Optimization of CCUS Supply Chains for Some European Countries under the Uncertainty

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Abstract: This paper develops a two-stage stochastic mixed integer linear programming model to optimize Carbon Capture, Utilization and Storage (CCUS) supply chains in Italy, Germany and the UK. Few works are present in the literature about this topic, thus this paper overcomes this limitation considering carbon supply chains producing different products. The objective of the numerical models is to minimize expected total costs, under the uncertainties of the production costs of carbon-dioxide-based compounds. Once carbon dioxide emissions that should be avoided are fixed, according to environmental protection requirements for each country, the optimal design of these supply chains is obtained finding the distribution of carbon dioxide captured between utilization and storage sections, the amount of different carbon-based products and the best connection between each element inside the system. The expected total costs for the CCUS supply chain of Italy, Germany and the UK are, respectively, 77.3, 98.0 and 1.05 billion €/year (1004, 613 and 164 €/ton CO₂ captured). A comparison with the respective deterministic model, analyzed elsewhere, is considered through the evaluation of the Expected Value of Perfect Information (EVPI) and the Value of Stochastic Solution (VSS). The former is 1.29 billion €/year, 0.18 million €/year and 8.31 billion €/year, respectively, for the CCUS of Italy, the UK and Germany. VSS on the other hand is equal to 1.56 billion €/year, 0 €/year and 0.1 billion €/year, respectively, for the frameworks of Italy, the UK and Germany. The results show that the uncertain production cost in the stochastic model does not have a significant effect on the results; thus, in this case, there are few advantages in solving a stochastic model instead of the deterministic one.

Keywords: CCUS supply chain; stochastic model; optimization; mathematical model

1. Introduction

The reduction of carbon dioxide emissions is a crucial international concern, considering that in 2018 emissions were 33.1 Gt [1]. Moreover, it is estimated that carbon dioxide emissions are increasing at an average rate of 0.6% from 2015 to 2040 [2]. However, a value of carbon dioxide concentration in the atmosphere lower than 550 ppm should be assured to maintain the mean global temperature rise below 2 °C by 2100, as established in the 21st United Nations Climate Change Conference (COP21) [3–5]. To reach this goal, reductions of carbon dioxide emissions of 40% by 2030 and of 80% by 2050 were proposed, compared to the level of 1990 [6]. A key role to achieve these objectives is attributed to carbon supply chains: Carbon Capture and Storage (CCS) supply chains, Carbon Capture and Utilization (CCU) supply chains and CCUS supply chains. In these systems, carbon dioxide is captured from large point sources, transported, generally via pipeline, and sent to the storage in the first case, to the utilization in the second case and to the storage and/or utilization sections in the last case [7].
The importance of these systems is made clear by some relevant data. For example, CCS could contribute up to a 32% reduction of carbon dioxide emissions by 2050, while CCUS could reduce greenhouse gas emissions by 7 Gt per year by 2050 [2]. These systems can also be integrated into a global low carbon system to generate negative emission [8]. It is evident that carbon supply chains play a crucial role together with promotion of sustainable energies from renewable sources.

Due to this strategic environmental role, it is important that each element inside the supply chain is connected with others in an optimal way: in fact, the connection of carbon sources at the right sites through the convenient capture technology is a combinatorial problem where the available solutions increase with the number of sites [9]. All solutions should be considered, and it is important to choose the one that minimizes total costs and/or carbon dioxide emissions.

In this context, mathematical models are developed with the aim to design the best system from both economic and environmental point of view. Generally, deterministic models are suggested and used in the literature to design CCUS supply chains in different countries: some significant papers published on this topic are mentioned among the literature references of this work [7,10–14] and were examined in details elsewhere [15].

For Germany, different deterministic models were developed by Ochoa Bique et al. [16], Leonzio et al. [9] and Leonzio et al. [17] with the aim to minimize the total costs. In [16], a carbon supply chain is integrated with a hydrogen supply chain in order to produce methanol. In [9], a CCUS supply chain is considered for methanol production via methane dry reforming. Three different case studies with different hydrogen production paths are considered, and it is found that, to maximize environmental benefits, it is preferable to produce hydrogen via water electrolysis utilizing renewable power sources. In fact, in this case, a lower environmental impact and a higher consumption of carbon dioxide is ensured. However, an amount of methanol higher than the national demand is produced: in [17], carbon dioxide is stored and used to produce different products as methanol, urea, polyurethane, wheat and calcium carbonate; for the treatment of lignin; and for concrete curing. It is the first tentative work to consider more carbon-dioxide-based products in a carbon supply chain. A similar work is considered for the UK, where three different CCUS supply chains with different storage sites (Bunter Sandstone, Scottish offshore and Ormskirk Sandstone) are compared in terms of net present value and payback period [18]. These systems are able to produce methanol, methane, polyurethane and calcium carbonate, as well as to improve concrete curing and tomatoes growing in greenhouses, with minimization of total costs. The results show that the best conditions are realized with Bunter Sandstone as storage site.

Only methane is produced in the CCUS supply chain for Italy through a power to gas system [19]. In this work, different supply chains with different storage sites are compared: the best case ensuring the lowest methane production costs and incomes (when carbon tax and economic incentives are taken into account) is that with Offshore Adriatic Sea as storage site. It is evident that the production of methane requires economic incentives to have a profitable process.

The above models consider a single objective optimization function considering the economic aspect of the carbon infrastructure. The solution of a multi-objective deterministic problem for a CCUS system is also addressed in the literature (see, for instance, [20]). The economic and environmental performances are simultaneously optimized using the Life Cycle Optimization framework.

In addition to deterministic models (with single or multiple optimization), stochastic models are considered for carbon supply chains. The advantages of stochastic models are the following: they are able to describe carbon systems in a more realistic way, because parameters assume a value with a defined probability; they make uncertainty explicit; and they make it easy to quantitatively take into account ranges and likely outcomes. However, a stochastic model is more complex than a deterministic one and is limited by computing resources as well as simulation errors.

In addition to carbon supply chains, stochastic models can be applied to different research areas: combined cooling, heating and power micro-grids [21,22], enzymatic hydrolysis of lignocellulosic biomass [23], home energy management [24] and other energy systems [25,26].
Different factors influence reliability of carbon supply chains planning. Regarding the storage site, uncertainties are related to permeability, capacity and porosity of reservoirs [27–29]. In addition to these, uncertainties are present inside a supply chain due to the fluctuation of carbon dioxide sources, variability of construction and operation costs, capture technology and unpredictable events [29–31]. In addition, external factors, such as carbon policy, technology, engineering performance and market forces can influence the design of these systems [32]. There are different ways to consider uncertainties in a supply chain: chance constrained programming [33], robust optimization [34], fuzzy mathematical programming [35] and the most popular two-stage stochastic model [36].

In the literature, stochastic models are mainly applied to CCS supply chains [37–40]. Han and Lee [39] considered a CCS infrastructure with uncertainties on carbon dioxide sources. In another work, the variability of operating and production costs is considered [38]. In [41], uncertainties are considered in the carbon dioxide price and tariff eligible per ton of carbon dioxide transported. Lee et al. [27] presented a stochastic mixed integer linear programming (MILP) model with multi-objective optimization for a CCS in South Korea. The system considers the minimization of costs, environmental impact and risk caused by uncertainty. The trade-off between cost and environmental impact in presence of uncertainties is suggested for decision makers. Their results show that uncertainties may be significant in the design of carbon frameworks. A multi-objective optimization based on a stochastic model was suggested by Zhang et al. [42] for a CCS supply chain in northeast China, where carbon tax is the variable parameter. Economic and risk objective functions are considered. The results show that, according to the value of risk level, CCS is suggested or not, with a specific value for carbon tax. A two-stage stochastic model for a system where the utility supply is integrated with a CCS considering the uncertain utility demand was studied by Ahn and Han [43], while the uncertainty of utility demand and carbon dioxide reduction was reported by Ahn and Han [44]. In a recent study, an approach different from the stochastic model and based on mixed integer linear optimization was used by d’Amore et al. [3]. Uncertainties of storage capacity for a CCS supply chain in Europe are considered, while the system is optimized in terms of resilience on risk (quantified as additional infrastructure costs). It is found that the supply chain designed and optimized is intrinsically resilient to the uncertainty. In addition, the results show that the risk due to storage capacity is negligible compared to the overall cost of the system.

Few stochastic models are present for a CCUS supply chain. Lee et al. [45] developed a two-stage stochastic model for a CCUS supply chain producing polymers and bio-butanol in Korea. The annual profit is maximized, while the environmental impact and risk due to the uncertainties are minimized simultaneously. Operating costs, carbon dioxide sources and energy consumption are the stochastic parameters. The model suggests solutions for decision makers according to their aptitude to risk. A different stochastic simulation for a CCUS supply chain with CO$_2$-EOR in Denmark was presented by Suicmez [46]: the price of oil and carbon dioxide, discount and hydrocarbon tax rates are changed. The results show that the net present value is between $-415$ and $1018$ million€. Uncertainties on coal price and carbon trading price were considered for a CCUS supply chain with CO$_2$-EOR in China by Fan et al. [47].

The aim of this research work is to overcome the present limitation in the development of stochastic models for CCUS supply chains producing a variety of carbon-based products: a two-stage stochastic model is used to re-design the CCUS supply chains that we developed elsewhere for Germany, Italy and the UK, as shown in Figure 1, where carbon dioxide is captured at the respective flue gas source, transported via pipeline and stored or utilized in different routes according to the principles of circular economy [16–18].

The above countries are chosen due to the highest carbon dioxide emission value in Europe (carbon dioxide emissions were of 419.820, 719.883 and 320.411 Mton, respectively, in the UK, Germany and Italy in 2014) [18].

As explained above, these CCUS supply chains take into account more carbon-dioxide-based products compared to those considered in previous works, such as polymers, bio-butanol and oil.
An additional point of novelty of this research is that the production cost of carbon dioxide products is considered as a stochastic parameter. This parameter is considered as stochastic one because it is a term of the objective function, thus directly influences the design of supply chains with a significant effect. Moreover, the production cost of carbon-dioxide-based products is influenced by the market during the year, thus it is not a fixed term but subjected to fluctuations. This parameter is important because it is related to carbon dioxide utilization, the core of CCUS supply chains aiming to the development of a circular economy: it is the main item to be considered in the optimization model.

Then, in this work, the variation in production costs of different carbon-dioxide-based products within certain limits is taken into account to generate stochastic parameters with a discrete normal probably distribution. The results obtained are compared with those of the respective deterministic model in order to evaluate the influence of these uncertainties on the design of carbon systems.

![Figure 1. Scheme of the CCUS supply chain of: (a) Germany; (b) the UK; and (c) Italy.](image)

2. Materials and Methods

2.1. Problem Statement

A two-stage stochastic programming model for the design of CCUS supply chains is presented in this section. In this approach, some decisions, as recourse actions, are made after uncertainty is disclosed [48].

The mathematical model is developed according to the main assumptions described by Leonzio and Zondervan [19] for the framework of Italy, Leonzio et al. [17] for the framework of Germany and
Leonzio et al. [18] for the framework of the UK, considering, however, the uncertainty and then a random nature for the production cost of carbon-dioxide-based products.

Overall, it is supposed that: (i) capture plants and carbon dioxide sources are located at the same place; (ii) one source node can be connected to only one capture node in the storage and utilization section [9]; (iii) carbon dioxide is transported via pipeline [9]; (iv) the system structure is designed over a period of 25 years, considering the uncertainty of production costs [16]; (vi) constant rate of compound production over time [16]; (vii) the stochastic parameters have a normal discrete probability distribution, with mean value defined by the previous deterministic treatment (stationary conditions) and standard deviation of ±20% with respect to the stationary condition [44,49]; and (viii) the stochastic parameters are defined under different scenarios [50].

Information is also provided about each element inside the supply chain [19]. In particular, this information concerns locations, costs, capture materials/technologies, carbon dioxide concentration in the flue gas and respective flow rate, carbon dioxide conversion factors in the production of chemicals, distances between different sites, production costs of carbon-dioxide-based products, etc.

Under uncertainty, given the above information, the best connection between each element of the supply chain is found to minimize the objective function (expected total costs).

Three different optimizations are considered, one for each country.

2.2. CCUS Supply Chain Model

A MILP model is suggested for the stochastic problem, defining sets, variables, constraints, equations and the objective function.

2.2.1. Sets

An index is introduced to define each element of carbon framework [17,18], as reported in the nomenclature, and an index “s” is considered to define a scenario of the stochastic problem, with the respective probability.

2.2.2. Parameters

The same parameters used to describe the deterministic supply chains in [17–19] are considered in the suggested stochastic model, as also reported in the nomenclature.

2.2.3. Variables

According to the stochastic formulation, decision variables are classified into first stage (here and now) variables and second stage (wait and see) variables [50]. First stage variables are design variables, thus insensitive to the uncertainty, and defined before the realization of the random parameter. In this work, these first stage variables are the binary variables $X_{i,j,k,s}$ suggesting the storage site for each scenario and $Y_{i,j,k,s}$ suggesting the capture system in each scenario. Second stage variables are operation variables, defined after having known the uncertainty. They compensate and correct the decision taken at the first stage, in order to reach the best compromise. In the stochastic model, second stage variables define the carbon dioxide flow rate to the utilization and storage section, respectively. These (reported in the nomenclature) are continuous variables, which define the amount of carbon dioxide required to produce a unit mass of each product in the utilization section.

2.2.4. Constraints

For the supply chains considered in this work, common constraints are considered. Carbon dioxide flow rate cannot be divided among multiple storage sites and also the one to one coupling principle should be considered for the storage site, as expressed by this relation (see Equation (1)):

$$\sum_{(j,k)\in(J,K)} X_{i,j,k,s} \leq 1 \ \forall \ (i, s) \in (I, S) \quad (1)$$
where $X_{i,j,k,s}$ are binary variables defined above. The storage site has a maximum capacity to store emissions, as considered in this relation (see Equation (2)):

$$\sum_{(j,k) \in (J,K)} CS_i \cdot FR_{i,j,k,s} \leq \frac{C_{k}^{\text{max}}}{\text{TH}} \quad \forall (i,s) \in (I,S)$$

(2)

where $CS_i$ is the amount of carbon dioxide from the selected source “$i$”, $C_{k}^{\text{max}}$ is the maximum amount of carbon dioxide that can be stored at the storage site “$k$”, TH is the time horizon of the framework in years and $FR_{i,j,k,s}$ is defined above.

The supply chain is considered in order to reduce carbon dioxide emissions at least according to the minimum target set by the environmental policies, as stated in this relation (see Equation (3)):

$$\text{Total captured CO}_2 \geq CR^\text{min} \quad \forall s \in S$$

(3)

where $CR^\text{min}$ is the minimum amount of carbon dioxide emission that should be reduced, while the total carbon dioxide captured in each scenario is defined considering the carbon dioxide emissions sent to the utilization and storage section (in particular, the total carbon dioxide captured is given by $\sum_{i,j,k} CS_i \cdot FR_{i,j,k,s} + CS_i \cdot \text{Utilization}_{i,j,k,s}$ for the framework in Germany and the UK and by $\sum_{i,j,k} CS_i \cdot FR_{i,j,k,s} + CS_i \cdot MR_{i,j,k,s}$ for the framework in Italy).

From a selected source, no more than 90% of carbon dioxide is captured from the flue gas, as follows (see Equation (4)):

$$\text{Fraction of captured CO}_2 \text{ in a source}_s \leq 0.9 \quad \forall s \in S$$

(4)

where the fraction of carbon dioxide captured from a specific source “$i$” is defined as $\sum_{i,j,k} CS_i \cdot FR_{i,j,k,s} + \text{Utilization}_{i,j,k,s}$ for the framework in Germany and the UK and as $\sum_{i,j,k} CS_i \cdot FR_{i,j,k,s} + MR_{i,j,k,s}$ for the framework in Italy.

To obtain carbon dioxide with a purity equal to or higher than 90%, its content in the flue gas streams should be constrained between a minimum ($XL_{j}$) and maximum ($XH_{j}$) level (in mole%, see Equation (5)):

$$\sum_{(k) \in (K)} (XH_{j} - XS_{i}) \cdot (XS_{i} - XL_{j}) X_{i,j,k,s} \geq 0 \quad \forall (i,j,s) \in (I,J,S)$$

(5)

where $XS_{i}$ is carbon dioxide composition in flue gas emissions from source “$i$” (mole%) and $j$ indicates the capture plant. This relation is valid for the storage section, while different or higher purities are needed in the utilization sites and these are assumed to be obtained at the respective production site.

One capture system is assumed for each carbon dioxide source, as follows (see Equation (6)):

$$\sum_{(j,k) \in (J,K)} Y_{i,j,k,s} \leq 1 \quad \forall (i,s) \in (I,S)$$

(6)

For the framework of Germany, it is assumed that the amount of different products should be higher than the national demand, as defined in this relation (see Equation (7)):

$$\text{Produced amount of a product}_s \geq \text{National demand} \quad \forall s \in S$$

(7)

This assumption is not taken into account for the framework of Italy and the UK because the carbon dioxide captured is lower than that required to produce methane according to the national demand in these cases.
Overall, the mathematical model so developed is made linear by using the Glover linearization, as expressed by the following constraints (see Equations (8)–(10)):

$$0 \cdot Y_{i,j,k,s} \leq \text{Utilization}_{i,j,k,s} \leq 0.9 \cdot Y_{i,j,k,s} \quad \forall \, (i, j, k, s) \in (I, J, K, S) \quad (8)$$

$$0 \cdot Y_{i,j,k,s} \leq \text{MR}_{i,j,k,s} \leq 0.9 \cdot Y_{i,j,k,s} \quad \forall \, (i, j, k, s) \in (I, J, K, S) \quad (9)$$

$$0 \cdot X_{i,j,k,s} \leq \text{FR}_{i,j,k,s} \leq 0.9 \cdot X_{i,j,k,s} \quad \forall \, (i, j, k, s) \in (I, J, K, S) \quad (10)$$

with the continuous (Utilization$_{i,j,k,s}$ and MR$_{i,j,k,s}$) and binary (X$_{i,j,k,s}$ and Y$_{i,j,k,s}$) variables defined above, while 0.9 indicates that at most 90% of carbon dioxide is captured from a selected source.

For the CCUS framework of Germany and the UK, carbon dioxide sent to the utilization section is distributed to the several production sites as follows (see Equations (11) and (12)):

$$\text{Utilization}_{i,j,k,s} = \text{Concrete}_{i,j,c,s} \cdot n_{\text{sites,c,s}} + \text{Wheat}_{i,j,w,s} \cdot n_{\text{sites,w,s}} + \text{Lignin}_{i,j,l,s} \cdot n_{\text{sites,l,s}} + \text{Polyurethane}_{i,j,p,s} \cdot n_{\text{sites,p,s}} + \text{Calcium Carbonate}_{i,j,c,c,s} \cdot n_{\text{sites,c,c,s}} + \text{Urea}_{i,j,u,s} \cdot n_{\text{sites,u,s}} + \text{Methanol}_{i,j,m,s} \cdot n_{\text{sites,m,s}} + \text{Concrete By Red Mud}_{i,j,cr,s} \cdot n_{\text{sites,cr,s}} \quad \forall \, (i, j, k, c, w, l, p, cc, u, m, cr, s) \in (I, J, K, C, W, L, P, CC, U, M, CR, S) \quad (11)$$

where Utilization$_{i,j,k,s}$, Concrete$_{i,j,c,s}$, Wheat$_{i,j,w,s}$, Lignin$_{i,j,l,s}$, Polyurethane$_{i,j,p,s}$, Calcium Carbonate$_{i,j,c,c,s}$, Urea$_{i,j,u,s}$, Methanol$_{i,j,m,s}$ and Concrete by red mud$_{i,j,cr,s}$ are the second stage variables, while $n_{\text{sites,c,s}}$, $n_{\text{sites,w,s}}$, $n_{\text{sites,l,s}}$, $n_{\text{sites,p,s}}$, $n_{\text{sites,c,c,s}}$, $n_{\text{sites,u,s}}$, $n_{\text{sites,m,s}}$ and $n_{\text{sites,cr,s}}$ are the number of sites for each carbon compound in Germany.

$$\text{Utilization}_{i,j,k,s} = \text{Concrete}_{i,j,c,s} \cdot n_{\text{sites,c,s}} + \text{Tomato}_{i,j,t,s} \cdot n_{\text{sites,t,s}} + \text{Polyurethane}_{i,j,p,s} \cdot n_{\text{sites,p,s}} + \text{Calcium Carbonate}_{i,j,d,s} \cdot n_{\text{sites,d,s}} + \text{Methanol}_{i,j,m,s} \cdot n_{\text{sites,m,s}} + \text{Methane}_{i,j,g,s} \cdot n_{\text{sites,g,s}} \quad \forall \, (i, j, k, c, t, p, d, m, g, s) \in (I, J, K, C, T, P, D, M, G, S) \quad (12)$$

where Utilization$_{i,j,k,s}$, Methanol$_{i,j,m,s}$, Methane$_{i,j,g,s}$, Polyurethane$_{i,j,p,s}$, Tomato$_{i,j,t,s}$, Concrete$_{i,j,c,s}$ and Calcium Carbonate$_{i,j,d,s}$ are the second stage variables defined above, while $n_{\text{sites,c,s}}$, $n_{\text{sites,t,s}}$, $n_{\text{sites,p,s}}$, $n_{\text{sites,d,s}}$, $n_{\text{sites,m,s}}$ and $n_{\text{sites,g,s}}$ are the number of sites for each carbon compound in the UK.

In addition to the above constraints, the non-anticipativity constraints are assumed for the first stage variables: their value is the same for all scenarios [51,52]. With these constraints, it is assumed that the decision should depend only on information available at the time of the decision and not on future observations [53,54].

2.2.5. Equations

In addition to constraints, equations are used in the two-stage stochastic model to define carbon dioxide capture costs, carbon dioxide transportation costs and carbon dioxide storage costs. Carbon dioxide capture and compression costs (€/year) are obtained from this general equation (see Equation (13)):

$$\text{CC} = \text{CDC} + \text{CIC} + \text{COC} \quad (13)$$

where CDC, CIC and COC are, respectively, the flue gas dehydration costs, investment costs and operating costs [19]. For the dehydration of gas (not required for amine absorption), tri-ethylene glycol absorption is used and this operation costs 9.28 €/ton CO$_2$ (including capital and investment costs) [55]. Investment and operating costs are defined as [56,57] (see Equation (14)):

$$\text{CIC or COC} = (\alpha + \beta x_{\text{co2}} + \gamma) \cdot F^m \quad (14)$$
where $\alpha$, $\beta$, $\gamma$, $n$ and $m$ are fixed parameters depending on technology and material (reported in Table S4) [58], $x_{\text{CO}_2}$ is carbon dioxide molar fraction in the flue gas and $F$ is flue gas flow rate in mol/s. For the ionic liquid (IL) absorption, this relation is suggested [59] (see Equation (15)):

$$CIC \text{ or } COC = (\alpha \cdot F + \beta)x_{\text{CO}_2} + \gamma \cdot F^m$$  \hspace{1cm} (15)

where parameter $\alpha$, $\beta$, $\gamma$ and $m$ are defined as in Table S4 [59] and $x_{\text{CO}_2}$, carbon dioxide molar fraction in the flue gas and $F$ flue gas flow rate are in mol/s.

Carbon dioxide transportation costs (TC) (€/year) consist of investment (TIC) and operating costs (TOC) (see Equation (16)) [19]:

$$TC = CCR \cdot TIC + TOC$$  \hspace{1cm} (16)

where $CCR$ is the capital cost recovery. Investment costs are defined using the relation suggested by Serpa et al. [60] (see Equation (17)):

$$TIC = (\alpha_t \cdot F_{\text{CO}_2} + \beta_t) \cdot F_T \cdot (D + 16)$$  \hspace{1cm} (17)

with $\alpha_t$ equal to 0.019 and $\beta_t$ equal to 0.533 [60]. $F_{\text{CO}_2}$ is carbon dioxide flow rate; $D$ is the distance among carbon dioxide sources, utilization and storage sites according to the latitude and longitude [55]; $F_T$ is a terrestrial factor equal to 1.2 [61]; and 16 km is an additional distance to consider paths related to process [62]. Operating costs are considered as 4% of the investment costs (see Equation (18)):

$$TOC = 0.04 \cdot TIC$$  \hspace{1cm} (18)

Carbon dioxide storage costs (CS) (€/year) consist of investment (SIC) and operating (SOC) costs [19,48] (see Equation (19)):

$$CS = CCR \cdot SIC + SOC$$  \hspace{1cm} (19)

where $CCR$ is the capital cost recovery. The investment costs are defined by the following relation [19,63] (see Equation (20)):

$$SIC = (m \cdot d_{\text{well}} + b) \cdot N_{\text{well}}^{\text{build}}$$  \hspace{1cm} (20)

where $m$ is 1.53 M€/km and $b$ is 1.23 M€ [63], $d_{\text{well}}$ is the depth of the well and $N_{\text{well}}^{\text{build}}$ is the number of wells which need to be built, as (see Equation (21)):

$$N_{\text{well}}^{\text{build}} = \frac{\text{Stored } \text{CO}_2}{IC}$$  \hspace{1cm} (21)

where $IC$ is the maximum injection capacity for well. Operating costs are 4% of investment costs [47] (see Equation (22)):

$$SOC = 0.04 \cdot SIC$$  \hspace{1cm} (22)

2.2.6. Objective Function

When considering a deterministic equivalent problem for the two-stage stochastic model of the supply chains, the objective function is defined by the following relation [53,54,64] (see Equation (23)):

$$\phi = \sum_s \text{probability}_s \cdot \text{Total costs}_s$$  \hspace{1cm} (23)

with the value of probability for each scenario and the value of total costs of carbon framework in each scenario. Each scenario is multiplied by scenario probability of occurrence [65]. The probability is obtained considering that the random production costs have a discrete normal probability distribution with a defined number of realizations sampled randomly using Monte Carlo method [42,52,66]. Real data about these parameters are not present, thus this method is suggested. To this aim, RiskAMP
in Excel is used. The total costs are provided by the sum of carbon dioxide capture and compression costs, carbon dioxide transportation costs, carbon dioxide storage costs and production costs of different products. This objective function is brought at the minimum value in order to provide an expected annual value of the total costs and design the supply chain under the uncertainty. The optimal level of various decision variables that minimizes the expected total costs is suggested for the stochastic MILP model, solved by using AIMMS software.

2.3. Case Studies

2.3.1. CCUS Supply Chain of Italy

The CCUS framework of Italy was described in details by Leonzio and Zondervan [19], where ten regions with higher carbon dioxide emissions are taken into account: Puglia (68.64 MtonCO$_2$/year), Lombardy (46.8 MtonCO$_2$/year), Sicily (41.53 MtonCO$_2$/year), Lazio (28.16 MtonCO$_2$/year), Sardinia (26.4 MtonCO$_2$/year), Veneto (22.5 MtonCO$_2$/year), Emilia Romagna (21.82 MtonCO$_2$/year), Piedmont (19.71 MtonCO$_2$/year), Liguria (17.6 MtonCO$_2$/year) and Tuscany (16.9 MtonCO$_2$/year) [19], as also shown in Table S1. The storage site is located in Offshore Adriatic Sea, while the utilization site producing methane with a power to gas process is set in Verbania. For the system in Italy, methane is proposed to be produced because of the high economic and industrial potential of power to gas installations in Italy was reported by Guandalini et al. [67,68]. Methane in Italy is largely used by industry, in private homes for heating and cooking and by the transportation sector, with a capillary network linking suppliers and utilizers.

The minimum target for the reduction of carbon dioxide emission is 77 Mton/year. MEA absorption, membrane (FSC-PVAm), PSA and VSA with 13X zeolite and ionic liquid (1-butyl-3-methylimidazolium acetate) absorption are the capture technologies considered in the model [19]. In stationary conditions, the methane production cost is fixed at 300 €/MWh, while a standard deviation of ±20% of this expected value is considered under the uncertainty [44,49]. With this assumption, the discrete normal distribution of the stochastic parameter is obtained through Monte Carlo sampling technique [41], as shown in Figure 2.

Twenty-one scenarios with the respective probability are considered.

![Figure 2. Discrete normal distribution for the stochastic parameter methane production cost for the CCUS supply chain of Italy.](image-url)
2.3.2. CCUS Supply Chain of the UK

A detailed description for the CCUS framework of the UK is presented in Leonzio et al. [18], considering these regions as carbon sources: Wales (14.2 MtonCO$_2$/year), Scotland (13.3 MtonCO$_2$/year), North West (15.5 MtonCO$_2$/year) and Yorkshire and the Humber (18 MtonCO$_2$/year) [18], as reported in Table S3. The storage site is set at Bunter Sandstone, while methane, methanol, polyurethane, tomato (growing in greenhouses), concrete curing and calcium carbonate are considered in the utilization section. Except for methane and methanol, two important products obtained from carbon dioxide hydrogenation reactions, other carbon-based compounds are taken into account, chosen by evaluation of the respective market demand in 2030 and of the relatively high technology readiness level of the respective production processes [69].

Different production sites are suggested. For methanol production, Billingham is selected; for methane production, Isle of Grain and Avonmouth are selected, for polyurethane production, Manchester and Alfreton are suggested; for tomato growing, Teesside and Isle of Wight are considered; for concrete curing, York and Wallasey are selected; and, for calcium carbonate production, Lifford, Birmingham and Fort William are suggested [18].

The minimum value for carbon dioxide reduction is 6.4 Mton/year [18].

Different technologies/materials are considered in the model. The absorption with monoethanolamine, piperazine and ionic liquid (1-butyl-3-methylimidazolium acetate) are proposed. POE1, POE2 and FSCPVAm membrane are indicated. 13X, AHT, MVY and WEI zeolites are suggested for pressure swing adsorption (PSA) and vacuum swing adsorption (VSA). The production costs of methanol, methane, polyurethane, tomatoes, concrete curing and calcium carbonate are, respectively, of 608 €/ton, 300 €/MWh, 1349 €/ton, 0.85 €/kg, 21.8 €/ton and 65.2 €/ton [18]. However, an uncertainty with the standard deviation of ±20% with respect to these expected values is considered [49,50], obtaining for each scenario a value of probability distribution, as shown in Figure 3. Monte Carlo sampling technique is used to obtain the discrete normal distribution of production cost for each compound. The normal distribution for the production cost of methane in the UK is different from that of Italy, because these curves are obtained with Monte Carlo technique, based on generation of random numbers.

![Figure 3. Cont.](image-url)
Figure 3. Cont.
The production cost of concrete, wheat, lignin, polyurethane, calcium carbonate, urea, methanol and concrete by red mud are fixed, respectively, at 21.8, 159, 15.4, 6377, 65.2, 257, 608 and 20.95 €/ton [17]. These values were considered in a stationary condition. However, an uncertainty of ±20% of the expected value (applied in the deterministic model) is now followed: for concrete curing 5.32 Mton/year, wheat 21.5 Mton/year, lignin 0.41 Mton/year, polyurethane 12.22 Mton/year, calcium carbonate 65.4 Mton/year, urea 1.48 Mton/year, methanol 940 kton/year and concrete by red mud 21.8 Mton/year [16]. The minimum target for reduction of carbon dioxide emission is 160 Mton/year. Absorption with MEA, PZ and ionic liquid (1-butyl-3-methylimidazolium acetate); membrane with POE1, POE2 and FSCPVA; and vacuum swing adsorption and pressure swing adsorption with 13X, AHT, MVY and WEI are the available capture technologies for this supply chain. The production cost of concrete, wheat, polyurethane, calcium carbonate, urea, methanol and concrete by red mud are fixed, respectively, at 21.8, 159, 15.4, 6377, 65.2, 257, 608 and 20.95 €/ton [17]. These values were considered in a stationary condition. However, an uncertainty of ±20% of the products are considered, as suggested by Patricio et al. [69]. Among them, lignin is obtained through the extraction from black liquor, obtained as a byproduct in the pulp and paper industry, at a pH value between 13 and 14. However, to use it as raw material, a pH of about 8 should be achieved by means of carbon dioxide addition [69]. In this carbon system, lignin is utilized in polyethylene production [70]. Regarding concrete, carbon dioxide is used for curing or to reduce the pH value of red mud; after treatment with carbon dioxide, the mechanical properties of concrete are improved [69].

2.3.3. CCUS Supply Chain of Germany

This CCUS supply chain was described by Leonzio et al. [17]. Carbon sources are the regions with higher emissions: Northrhine-Westphalia (307.3 MtonCO2/year), Bavaria (80 MtonCO2/year), Baden-Württemberg (69.3 MtonCO2/year), Lower Saxony (69 MtonCO2/year), Brandenburg (55 MtonCO2/year), Saxony (48.7 MtonCO2/year), Hesse (42.9 MtonCO2/year), Saxony-anhalt (27.4 MtonCO2/year), Berlin (19.8 MtonCO2/year) and Saarland (19.1 MtonCO2/year) (see Table SI). The storage site is located in Altmark, while methanol, urea, concrete, wheat, polyurethane, calcium carbonate and lignin are produced/treated in different utilization sites. These carbon-based products are considered, as suggested by Patricio et al. [69]. Among them, lignin is obtained through the extraction from black liquor, obtained as a byproduct in the pulp and paper industry, at a pH value between 13 and 14. However, to use it as raw material, a pH of about 8 should be achieved by means of carbon dioxide addition [69]. In this carbon system, lignin is utilized in polyethylene production [70]. Regarding concrete, carbon dioxide is used for curing or to reduce the pH value of red mud; after treatment with carbon dioxide, the mechanical properties of concrete are improved [69].

Ennigerloh and Hannover are selected for concrete curing, Munich and Hannover for wheat cultivation, Cologne and Münchsmünster for lignin extraction and utilization, Schwarzheide and Leverkusen for polyurethane production, Salzgitter and Bremen for calcium carbonate production, Kassel and Hagen for urea production, Leuna and Wesseling for methanol production and Rackwitz and Hamburg for concrete production by red mud [17]. The national demand for each product is defined as follows: for concrete curing 5.32 Mton/year, wheat 21.5 Mton/year, lignin 0.41 Mton/year, polyurethane 12.22 Mton/year, calcium carbonate 65.4 Mton/year, urea 1.48 Mton/year, methanol 940 kton/year and concrete by red mud 21.8 Mton/year [16]. The minimum target for reduction of carbon dioxide emission is 160 Mton/year. Absorption with MEA, PZ and ionic liquid (1-butyl-3-methylimidazolium acetate); membrane with POE1, POE2 and FSCPVA; and vacuum swing adsorption and pressure swing adsorption with 13X, AHT, MVY and WEI are the available capture technologies for this supply chain. The production cost of concrete, wheat, lignin, polyurethane, calcium carbonate, urea, methanol and concrete by red mud are fixed, respectively, at 21.8, 159, 15.4, 6377, 65.2, 257, 608 and 20.95 €/ton [17]. These values were considered in a stationary condition. However, an uncertainty of ±20% of the
expected value (applied in the deterministic model) is now considered for each production cost \([44,49]\), obtaining for each scenario a value of probability, as reported in Figure 4.

The probability of each product is obtained with Monte Carlo technique, supposing a discrete normal distribution. Seven scenarios are considered for the two-stage stochastic model. Here, only seven scenarios are considered to avoid a numerical model too big to converge without serious problems. As in the previous case, the overall probability for each scenario is evaluated as the product of the probability of each product.

![Figure 4](image-url)
Figure 4. Cont.
Figure 4. Discrete normal distribution for the stochastic parameter: (a) concrete by red mud production cost; (b) urea production cost; (c) calcium carbonate production cost; (d) polyurethane production cost; (e) lignin extraction cost; (f) wheat production cost; (g) concrete curing cost; and (h) methanol production cost for the CCUS supply chain of Germany.

2.4. Monte Carlo Method

Monte Carlo method is a computer simulation technique used to have an estimation of the entire probability distribution of an outcome, in this case of a random parameter utilized in the CCUS supply chain. Common probability distributions include normal, lognormal, uniform, triangular, pert and discrete. The most common used distribution is the normal one, according to the following relation (see Equation (24)):

\[ f(x) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \]  

(24)

with \( \sigma \) standard deviation and \( \mu \) mean. Different steps are followed to build the probability distribution curve of a stochastic parameter. At first, it is necessary to choose the probability distribution law and the value of its characteristic parameters are defined (in our case, standard deviation and mean for the normal distribution). After that, a random number between 0 and 1 is associated and the value of the investigated stochastic parameter is found (the value of \( x \) according to Equation (24)). These steps are repeated 1000 times. The values so obtained are used to evaluate the frequency of sampling and then the probability distribution curve.
3. Results and Discussion

The results of these supply chains were obtained solving the MILP model using CPLEX 12.7.1 solver. The computer processor was 2.5 GHz while the memory was 4 GB [19].

3.1. Results for the CCUS Supply Chain of Italy

The model is set up as a MILP model and it is solved in 0.38 s, through 980 iterations.

When the information about methane production cost is changed at random, it is found that the expected value of the objective function and then the expected value of the total costs for the CCUS framework with Offshore Adriatic Sea as storage site is equal to 77.3 billion€/year (1004 €/tonCO$_2$ captured).

First and second stage variables are calculated. Regarding the first stage variable related to the choice of storage site, it is found that the carbon dioxide should be captured from Lombardy region by using MEA absorption and sent to storage site. Regarding the first stage variable related to the choice of capture technology, it is preferable to capture carbon dioxide with PSA adsorption, as also suggested by Kalyana rengan Ravi et al. [55]. However, after knowing the uncertainty, recourse actions are taken, and the second stage variables are defined for each scenario.

It is found that, for each scenario under the uncertainty, an overall amount of 77 Mton/year of carbon dioxide is captured: 44.2 Mton/year are utilized, while 32.8 Mton/year are stored. Overall, 16.1 Mton/year of methane are obtained. Even if the amount of carbon dioxide captured is the same for all scenarios, different carbon sources and capture technologies are suggested (MEA and IL absorption, membrane, PSA and VSA). In this case, MEA absorption is the most used capture technology due to lower costs [17,19]. This solution illustrates that it is impossible, under uncertainty, to find a solution that is ideal for all circumstances. However, in all cases, carbon dioxide is distributed between the utilization and storage section in order to reduce emissions according to the target suggested. Then, capturing a higher amount or choosing only the utilization option would never take place with a perfect forecast.

It is interesting to analyze the cost distribution and then the value of the total costs for each scenario, as in Figure 5, where the respective probabilities are considered.

![Figure 5. Costs distribution for the CCUS supply chain of Italy obtained from the solution of the stochastic problem.](image-url)
The structure of the framework for the scenario with the highest probability is shown in Table 1 (Scenario 11 with a probability of 0.135) and in Figure S1. In this case, the total costs of supply chain are of 75 billion €/year while 16.1 Mton/year of methane are produced.

Table 1. Topology of the CCUS supply chain in Italy for the scenario with the highest probability.

| CO₂ Source | CO₂ Capture Technology | CO₂ Amount (Mton/Year) |
|------------|------------------------|------------------------|
| Lombardy   | MEA absorption         | 33                     |
| Emilia Romagna | MEA absorption     | 20                     |
| Piedmont   | MEA absorption         | 18                     |
| Veneto     | Membrane              | 7                      |

In this scenario, carbon dioxide is captured from Lombardy through MEA absorption and sent to the storage section. In addition, carbon dioxide is captured from Emilia Romagna and Piedmont through MEA absorption and from Veneto from membrane and sent to the utilization section in Verbania for methane production. In this case, membrane technology is used due to the higher carbon dioxide content in flue gas [18,19].

Some parameters are calculated in order to compare the results of the stochastic model with that of the deterministic model. These parameters are the Expected Value of Perfect Information (EVPI) and the Value of Stochastic Solution (VSS).

EVPI is about the knowledge of the future evolution of the system with certainty, in particular the cost that a decision maker could pay to have a perfect information about the future before that the uncertainties will be bared [71]. This parameter is obtained as the difference between the wait and see (WS) solution and the stochastic here and now solution (HN). The first, wait and see solution is calculated by weighting each deterministic scenario with its corresponding probability. For the CCUS framework of Italy with Adriatic Sea as storage site, it results that the wait and see solution is 78.6 billion €/year. This suggests that if it were possible to learn about the future with certainty, the total system costs would only be 78.6 billion €/year. However, the future is not predictable; thus, by solving the stochastic program, it is found for the supply chain an expected value of the costs equal to 77.3 billion €/year. The EVPI of 1.3 billion €/year suggests how beneficial it is to know the future with certainty. In particular, the EVPI/WS ratio of 1.64% shows not a big influence of the uncertainty, thus it is not worthwhile to have a better forecast about the different scenarios [72]. To confirm this result, a value of EVPI of 1.66% of the stochastic solution underlines that an extra effort is not required to have information about the future. VSS suggests the possible gain for solving the stochastic model over a deterministic one, in particular the cost of ignoring the uncertainty for a decision maker. This indicates the importance of solving a stochastic problem. VSS is calculated as the stochastic here and now solution less EEV, defined as the expectation of the expected value (EV) solution [71]. Two steps are required: at first, the EV solution is calculated, and then the EEV solution is found. In particular, the EV solution is obtained by solving a single deterministic problem that uses the expected value of random variables. Afterwards, the solutions for the first stage variables obtained in the first step are set in the stochastic problem that provides in this way the EEV solution [73].

For the considered CCUS framework of Italy, a value for VSS of 1.6 billion €/year is found (the respective value of EEV is of 75.7 billion €/year): solving the stochastic problem rather than the corresponding deterministic problem, 1.6 billion €/year can be saved. It is interesting to evaluate the VSS/EEV ratio, equal to 2.06%, that is the gain of the two-stage stochastic model over the deterministic one [72]. Due to the low value of this ratio, it is not recommended to solve a complex problem as the stochastic one. In fact, as found above, the uncertainty does not have a big influence on the results obtained.
3.2. Results for the CCUS Supply Chain of the UK

The MILP model developed for the CCUS framework of the UK is solved in 15.94 s with 1402 iterations. Random data are provided about the production cost of different compounds (methanol, methane, polyurethane, tomato, concrete and calcium carbonate). The expected value for the objective function, i.e., the total costs of the system, is found equal to 1.05 billion€/year (164 €/tonCO₂ captured), a much lower value than the corresponding ones for the supply chains of Germany and Italy, mainly due to the lower amount of carbon dioxide emissions treated in this case. In the optimized system, the first stage variables are the same for all scenarios. Regarding the binary variable related to the definition of the storage section, it is found that carbon dioxide is captured from the Yorkshire and Humber region by using the VSAWEI capture system and sent to the Bunter Sandstone storage site. Regarding the variable characterizing the choice of capture technology, the PZ absorption is the preferable choice, due to a lower cost compared to the MEA absorption [55]. Second stage variables are, instead, different for each scenario and are related to the recourse actions that should be taken after knowing the uncertainty. Second stage variables define the amount of carbon dioxide that is stored or utilized. Under uncertainty, it is suggested to capture an amount of carbon dioxide that allows to achieve the minimum target for reduction of emission (6.4 Mton/year). In particular, 6 Mton/year of carbon dioxide are utilized, while 0.4 Mton/year of carbon dioxide are stored. This picture is the same for each scenario. However, different amounts of calcium carbonate and polyurethane are obtained in each scenario, as shown in Figure 6. Other carbon-dioxide-based compounds are not produced. In addition, in each scenario, different carbon sources are selected to capture carbon dioxide, although PZ absorption is the capture technology mainly used in the utilization section while VSAWEI is the capture system used in the storage section. The PZ absorption technology is chosen as explained above, while VSAWEI is selected due to the relatively low flow rate and higher carbon dioxide composition [10,52].

![Figure 6](image-url)  
**Figure 6.** Quantity of compounds produced in different scenarios in the two-stage stochastic problem for the CCUS supply chain of the UK.

In this case of study, with random variables, it is impossible to find an ideal solution for all scenarios under all circumstances, even though for all scenarios carbon dioxide is distributed between the utilization and storage section in the same measure, achieving the minimum target for emission reduction. Thus, with a perfect forecast, it is preferable to have both utilization and storage sections, then the importance of providing a storage site, as found by Leonzio and Zondervan [19].
Figure 7 shows the cost distribution for the CCUS supply chain of the UK: for each scenario, the value of the total costs and the respective probability are reported (the scenarios with a probability equal to zero are not taken into account in this plot). Scenario 11 has the highest probability of 0.32, while the respective costs are equal to 1.04 billion€/year. For this case, the topology of the supply chain is reported in Table 2.

![Costs distribution for the CCUS supply chain of the UK obtained with the stochastic problem.](image)

**Figure 7.** Costs distribution for the CCUS supply chain of the UK obtained with the stochastic problem.

**Table 2.** Topology of the CCUS supply chain in the UK for the scenario with the highest probability.

| CO₂ Source | CO₂ Capture Technology | CO₂ Amount (Mton/Year) |
|------------|------------------------|------------------------|
| Leeds      | VSAWEI                 | 0.4                    |
| Leeds      | PZ absorption          | 6                      |

For this scenario, carbon dioxide is captured from Leeds and sent to utilization (6 Mton/year) and to storage (0.4 Mton/year) section. PZ absorption is used in the utilization section, while VSAWEI is used in the storage section, as explained above.

The performance of the stochastic model is measured calculating the expected value of perfect information and the value of stochastic solution, the respective meanings of which were explained in the previous case study.

When considering three significant digits to express the expected total costs and related economic indices, the model does not detect any difference between the wait and see and the here and now solutions, for the EVPI calculation; when assuming numerical errors much smaller than this level of outputs precision, a difference of 0.18 million€/year is detected, over an expected total cost of 1.05 billion€/year, negligible in relative terms. Then, in this second case, 0.18 million€/year, the EVPI value, is the amount that a decision maker could pay for having a perfect information in advance on how uncertainties will be revealed. This rather small value suggests that the uncertainty on the solution is not significant in this case. Regarding VSS, the value of the expectation of the expected value is equal to the stochastic here-and-now solution (1.05 billion€/year). Then, the value of VSS is 0: it is not necessary to solve the more complex stochastic problem, as also found before considering EVPI. The uncertainty is not significant. It is not advantageous to use the stochastic modeling approach
to design the supply chain, when production costs of carbon-dioxide-based products are stochastic parameters, as in the case examined here.

3.3. Results for the CCUS Supply Chain of Germany

In addition, for the CCUS framework of Germany, the two-stage stochastic program is developed as a MILP model and the optimal solution is calculated in 114.33 s through 10,112 iterations.

In the model, the production costs of methanol, concrete, wheat, lignin, polyurethane, calcium carbonate and urea are random and are not defined by a fixed value. In this condition, the expected value of the objective function expressing the total costs of the system is equal to 98.0 billion €/year (613 €/ton CO\textsubscript{2} captured).

First and second stage variables are also evaluated. The first are the same as those of the previous study case, thus suggesting the selection of storage site and the capture technology. These are equal for all scenarios. It results that for the selection of the storage site carbon dioxide is captured from Magdeburg through PZ absorption and sent to Altmark storage site. Regarding the capture technology, PZ absorption is preferred for the selected carbon sources, due to its lower cost [55]. Second stage variables, suggesting carbon dioxide utilized and stored, are related to the recourse actions that a decision maker takes after knowing the uncertainty. Figure 8 shows the amount of carbon dioxide utilized or stored.

The results show that only for Scenarios 1, 2, 6 and 7 all captured carbon dioxide (160 Mton/year) is sent to the utilization section for the production of different compounds. For other scenarios, carbon dioxide captured is used (140 Mton/year) and stored (20 Mton/year). In both cases, carbon dioxide is captured in an amount achieving the minimum target for emission reduction. Only in few scenarios the whole carbon dioxide captured is completely utilized: with a perfect forecast, it is preferable to have a storage and a utilization section inside the supply chain, as in the previous case studies.

![Figure 8](image_url)

Figure 8. Amount of carbon dioxide sent to the utilization and storage section, respectively, and the whole amount of carbon dioxide captured, as defined with the second stage variables of the stochastic problem for each scenario in the CCUS supply chain of Germany.

The amounts of different products in each scenario are reported in Figure 9.
Methanol, concrete curing, polyurethane, urea and concrete by red mud are characterized by constant production rate in each scenario, respectively, of 0.85, 4.8, 11, 1.3 and 19.15 Mton/year. Wheat, lignin and calcium carbonate show a variation in their production rate in some scenarios.

Figure 10 shows the cost distribution for the CCUS framework of Germany with the respective probability (scenarios with a probability equal to 0 are not taken into account in this plot). Scenario 4 has the highest probability, equal to 0.97, while the total costs of the system are equal to 98.1 billion€/year. In this case, the topology of the system is shown in Table 3 and Figure S3: in the utilization and storage section carbon dioxide is captured with PZ absorption, for reasons explained above.
Table 3. Topology of the CCUS supply chain in Germany for the scenario with the highest probability.

| CO₂ Source | CO₂ Technology | CO₂ Amount (Mton/Year) |
|------------|----------------|------------------------|
|            | To storage     |                        |
|            | Madgeburg      | PZ absorption          | 20                      |
|            | Munich         | PZ absorption          | 1                       |
|            | Hannover       | PZ absorption          | 52                      |
|            | Dresda         | PZ absorption          | 44                      |
|            | Wiesbaden      | PZ absorption          | 39                      |
|            | Madgeburg      | PZ absorption          | 4                       |
|            | To utilization |                        |

In particular, 20 Mton/year of carbon dioxide are captured from Magdeburg and sent to the Altmark storage site, while an overall amount of 140 Mton/year of carbon dioxide is captured from Munich, Hannover, Dresda, Wiesbaden and Magdeburg and sent to production of goods.

EVPI and VSS are evaluated for this supply chain as well, in order to analyze the importance of uncertainty. It is found that the EVPI for the stochastic model is 8.31 billion€/year (this amount should be paid by a decision maker to know future evolution with certainty), while the wait and see solution is 106 billion€/year (this is the cost of the system if it were possible to know perfectly its future evolution). In particular, the EVPI solution is 8.48% of the objective function value, then there is not a big influence of uncertainty on the solution and the effort to have information about future is not recommended. In fact, the EVPI/WS ratio is only 7.81%.

Regarding the VSS parameter, a value of 0.1 billion€/year is found, as the possible gain when solving the stochastic model over the deterministic one (the value of the EEV is of 97.9 billion€/year). Negligible values are related to the VSS/EEV ratio and the percentage of VSS over the stochastic objective function: few advantages are obtainable solving the stochastic problem over the deterministic one. In fact, as found with EVPI, the uncertainty on the solution is not so significant.

4. Conclusions

Carbon supply chains are not static processes, but are characterized by uncertainties providing a dynamic aspect to them. In fact, uncertainties are due to variability on carbon sources, operating costs, market, carbon policy, etc. Few works are present in the literature regarding the modeling of CCUS supply chains by means of a stochastic model. This paper aims to overcome this gap, considering supply chains (for Italy, Germany and the UK) that we developed elsewhere and that produce different products.

In Italy, methane via power to gas is produced. In the UK methanol, methane, concrete, tomatoes, polyurethane and calcium carbonate are obtained from carbon dioxide captured. In Germany, carbon-dioxide-based methanol, urea, polyurethane, concrete curing, wheat, lignin extraction and calcium carbonate are considered.

In this research, a two-stage stochastic model with recourse actions is implemented for these carbon frameworks with the aim to find an optimal network and then assist the decision-making process. The production costs of different carbon-based compounds are the stochastic parameters, for which a probability normal distribution is obtained by means of Monte Carlo technique. This parameter is the main item in the objective function and related to the circular economy, thus is chosen in our study providing, also a novelty to the work.

For the CCUS framework of Italy and the UK, 21 scenarios are considered while seven scenarios are considered for the CCUS of Germany. The expected costs of these systems are minimized under the condition to reduce carbon dioxide emissions at least to the value suggested by environmental policies. AIMMS software is used to solve the stochastic mixed integer linear programming model, described utilizing the equivalent deterministic problems linked to non-anticipativity constraints.
It is found that the expected total costs for the CCUS framework of Italy, Germany and the UK are, respectively, 77.3, 98 and 1.05 billion €/year.

The comparison with the respective deterministic model is made evaluating EVPI and VSS. For the CCUS framework of Italy, EVPI and VSS are, respectively, 1.29 and 1.56 billion €/year. For the CCUS framework of the UK, the values of EVPI and VSS are, respectively, 0.18 million €/year (assuming numerical errors much smaller than a reasonable level of outputs precision, equal to 0.1%) and 0 €/year, while it was found that the values of EVPI and VSS are, respectively, 8.31 and 0.1 billion €/year for the CCUS supply chain of Germany.

Overall, the results show that the uncertainties in production costs, under the considered assumptions (quite high technology readiness level, reducing the range of costs variability to a maximum ±20% of the expected one), do not have a big influence on the modeling outputs of these carbon systems, thus only limited benefits are obtained solving the stochastic problem over the deterministic one, when considering the fluctuation of the stochastic parameters investigated here: the production cost of carbon-dioxide-based compounds.

Another insight that can be found is that the variability or fluctuation of carbon-dioxide-based products can be neglected during the design of a CCUS supply chain network and the expected costs can be considered in this calculation. For this reason, it is possible to save time during the building of the mathematical model on finding the cost distribution of carbon-dioxide-based products. It is suggested to use the cost of last years in the market.

Policy-makers, then, in this situation, can use a deterministic model to design the supply chain and not a more complex stochastic model. This can save authors the time and money.

On the extreme case, if carbon-dioxide-based product costs have a big influence (may be affected by much higher uncertainty than that considered in this research), a more detailed model should be considered, such as a stochastic one, after a higher effort in finding data about the fluctuation of this parameter inside the market. This is also what happens for newly synthesized products, or those which were not produced before on a large industrial scale or did not yet enter the international market. Although this mathematical modeling is time consuming, it allows a more realistic description of CCUS supply chains frameworks.

Of course, considering different stochastic parameters may lead to more significant differences between the deterministic and the stochastic approach (a broader analysis extended to other parameters that may vary would be necessary here).

Supplementary Materials: The following are available online at http://www.mdpi.com/2227-9717/8/8/960/s1, Figure S1: Topology of the CCUS supply chain of Italy for the scenario with the highest probability, Figure S2: Topology of the CCUS supply chain of the UK for the scenario with the highest probability, Figure S3: Topology of the CCUS supply chain of Germany for the scenario with the highest probability, Table S1: Data about CO2 source sites for the CCUS supply chain of Italy, Table S2: Data about CO2 source sites for the CCUS supply chain of Germany, Table S3: Data about CO2 source sites for the CCUS supply chain of the UK, Table S4: Data cost for capture and compression technologies, Table S5: Maximum storage capacity of storage site in the CCUS supply chain of Italy, Germany and the UK.

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Nomenclature

Indices

c  concrete production site
cc calcium carbonate production site
cr concrete by red mud production site
d  calcium carbonate production site
g  methane production site
i  carbon dioxide sources
j  carbon dioxide capture technologies
k  carbon dioxide storage and overall utilization sites
l  lignin production site
m  methanol/methane production site
p  polyurethane production site
s  scenario
t  tomatoe growing site
u  urea production site
w  wheat production site

Abbreviation

AIMMS  Advanced Interactive Multidimensional Modeling
CC  Capture Costs (€/year)
CCUS  Carbon Capture Utilization and Storage
CCU  Carbon Capture Utilization
CDC  Flue gas dehydration costs (€/year)
CIC  Capture Investment Costs (€/year)
COC  Capture Operative Costs (€/year)
CO2-EOR  CO2-enhanced oil recovery
CS  Storage Costs (€/year)
F  Flue gas flow rate (mol/s)
F\textsubscript{CO2}  amount of carbon dioxide that is transported (ton/year)
IC  Injection Capacity per well
MEA  Monoethanolamine
MILP  Mixed Integer Linear Programming
N\textsubscript{build\ well}  Number of well
PSA  Pressure Swing Adsorption
PZ  Piperazine
SIC  Storage Investment Costs (€)
SOC  Storage Operative Costs (€/year)
TC  Transportation Costs (€/year)
TH  Time Horizon
TIC  Transportation Investment Costs (€)
TOC  Transportation Operative Costs (€/year)
VSA  Vacuum Swing Adsorption

Parameters

b  parameter in SIC (M€)
Calcium Carbonate\textsubscript{dem}  National calcium carbonate demand (ton/year)
Concrete\textsubscript{dem}  National concrete demand (ton/year)
Concrete by red mud\textsubscript{dem}  National concrete by red mud demand (ton/year)
Ck\textsubscript{max}  Maximum storage capacity at the storage site k (ton)
CR\textsubscript{min}  Minimum target for carbon dioxide reduction (ton/year)
CS\textsubscript{i}  Total carbon dioxide emission from each source i (ton/year)
D  distance (km)
d\textsubscript{well}  depth of well
F\textsubscript{i}  Total feed flue gas flow rate from each source i (mol/s)
F\textsubscript{T}  Terrestrial factor
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Lignin\textsuperscript{dem}

National lignin demand (ton/year)

m

parameter in SIC (M€/km), CIC and COC

MeOH\textsuperscript{dem}

National methanol demand (ton/year)

n

parameter in CIC and COC

Polyurethane\textsuperscript{dem}

National polyurethane demand (ton/year)

x\textsubscript{CO2}

Carbon dioxide molar fraction

X_{Si}

Carbon dioxide composition in the flue gas emission from source i

(mol%)

XL\textsubscript{i}

Lowest carbon dioxide composition processing limit for the capture plant j (mol%)

XH\textsubscript{i}

Highest carbon dioxide composition processing limit for the capture plant j (mol%)

Urea\textsuperscript{dem}

National urea demand (ton/year)

Wheat\textsuperscript{dem}

National wheat demand (ton/year)

Variables

Binary

X_{i,j,k,s} 1 if carbon dioxide is captured from source i with technology j and sent to storage site k in the scenario s, otherwise 0

Y_{i,j,k,s} 1 if carbon dioxide is capture from source i with technology j and sent to storage/utilization site k in the scenario s, otherwise 0

Continuous

Calcium carbonate\textsubscript{i,j,cc,s} fraction of captured carbon dioxide from source i with technology j sent to calcium carbonate production site cc in the scenario s

Calcium Carbonate\textsubscript{i,j,d,s} fraction of capture carbon dioxide from source i with technology j sent to calcium carbonate production site d in the scenario s

Concrete\textsubscript{i,j,cr,s} fraction of captured carbon dioxide from source i with technology j sent to concrete production site by red mud cr in the scenario s

Concrete\textsubscript{i,j,c,s} fraction of captured carbon dioxide from source i with technology j sent to concrete production site c in the scenario s

FR\textsubscript{i,j,k,s} fraction of captured carbon dioxide from source i with technology j sent to storage site k in the scenario s

Lignin\textsubscript{i,j,l,s} fraction of captured carbon dioxide from source i with technology j sent to lignin production site l in the scenario s

Methane\textsubscript{i,j,g,s} fraction of captured carbon dioxide from source i with technology j sent to methane production site g in the scenario s

Methanol\textsubscript{i,j,m,s} fraction of captured carbon dioxide from source i with technology j sent to methanol production site m in the scenario s

MR\textsubscript{i,j,k,s} fraction of captured carbon dioxide from source i with technology j sent to methane production site k in the scenario s

Polyurethane\textsubscript{i,j,p,s} fraction of captured carbon dioxide from source i with technology j sent to polyurethane production site p in the scenario s

Tomato\textsubscript{i,j,t,s} fraction of captured carbon dioxide from source i with technology j sent to tomato growing t in the scenario s

Urea\textsubscript{i,j,u,s} fraction of captured carbon dioxide from source i with technology j sent to urea production site u in the scenario s

Utilization\textsubscript{i,j,k,s} fraction of captured carbon dioxide from source i with technology j sent to overall utilization site k in the scenario s

Wheat\textsubscript{i,j,w,s} fraction of captured carbon dioxide from source i with technology j sent to wheat production site w in the scenario s

Greek Letters

\( \alpha \) parameter in CIC and COC

\( \alpha_t \) parameter in TIC

\( \beta \) parameter in CIC and COC

\( \beta_t \) parameter in TIC

\( \gamma \) parameter in CIC and COC
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