>2</sub> needed to produce acetic acid, considering the yield and the proposed system configuration (28.9 t/h), was calculated using a mass balance. This stream was mixed with the H<sub>2</sub> stream in MIX 1 before being fed into the reactor (Figure 6). Next, the potential streams within the acetic acid production system were evaluated iteratively by calculating the individualized environmental model results without any applied integration. The process arrangements regarding consumption and emissions were reproduced using the SimaPro v 9.3 software (PreSustainability, Amersfoort, NL, USA), a tool routinely employed to support LCA studies. Thus, the first evaluated stream was the CO<sub>2</sub>-rich one generated alongside the furnace emissions that sustained the CH<sub>3</sub>COOH synthesis. The furnace that held the acetic acid displayed the same standardization and modeling as those that made up the ethanol and urea production model, burning natural gas and, among the specific modeling assumptions, using O<sub>2</sub> for burning instead of atmospheric air.

The emissions in Table 1 originate from the furnace that is part of the acetic acid plant. Considering this system's characteristics, an emanation of 77.8 g of combustion gases was estimated for every 1.0 MJ of thermal energy produced. On the other hand, an integrated plant that operates according to the technical-procedural characteristics indicated above and produces 35.6 t/h of ethanol and 16.8 t/h of urea must synthesize 25.1 t/h of acetic acid to equalize its overall mass balance (Figure 5).

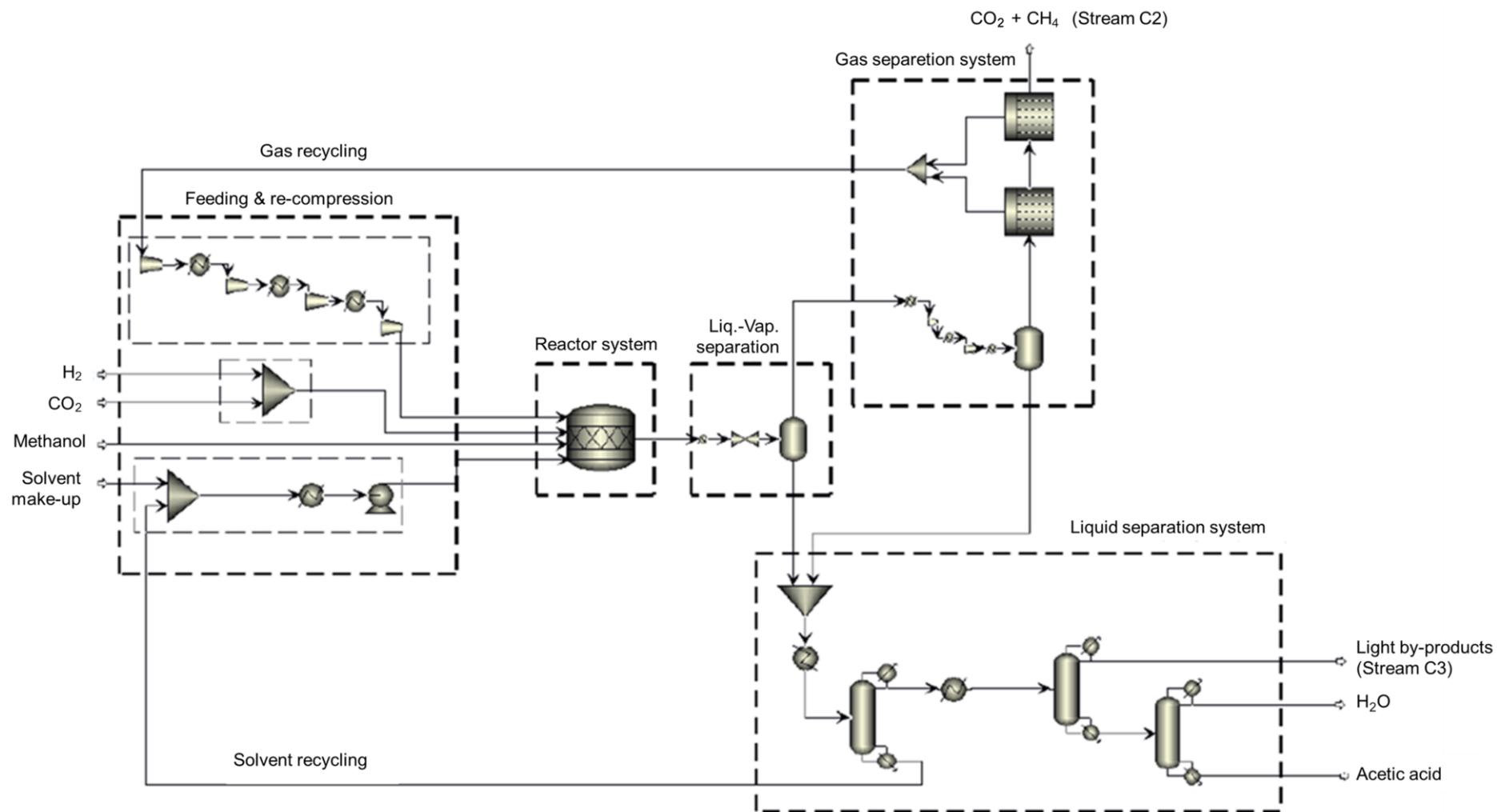


Figure 4. Acetic acid synthesis process via methanol hydroxycarboxylation [37].

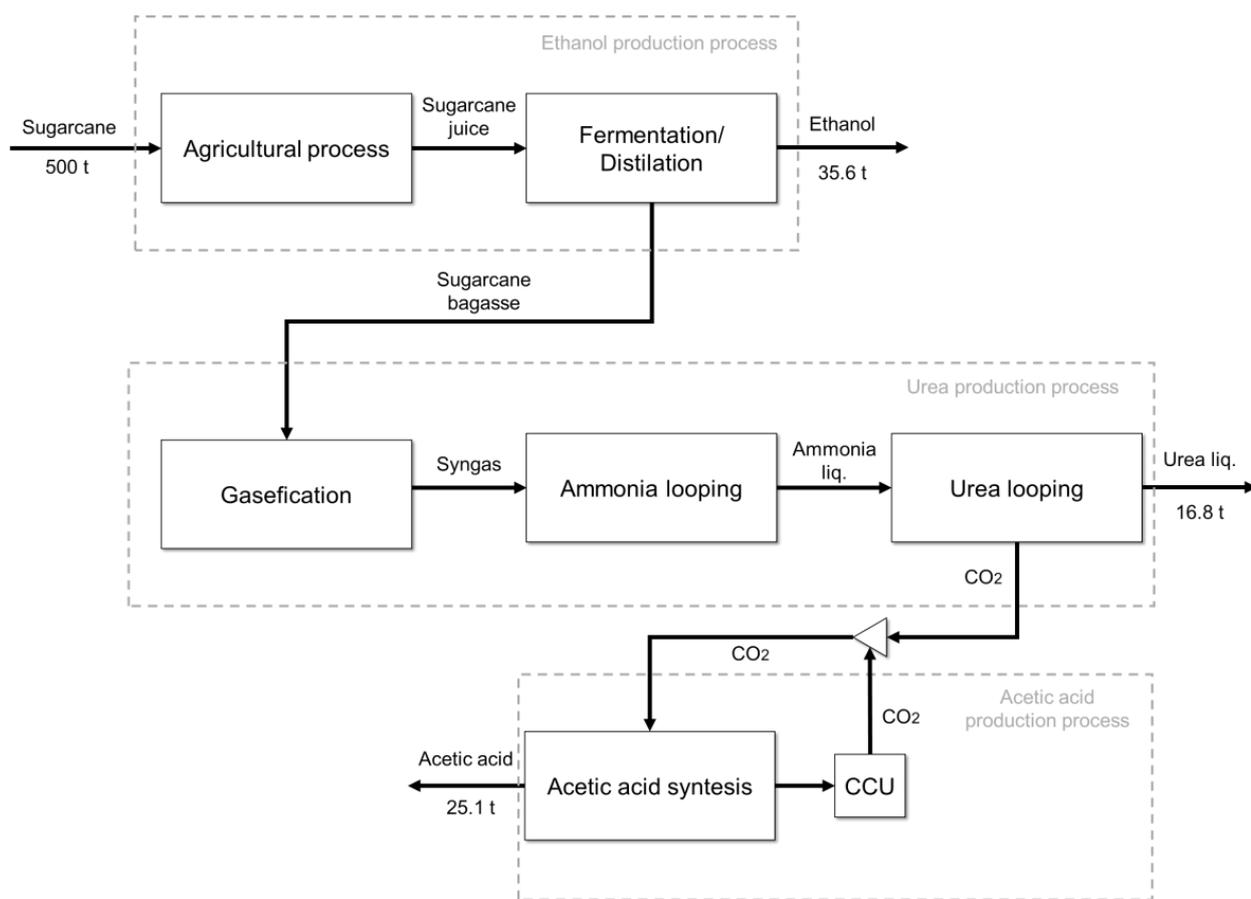


Figure 5. Overview of the integrated arrangements investigated herein.

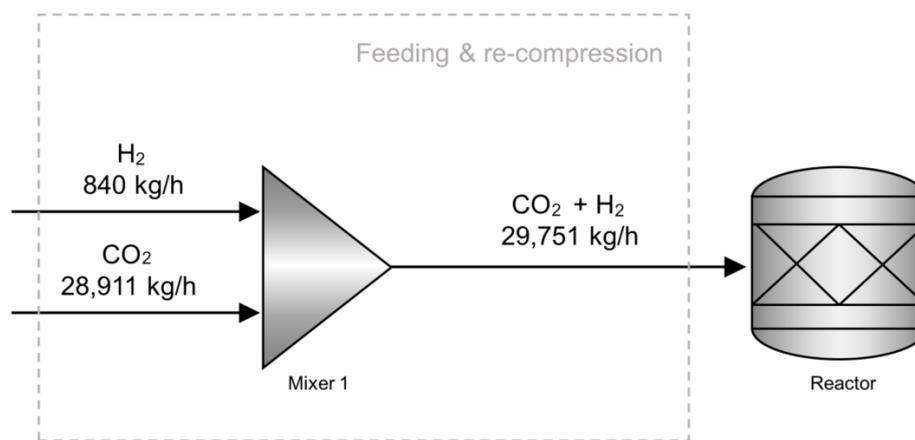


Figure 6. Overview of the mixer of CO<sub>2</sub> and H<sub>2</sub> in the acetic acid synthesis plant.

Table 1. The composition of combustion gas produced from generating 1.0 MJ of heat.

Component	Mass Flow Rate	Unit	Concentration (%) <i>v/v</i>
CO	2.00	mg/h	0.00
CO <sub>2</sub>	76.4	g/h	98.0
CH <sub>4</sub>	1.45	g/h	1.90
N <sub>2</sub> O	1.00	mg/h	0.01
Flue gas	77.8	g/h	100

This processing requires 208 GJ /h of heat, the generation of which also results in 16.2 t/h of combustion gases with 98% *v/v* CO<sub>2</sub>, as the burning of natural gas is carried out with pure O<sub>2</sub>. Such conditions make this flow eligible to meet (partially) the CO<sub>2</sub> demand for manufacturing CH<sub>3</sub>COOH (28.9 t).

As indicated in Figure 4, acetic acid synthesis also produces carbon dioxide in the gas and liquid separation subsystems. Consequently, C2 and C3 can be reinserted into the process after reaching the CO<sub>2</sub> purity grade required to act as reactants in that transformation. This is possible after treating those streams with CCU technology focused on CO<sub>2</sub> capture, purification, transport, and revaluation as an input to supply carbon in chemical production processes. Especially in this case, the purification of the CO<sub>2</sub> existing in C2 and C3 was only possible by installing Pressure Swing Adsorption (PSA). PSA was selected to perform this function because it reaches high gas concentration rates with a low electricity consumption [38].

We estimate the PSA energy consumption for the C2 and C3 treatments based on the similarities of their behaviors with that of a unit for H<sub>2</sub> removal from a stream formed predominantly by CH<sub>4</sub> and CO<sub>2</sub>. In that situation, PSA consumed 0.5 kWh/kg of gas to achieve a purification efficiency of  $\eta \sim 91\%$  and generate a product with 95 to 99% *v/v* of H<sub>2</sub> [38]. The strategy was reproduced for PSA 2 and PSA 3 (Figure 7), restricting so that their upper output streams 'CO<sub>2</sub> PSA 2' and 'CO<sub>2</sub> PSA 3' reached a 98% *v/v* CO<sub>2</sub> purity. This procedure projected 2.42 MWh/4.84 t CO<sub>2</sub> consumption in the operation of PSA 2 and 2.03 MWh/4.06 t CO<sub>2</sub> for PSA 3. Table 2 describes the effects of the interventions carried out at PSA regarding changing the streams' composition involved in the purification processes.

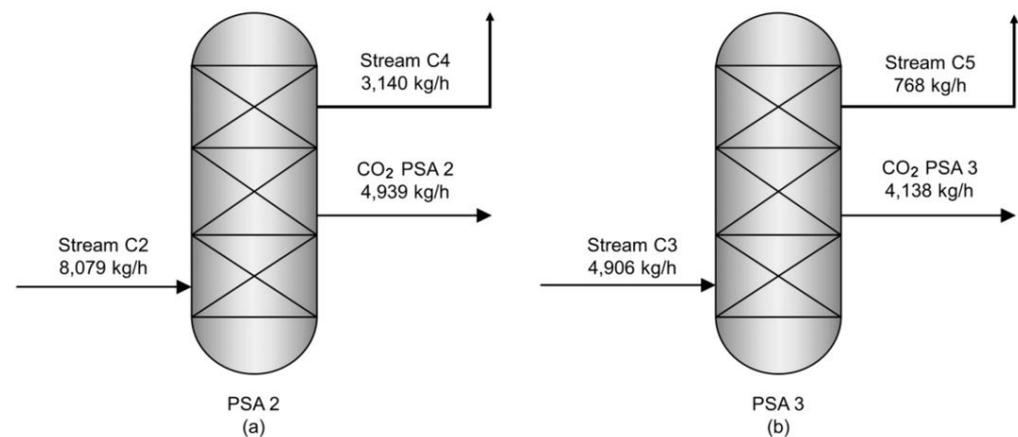


Figure 7. Diagram for CO<sub>2</sub>-rich purification systems, for the C2 (a) and C3 streams (b).

Table 2. Composition of the analyzed streams on a mass basis.

Streams	Composition (% <i>m/m</i> )				
	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>3</sub> COOH	H <sub>2</sub>	H <sub>2</sub> O
C2 stream	21.0	66.3	0.29	12.3	0.17
CO <sub>2</sub> PSA 2	1.89	98.1	0.00	0.00	0.00
C4 stream	51.1	16.2	0.75	31.5	0.43
C3 stream	8.27	91.4	0.06	0.00	0.23
CO <sub>2</sub> PSA 3	1.89	98.1	0.00	0.00	0.00
C5 stream	42.6	55.5	0.42	0.00	1.47

In addition to employing the C2 and C3 streams, another 3.64 t/h of CO<sub>2</sub> is still required to produce the 25.1 t/h CH<sub>3</sub>COOH. This difference was filled using 4.05 t/h of the flue gas released (98.1% CO<sub>2</sub>) from the furnace that supplies the urea production unit. The gaseous stream surplus not used in production was considered to be an atmospheric emis-

sion. Furthermore, the furnace of the urea production system is similar to that employed by the acetic acid system, so the exit gas composition is identical to that described in Table 1.

### 3.4. Environmental Assessment Scenario Development

Initially, we planned to evaluate the integrated plant's environmental performance by comparing its impacts in this domain with the sum of the results achieved with individual sugarcane ethanol, urea, and acetic acid productions. To this end, conventional production technologies would carry out the specific processes. However, a parametric analysis of the integrated process revealed that the CCU technology adopted for PSA 2 to obtain CO<sub>2</sub> PSA 2, the stream of interest for CH<sub>3</sub>COOH synthesis, significantly influenced the arrangement's environmental performance. This led to the development of six scenarios (S1–S6) for the integrated unit, which differed in how PSA 2 and its derived streams (CO<sub>2</sub> PSA 2 and C4) could be considered. A brief description of each of these alternatives is presented below.

Baseline scenario (BS): consisting of non-integrated plants producing ethanol (alcoholic fermentation followed by distillation), urea (Total-Recycle), and acetic acid (Methanol carbonylation);

S1: the C4 stream, from the background of PSA 2 (Figure 7), is released into the environment in the form of atmospheric emissions. In this context, in addition to the negative impacts, the production of 25.1 t/h CH<sub>3</sub>COOH results in the disposal of 3.14 t/h of gases with a high energy content (Table 2), which, if burned, would increase the supply of heat for the process;

S2: C4 is now treated as a by-product of PSA 2, with the potential to be reclaimed to become an input for processes outside the integrated plant. From a strictly conceptual LCA perspective, this condition means that C4 is no longer an emission that burdens the manufacture of acetic acid in environmental terms and, therefore, the other processes in the integrated plant. Conversely, this stream does not receive any environmental loads generated during the production of CH<sub>3</sub>COOH, meaning that all the adverse contributions are attributed to the CO<sub>2</sub> PSA 2 stream;

S3–S5: These scenarios repeat the circumstances established for S2, but consider C4 as a co-product of PSA 2 with well-defined applications outside the integrated plant. This status characterizes a multifunctional PSA 2 situation between CO<sub>2</sub> PSA 2 and C4, which must be treated by allocation because the study applies LCA in the attributional mode [39]. The load partitioning adopted for S3, S4, and S5 is governed by criteria based on physical relationships in the form of mass, CO<sub>2</sub> content, and energy value. The allocation factors used in each scenario are described in Table 3.

**Table 3.** Allocation criteria defined to solve the multifunctional situation in PSA 2.

Scenarios	S3	S4	S5
Allocation criteria	Mass flow	CO <sub>2</sub> content	Energy Content
	(relative values, %)		
CO <sub>2</sub> PSA 2	61.1	90.5	0.00
C4	38.9	9.50	100

S6: C4 is considered to be a system emission, as occurs in S1. However, before being released into the environment, these gases undergo complete combustion in a flare to reduce their Global Warming Potential by converting CH<sub>4</sub>, a high GWP contributor, into CO<sub>2</sub>, a lower one. The amounts of CO<sub>2</sub> and H<sub>2</sub>O resulting from the burning are indicated in Table 4.

**Table 4.** Mass flows and respective flare emission compositions.

Component	Mass Flow Rate (kg/h)	Composition (% w/w)
CO <sub>2</sub>	4954	28.3
H <sub>2</sub> O	12,549	71.7

A brief description of each scenario set up to examine the environmental performance of the integrated plant is shown in Table 5.

**Table 5.** Summary scenarios for each environmental assessment investigated herein.

Scenario	Description
Baseline	Conventional ethanol + urea + acetic acid route with no integration
S1	No allocation. C4 is considered an emission to air
S2	Hypothetical scenario, without allocation, but with by-product recognition
S3	Mass Allocation in the C4 stream
S4	Allocation by CO <sub>2</sub> content in the C4 stream
S5	Energy Allocation in the C4 stream
S6	No allocation. C4 is burned in flare before being emitted (variation of S1)

### 3.5. Life Cycle Modeling

The environmental performances of the scenarios under analysis were determined through Life Cycle Assessment in the attributional mode and for a ‘cradle-to-grave’ scope, which restricts this class of diagnosis to the anthropogenic interventions included in the production cycle. Following the methodological guidelines described in ISO 14044 [15], the technique was applied to a reference flow (RF), which consisted of ‘producing 35.6 t of anhydrous ethanol (99.5 w/w), 16.8 t of urea, and 25.1 t of acetic acid’. The analyses were carried out using secondary data from two sources: (i) the process indicators and operating parameters applied in the modeling of the integrated plant, from which scenarios S1–S6 were derived; and (ii) datasets compiled from the Ecoinvent<sup>®</sup> database to describe the environmental behavior of the typical processing of ethanol, urea, and acetic acid, which defined the baseline scenario. Ecoinvent databases were also employed in specifying the environmental loads associated with the agricultural production of sugarcane and generating electricity and heat.

In conceptual terms, the integration between processes is feasible because the surplus bagasse from ethanol production becomes a primary input for urea synthesis. This aspect served as an argument for selecting the state of São Paulo, the leading producer of biofuel in the country, as the Geographical Coverage for this study. The Temporal Coverage of the data referred to the 2019–2022 quadrennium, while the Technological Coverage comprised the transformation practices, operations, and techniques discussed in Sections 2.1–2.3.

The multifunctional situations identified in the systems—in the sugarcane milling (between bagasse and sugar juice), oil refining (diesel and other oil derivatives), and PSA 2 (CO<sub>2</sub> PSA 2 and C4, for scenarios S3–S5)—were dealt with by the allocation procedure, using criteria based on physical relationships.

A comparison between scenarios applying different impact categories and in which environmental performances differ in trends according to the analyzed effects becomes a complicated and often inconclusive task [40]. Thus, the environmental impact of each scenario was described as a fraction of the base scenario results to provide an immediate comparison. This practice has been successfully applied when scenario comparisons are required [41–44]. Observing the input origin, co-product characteristics, and emission destinations associated with the proposed production system, two impact categories were selected using the midpoint characterization method to verify the environmental performances of the established scenarios, namely the Global Warming Potential (GWP)

through the IPCC 2013 method GWP 100a V1.03 [45] and the Primary Energy Demand (PED) through the Cumulative Energy Demand method V1.09 [46].

The first method employed the model based on the time horizon of 100 years published by the Intergovernmental Panel on Climate Change (IPCC). The GWP values for specific gases given in successive IPCC reports are drawn from various sources that have used multiple techniques to derive the input parameters, which is, broadly, the “greenhouse” strength of a particular gas on a per molecule basis [45]. The PED includes all direct and indirect energy used to transform resources into inputs (or production goods) and that into products (consumer goods). It aims to investigate the energy use throughout the life cycle of a good or service. The CED indicator is divided into six subcategories: nuclear, fossil, primary Forest, biomass, solar, wind and geothermal, and water (kinetic energy). A premise common to all these approaches is that energy carriers should have an intrinsic value associated with them. The magnitude in terms of impact of this parameter is determined by the amount of energy taken from nature [46].

### 3.6. Life Cycle Inventory (LCI)

The preparation of the LCIs related to the processing of anhydrous ethanol, urea, and acetic acid consisted of adaptations of the following databases ‘*Ethanol, without water, in 95% solution state, from fermentation {BR} | sugarcane processing, modern autonomous plant | APOS, U*’ [47], ‘*urea production, as N RER*’ [48], and ‘*acetic acid production, product in 98% solution state RER*’ [48] available on the Ecoinvent® database for the process conditions practiced in Brazil, or in the exporting centers that meet their domestic demands. The criterion adopted for these choices was the technological similarity of the assemblies with the technologies considered in the study for the same processes. In the case of the manufacture of ethanol, the primary adaptation consisted of adjusting the environmental loads of the cogeneration system considered by the database, consisting of a boiler operating at 65 bar and 485 °C, therefore suitable for exporting electricity, for an equivalent arrangement but with a lower capacity (21 bar and 420 °C), and only capable of meeting the plant’s electrical and thermal demands. Within this same arrangement, adjustments were also made to the agricultural stage of sugarcane production.

The ‘*sugarcane production | APOS, U*’ database [47] was updated in terms of (i) the emissions derived from agricultural operations, which were estimated using the BR-Calc/ICVCalc tool, developed by Embrapa Environment [49], (ii) the percentages of the area subject to mechanized planting (64%) and mechanized harvesting (89%), and (iii) the type of agrochemicals and their derived emissions, determined using PestLCI Consensus V 1.0, parameterized for Brazil [50].

For the analysis, it was assumed that urea synthesis took place in Brazil. The database collected from Ecoinvent was then customized by incorporating local sources of electricity and heat. Direct emissions of ammonia, carbon dioxide, and particulate matter to air, ammonium ions, and nitrogen to water are included in data available at [51]. The premise that guided the modeling of the original Ecoinvent database dealing with acetic acid production was that the performance of methanol carbonylation technology would be acceptable with its installation in Brazil. On this basis, the sources of the electrical and thermal energy consumed by the process could be corrected for local conditions in the same way as before with the synthesis of  $\text{CO}(\text{NH}_2)_2$ .

The LCI developed to describe electricity generation was based on structuring terms from the ‘*Electricity, high voltage {BR} | production mix | APOS, U*’ database. However, the relative contributions of each source were adjusted for the base year of 2021, based on values collected in [28]. The life cycle associated with natural gas processing (i.e., the extraction, processing, and distribution of the finished product) was constructed using the study by Sakamoto et al. [40] as a reference. To this end, the databases ‘*Natural gas, high pressure {NL} | petroleum and gas production, off-shore | APOS, U*’ [52] and ‘*Natural gas, high pressure {RU} | natural gas production | APOS, U*’ [52] were collected to represent, respectively, the extraction of raw gas off the Brazilian coast, which corresponds to 61% of the domestic

supply of the product, and in the gas fields of Bolivia, from where the rest of the availability is exported.

#### 4. Environmental Results

The results of the comparison in terms of the GWP and PED of the routes described for the production of 35.6 t ethanol, 16.8 t urea, and 25.1 t acetic acid (values that balance, integrate, and connect the system to the crushing of 500 t of sugarcane) through the LCA methodology are presented in Table 6.

**Table 6.** Environmental performances of the scenarios under analysis, in absolute and relative values (in relation to the baseline).

Route	Environmental Performance (/RF)			
	Impact Category			
	GWP	GWP Relativized to BS	PED	PED Relativized to BS
	(t. CO <sub>2eq</sub> )	(%)	(TJ)	(%)
BS	71.1	100%	4.54	100%
S1	118	166%	2.47	54%
S2	68.1	96%	2.47	54%
S3	50.1	70%	1.96	43%
S4	61.8	87%	2.29	50%
S5	39.5	56%	1.67	37%
S6	73.0	103%	2.47	54%

Legend: RF: Reference Flow; BS: Baseline Scenario; GWP: Global Warming Potential; and PED: Primary Energy Demand.

Scenario S5 was shown to be the least impactful alternative in the entire series analyzed, as it simultaneously recorded the best cumulative performances in terms of GWP and PED. On the other hand, at the opposite end of the scale, S1 had the worst GWP result, while BS was the most aggressive in terms of PED. The technical arguments that justify such performances, as well as the similarities and fired values with similar results available in the available technical literature on the subject, are presented in the following sections.

#### 5. Results Discussion and Recommendations

##### 5.1. Scenario Analysis

S1 describes the GWP and PED impacts of the integrated plant when C4, the bottom stream from PSA 2, is discharged into the environment. This action releases significant quantities of CH<sub>4</sub> and CO<sub>2</sub> into the atmosphere (51% and 16% of the C4 stream, respectively), contributing significantly to the increase in GWP compared to the impact of the baseline scenario for the same category. Influenced directly by the release of C4, the CH<sub>4</sub> emissions were responsible for 70% of S1's contributions to GWP. As with the other scenarios involving the integrated plant, S1 achieved much better results than BS regarding GWP. This finding only confirms that the integration of ethanol, urea, and acetic acid processing is positive in energy terms. In addition, using PSA as a CCU technology proved to be a correct choice from the same perspective due to its low electrical demand.

Initially, it would have been expected that the GWP and PED impacts would show similar behavioral trends for the scenarios involving the integrated plant, precisely because they correspond to variations in the same arrangement. However, we observed a significant interference in how C4 was disposed of on GWP performance, which was not corroborated in terms of PED. S1 is one of the clearest examples of this dissonance, since its contributions to Global Warming come from methane emanations, which, however, have not been extracted from the Biosphere to have their energy content used. This finding only reinforces the thesis that the indiscriminate draining of gases composed of GWP precursors into the air is a practice that cannot be recommended.

When C4 is treated as a revalued current of the process—as in S2—failing to penalize the performance of the integrated plant, but still without sharing environmental loads with CO<sub>2</sub> PSA 2, the performance of the set to GWP significantly improves, exceeding the achieved BS by about 4.0%. Simultaneously, the system performance for PED in this scenario remains identical to that of S1, reaffirming the detachment of behaviors between GWP and PED.

According to Table 6, S3 provides 30% less impact on GWP than BS. When the comparison is made for PED, this difference reaches 57% in favor of the integrated plant. Such benefits are justified by the decision to give C4 the status of a process coproduct, as already occurs with CO<sub>2</sub> PSA 2. According to ISO 14044 [15], coproducts at a particular stage of the Product System characterize a multifunctional situation, which, from the perspective of attributional LCA, will be dealt with by applying the allocation procedure. In S3, it was decided to allocate the environmental loads generated by the system between C4 and CO<sub>2</sub> PSA 2 in terms of mass criteria. As a result, C4 crossed the boundaries of the product system into another anthropic arrangement, carrying 39% of the environmental loads generated by the integrated plant until the arrangement stage in which multifunctionality was configured. This performance corroborates the findings of Luo et al. (2009) [39] for a similar processing of acetic acid.

S4 and S5 follow similar conceptual paths to S3 in considering C4 as a co-product of PES 2. In this respect, S5 stands out from the others in that it adopts energy content as an allocation criterion, so that C4 reduces the GWP impacts of the integrated plant by ~60%. The treatment of multifunctionality by energy criterion is intense enough that the impact as a PSA is also affected, as its precursors are distributed in the same proportions. As a result, S5 is 63% less impactful in the category than BS.

On the other hand, the results accumulated by S4 are the least attractive among the scenarios that evaluate the influence of the allocation procedure. This outcome is not surprising, however, since the remaining CO<sub>2</sub> content in C4 tends to be minimal, given the efficiency of PSA in terms of its separation. The comparison between the performances of S3–S5 in terms of GWP illustrates the influence that the selection of the allocation criterion has on the overall results of a given impact. Because of this, the treatment of multifunctionality situations continues to be one of the main areas of subjectivity when carrying out an LCA study.

Finally, S6, which considers C4 stream emissions after burning, presents a GWP about 3.0% greater than the sum of the individual contributions to the Global Warming of the conventional routes. This result can be considered as a technical draw with BS, given the uncertainty associated with the applied models. Conversely, a significant reduction in GWP is observed in S6 compared to S1. This was expected, since the combustion of gases from the C4 and C5 streams converts methane into CO<sub>2</sub>, and, despite this step increasing the mass flow of the emission, each kg of fossil methane converted into CO<sub>2</sub> reduces GWP by approximately 30.5-fold [7]. Regarding PED, S6 exhibited a similar performance to S1 and S2, with a 46% reduction in BS. This behavior is justified by the use of bagasse provided by ethanol production as an input into the urea production process without the allocation of any environmental loads between the CO<sub>2</sub> PSA 2 and C4 streams.

To pick up on an essential point in this analysis, the PED reduction observed in all scenarios related to the integrated plant is mainly associated with the contribution of the alternative ethanol production model compared to the conventional one, as the most significant energy demand contribution is related to the use of sugarcane as an input. Therefore, when part of this biomass, in the form of bagasse, is allocated to the urea synthesis, its intrinsic environmental loads leave the ethanol production, reducing the Primary Energy Demand for this product. On the other hand, loads associated with bagasse are attributed to the urea production process. Although this action reduces the PED associated with ethanol, the allocation increases the impact transferred to the urea to the same extent, which would keep the contribution size in the integrated ethanol–urea–acetic acid process, were it not for the fact that the PED intrinsic to bagasse is much smaller

than that associated with the natural gas, a conventional raw material for urea production, which is replaced by sugarcane bagasse as an input.

The similarity in the PED values observed for S1, S2, and S6 is justified by (i) the absence of environmental load allocation between the gaseous streams in the scenarios and (ii) because the gas management of the PSA output (direct release, commercialization without environmental loads, or burning of C4 stream, respectively) neither consumes nor generates energy. For S3, S4, and S5, the environmental load partitioning is determined by different physical amounts, resulting in PED impact reduction variations.

### 5.2. LCA of Ethanol, Urea, and Acetic Acid Production Previous Studies

Comparing the results obtained by this study with the GWP values collected from the literature that deals with the environmental performances of productive arrangements of ethanol, urea, and acetic acid is restricted to individual processes. This is because the integration of these chains to form a unique structure based on Industrial Ecology precepts has yet to be explored in their potential. In any case, Table 7 shows the GWP values taken from official scientific records for the manufacture of these products. The significant variability in these indices is related to factors such as (i) the technical and operational versatility of technologies and (ii) the use of different methodological approaches, Temporal and Geographical coverage, and variables sensitive to the study of LCA.

**Table 7.** GWP impacts associated with ethanol, urea, and acetic acid processes available in the literature.

References	Ethanol Manufacturing	
	GWP (t CO <sub>2eq</sub> /t)	GWP (t CO <sub>2eq</sub> /35.6 t Ethanol)
(Muñoz et al., 2014) [53]	1.60	56.9
(Cavalett et al., 2013) [54]	0.60	21.3
(Caldeira-Pires et al., 2018) [55]	1.63	57.8
(Tsiropoulos et al., 2014) [56]	0.60	21.4
References	Urea Manufacturing	
	GWP (t CO <sub>2eq</sub> /t)	GWP (t CO <sub>2eq</sub> /35.6 t Ethanol)
(Shirmohammadi et al., 2023) [57]	1.54	25.9
(Kumar et al., 2021) [58]	0.71	12.0
(Galusnyak et al., 2023) [59]	0.68	11.4
(Wu et al., 2021) [60]	5.60	94.1
References	Acetic Acid Manufacturing	
	GWP (t CO <sub>2eq</sub> /t)	GWP (t CO <sub>2eq</sub> /35.6 t Ethanol)
(Budsberg et al., 2020) [34]	1.00	25.1
(Petrescu and Cormos, 2022) [61]	4.41	111

After conversion into the reference flow defined for this study, the sum of the GWP portions of each product varies between 57.8 and 263 t CO<sub>2eq</sub>/RF. A relativized and merely exploratory confrontation of the results obtained by this investigation with that universe showed that the impacts of the GWP of most scenarios would be close to the lower limit of the track. Unfortunately, the unavailability of data on PED performance invalidated the realization of an analysis in this context.

### 5.3. CCU Perspective

The treatment of gaseous streams is a critical aspect to address in this analysis. In the environmental modeling that supports the study, the selected CCU technology strongly influences the GWP performance in the alternative modeling of acetic acid (Figure 7). This occurs because it removes 7278 kg/h of CO<sub>2</sub> at a 98.1%*v/v* purity from the exhaust streams

coming from the boilers of the  $\text{CH}_3\text{COOH}$  production process, which corresponds to the sum of the streams  $\text{CO}_2$  PSA 2 and  $\text{CO}_2$  PSA 3. However, this stage also generates waste gas streams (C4), whose  $\text{CH}_4$ -rich compositions represent a considerable environmental impact, since hydrocarbon has a Global Warming Potential factor 30.5 times greater than  $\text{CO}_2$  [7].

It is essential to note the discussion concerning the insertion of CCU technology in industrial processes. Because it is still a developing technology, CCU effectiveness is very much questioned, as this is an energy-intensive process requiring a high consumption to adapt the  $\text{CO}_2$  from other waste streams in terms of purity for using it as an input in other synthesis processes.

On the other hand, the findings reported herein demonstrate that, even with the high energy demand of the PSA systems, process integration via CCU leads to a much better environmental performance than that of conventional routes. So much so that five of the six scenarios investigated exhibited positive results in terms of decreasing the GWP, and all of them reduced the PED. This can be partly explained by the fact that the electricity consumed in the process is provided (by 85%) from renewable sources. In addition, using PSA leads to less energy consumption than other technologies for purifying and concentrating gases of interest.

Some challenges are noted before CCU regarding implementation costs. However, suppose this technology obtains the necessary investments to mature, undergoing optimization processes. In this case, the possibility of further reducing energy consumption and optimizing operational and investment costs is perceived, making the synthesis of other products economically and environmentally viable from  $\text{CO}_2$  reuse in arrangements like those discussed in this research.

#### 5.4. Process Integration Perspective

Despite some potential advantages of integrating production systems in an industrial ecosystem arrangement, such as reduced GHG emissions, a smaller demand for transportation, integrated input management, a reduced need for equipment redundancy, and low waste disposal costs [62], this approach also shows some disadvantages. Among the most recurrent are the difficulty in managing through cooperation [63], the greater complexity of local supply networks, and the need to make production more flexible [64]. Integrated systems like the one proposed in this study require a high material flow management capacity so that one production line can operate by the product flows generated by the others. This is a significant challenge for traditional models. Developing a reliable input supply network is also an obstacle, since any failures in this system can cause systematic problems for a symbiotic model. However, the application of modern tools, such as artificial intelligence, more robust optimization models, and the development of reliable networks that could be integrated with adjacent chains, are adequate operational resources for reducing these difficulties [64–66].

## 6. Conclusions

The chemical industry is one of the economic sectors with the most significant environmental footprint [67]. To minimize its impacts, this prospective study proposes alternatives inspired by the concept of Industrial Ecology to integrate the production of ethanol, urea, and acetic acid, making them less aggressive for the environment than if they were carried out independently. The results obtained from the initiative corroborate the following statements:

- The integration of industrial processes has the potential to considerably reduce the contributions to Global Warming Potential (GWP) and Primary Energy Demand (PED) from the manufacture of those essential inputs;
- CCU technologies based on the use of Pressure Swing Adsorption (PSA) are viable alternatives for reducing environmental impacts in the chemical industry due to their low electrical operating demand, as well as for regions where electricity is mainly generated from renewable sources, as in the case of Brazil;

- The recovery of emissions in industrial processes generates significant environmental benefits and should always be encouraged.

As far as GWP is concerned, the integration of processes did not prove advantageous compared to individualized routes when the gaseous streams resulting from CO<sub>2</sub> purification become emissions and are released untreated into the atmosphere. On the other hand, when these streams came to be seen as co-products, giving rise to situations of multifunctionality in the system, the previous picture was reversed. When environmental loads are allocated in terms of physical criteria such as mass, carbon content, or energy content, there is a significant environmental gain from the integrated process compared to the accumulated performance of stand-alone plants in the same impact categories. Energy content proved to be the most promising alternative for reducing impacts under these conditions, as the revalorized stream leaving the system under analysis was rich in combustible gases.

The need to integrate the industrial processes under analysis becomes even more evident when comparing the SDP results, which indicated significant advantages of collective arrangements over their specific counterparts for all the scenarios analyzed. It is important to note that Brazil's predominantly renewable electricity matrix favors route integration due to its low associated charges, even for energy-intensive systems.

There are several possibilities for exploration concerning future studies derived from this initiative. The first is to check the technical and environmental viabilities of using other CO<sub>2</sub>-concentrated streams to produce acetic acid. Also, it would be best to check the technical possibilities of reusing the fuel-concentrated stream as a complementary source of thermal and electrical energy to be used by the plant. The complex's quest for energy self-sufficiency would bring about even more significant advantages in terms of environmental performance, despite the complexity that the operationalization of this measure could add to the process in terms of management.

Last but not least, an economic feasibility study of the integrated plant should be carried out, considering some of the variants explored in this environmental assessment. The association of this dimension with the others—technical and environmental—could serve as a criterion for designing interconnected multiproduction units.

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