Mathematical programming model for the optimal management of carbon intensity indicators in global supply chains

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Abstract

We propose a rigorous approach for the operational planning of supply chains considering carbon intensity limits in final products. Accurately tracking of these indicators along the value chain can be challenging when dealing with bulk products. Production, transportation, blending and separation of components yield a complex pooling problem within a network structure. A novel mixed-integer nonlinear model is developed to optimize shipping schedules, inventories, processing and distribution of products while complying with environmental constraints of different markets. The model allows for rigorous monitoring and managing of carbon indicators, as well as for drawing important conclusions about sourcing strategies. A decomposition algorithm is presented for this problem, which permits obtaining high quality solutions in reasonable times. A global scale case study is solved to illustrate the economic impact of operating under carbon intensity limits, as well as suggesting alternative operating modes when the penalties on exceeding carbon targets are high.

Keywords: supply chain, carbon intensity, optimization, planning, MINLP

1. Introduction

During the last two decades there has been a significant interest of organizations, researchers and governments to develop sustainable production and logistics systems worldwide. As public agencies work to establish safe criteria for controlling the environmental impacts of economic activities, consumers become more stringent and demand greener products and services. In this context, companies are striving to implement effective operations management strategies that rely on precise quantitative indicators and specific targets. The carbon footprint, defined as the amount of carbon dioxide and other greenhouse gases emitted by direct or indirect human activity, has been one of the most important indicators for controlling emissions and building environmental management strategies for procurement, production, transportation and inventory management across supply chains (Benjaafar et al., 2013). Increasingly, sustainability reports and strict regulations such as carbon trading systems, carbon cap and carbon taxes appear to be the most effective ways to promote carbon footprint reduction in value chains (Caritte et al., 2015). To meet these demands and stay competitive, companies need to evaluate several important factors. On the one hand, they need to assess and identify critical stages in the supply chain where they can implement operational changes to reduce environmental impact without compromising business goals. On the other hand, accurate

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tools are required to track indicators, define goals and measure the progress of changes while predicting network behaviors. Furthermore, it may be necessary to collaborate with suppliers of raw materials, intermediate products, or logistics services to effectively manage carbon indicators (Ghosh et al, 2020).

Although carbon footprint indicators are currently the primary focus of regulations, there are other indicators that can aid in identifying processes and guiding actions to enhance the environmental performance of supply chains. In fact, these indicators are increasingly being recognized as new benchmarks for evaluating the sustainability of production processes. Carbon intensity (CI) indicators seek to assess emissions per unit of economic activity or output of a process and are key elements in sustainable operations management. Carbon intensity labels of products and services seem to be one of the most promising and effective strategies for the future in terms of specifying the environmental quality of goods, providing transparency to consumers, partners and regulators (Burgess and Nye, 2008; Xu and Lin, 2021; Majer et al., 2022, Taufique et al., 2022). Furthermore, new perspectives are proposed from these indicators for analyzing operations (processing, storage, transportation) and related energy consumption to determine their specific contribution to unit emissions, and deciding on technological improvements to aid in supply chain planning. However, performing tasks in a cleaner way often requires increasing operating costs, reducing throughput or affecting delivery times, leading to a significant trade-off between economic performance and sustainability (Martí, 2015; Mala, 2022). Optimally planning operations in a value chain using rigorous tools allows organizations to respond to their customers in the timely delivery of goods and services, while respecting environmental constraints or goals. Nevertheless, for many industries, tracking carbon intensity indicators accurately along a supply chain is not trivial.

In this paper, we present a general mathematical programming model that allows planning production and logistic operations in an economical way considering carbon intensity constraints imposed by different markets. By means of a State-Network-Task (STN) representation (Kondili et al., 1993) we accurately monitor the carbon intensity of the products through the operations of the supply chain. This monitoring is particularly relevant when dealing with bulk products because different streams with different carbon intensities can be mixed to comply with restrictions, like in pooling problems (Castro, 2016). Thus, a nonlinear, non-convex formulation is obtained of the corresponding mixed-integer nonlinear programming model giving rise to serious challenges when seeking for optimal solutions. To tackle these challenges, an efficient decomposition is proposed to obtain high quality solutions to large-scale problems in reasonable times. First, a linear approximation of the CI is used to define the maritime transportation plan. Then, we refine and calculate precise CI indicators in a second subproblem. Given that global scale value chains can involve long-duration operations (in the order of weeks), the decomposition strategy is combined with a rolling horizon approach to be implemented over extended time horizons. We also discuss the challenges of accurately tracking CI, given that bilinear equalities are required to calculate the resulting values. The main contribution of this work lies in proposing a novel computational decision-making tool where carbon intensity indicators can be monitored, managed and limited stage by stage along the value chain. In this approach, the decision on how to execute each task can affect the amount of GHG emissions, while the combination of flows throughout the operations will finally lead to optimal carbon indicators at the points of delivery.

The following sections are structured as follows. First, we introduce the concept of carbon intensity in the management of sustainable supply chain operations, its usefulness, difficulties and need for strict monitoring. Next, the most important contributions in terms of planning and design of supply chains under environmental constraints are reviewed, showing that there is a strong gap in the management of operations with accurate monitoring of carbon intensity indicators. We also discuss the concept of optimization in supply chain planning and how it can be affected when explicit carbon intensity constraints are introduced at each stage. Subsequent sections formally define the problem and present the MINLP optimization model. Finally, illustrative and real-world case studies involving the transportation, storage and processing of energy products along a global supply chain are presented. Conclusions are drawn regarding the economic impact of CI constraints in supply chain planning and how carbon penalties can be planned on target overruns.

1.1 Carbon intensity indicators for sustainable supply chains

The operation of sustainable supply chains must be based on quantitative and reliable measures of their environmental impact. Carbon intensity indicators refer to a way of assessing the impact of industry operations in terms of total GHG emissions and/or consumption per mass unit of product being processed (typically measured in tons equivalent of CO_2 due to its predominance among GHG). The use of these indicators to evaluate the sustainability of supply chains are becoming increasingly prevalent, turning critical for companies that aim at commercializing products in stringent markets by meeting regulations, to avoid economic penalties and to remain competitive (Ghosh et al., 2020). Depending on the nature of the operations, technological specifications and equipment, companies may seek to manage carbon intensity indicators by finding more sustainable ways to perform their processing and/or logistics tasks, eventually optimizing their value chain. Once the objectives and constraints have been defined in terms of carbon intensity targets from business, adapting supply chain operations to new standards may require evaluating alternative configurations and to re-assess the economic viability of supply chains. In contrast to discrete manufacturing industries, the assessment of carbon indicators along the value chain in the process industry becomes more complex since in continuous and batch processes bulk components may come from different suppliers and are mixed together to yield a common product that is then manufactured through different operations. In such cases, the carbon intensity of inlet streams cannot only be different, but also vary over time, from which stringent criteria must be established to assess the carbon intensity in the final product. Computing carbon footprint per mass unit of product in these cases leads to the need of accurately assessing emissions through a *pooling problem* scheme (Foulds et al., 1992; Adhya et al., 1999) that must be integrated with the calculation of carbon intensity indicators from every activity along the supply chain.

Figure 1 shows a simplified superstructure of alternatives for the optimal operation of a global supply chain illustrating a wide variety of processing tasks, storage nodes and flows that may converge at different points. Accurate calculation of the carbon intensity (CI) indicator at the end of the value chain also requires computing it at intermediate points. In such nodes, inlet flows merge with the inventory of material available from previous periods, and all of these amounts may have different carbon footprint indicators. Keeping track of CI at end points requires managing upstream tasks on components that are often shared among products. Thus, a new dimension is added to modern supply chains, in particular for the operations management problem, raising the question on how to meet the demand for different products under required specification of environmental impact. The inclusion of quantitative environmental indicators in the commercialized products poses new challenges that must be rigorously addressed.

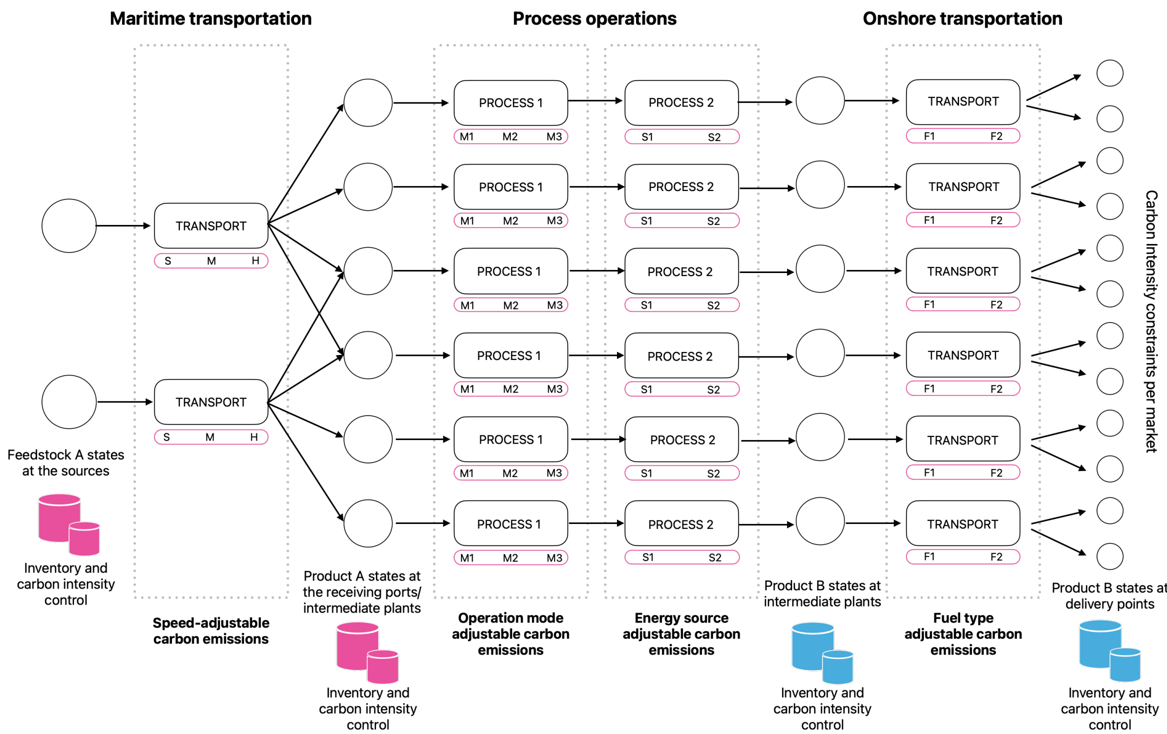

Figure 1 – Simplified superstructure for global supply chain operation

1.2 Literature review

In recent years, relevant work has been focused on developing best practices and gaining a better understanding of the effective management of supply chains in a sustainable manner. This trend can largely be attributed to the increasing concern of markets and governments to implement policies that restrict the environmental impact of operations and facilitate the attainment of objectives outlined by international agreements. One of the first clear definitions of sustainable supply chains is introduced by Hervani et al. (2005). The authors suggest that the combination of green procurement, environmental management of production and circulation across the network, marketing and reverse logistics is a key characteristic of a sustainable supply chain. Sundarakani et al. (2010) formally extend the concept by including new aspects such as supplier and sourcing selection, product design, packaging and end-of-life management. Carter and Easton (2011) survey and study the most important developments of the previous two decades showing a growing trend in the research community, and highlighting how the development of sustainable chains can become a license to operate businesses in the 21st century. The authors also highlight how the transportation stages are often the focus of attention due to their high impact on carbon footprint. Further on, a detailed review on the impact of sustainable practices in corporate performance is carried out by Younis et al. (2016). This paper explores the importance of decisions such as design, purchase, cooperation and reverse logistics on operational, environmental and social performance. Ghosh et al. (2020) analyze the impacts of sustainable supply chain management in different industries, recognizing a general shift toward adapting existing supply chains to a sustainable scheme rather than designing new ones. The authors identify an important gap in designing more specific indicators for planning cleaner processes and the need to incorporate social dimensions into the studies. Although these papers provide insights into the management of sustainable operations, they mainly conclude on qualitative implications. Nevertheless, most of them agree on the need to develop precise indicators and policies for the transformation of supply chain operations management.

Numerous contributions explore the trade-off between environmental sustainability and economic performance in supply chains (Azapagic and Clift, 1999; Joshi, 2022). From an operations research perspective, these contributions assess the impact of environmental constraints, carbon market conditions, technologies, and alternative strategies on the design and operation of supply chains. An approach that integrates mixed-integer mathematical programming and lifecycle analysis (LCA) has been proposed by Hugo and Pistikopoulos (2005) to optimize investments related to the design and planning of supply chains. The authors minimize total emissions along with design and operating costs. Subramanian et al. (2010) introduce a mathematical modeling approach to combine environmental considerations to manufacturing management decisions. In their work, the authors determine capacities, inventories and production volumes under environmental goals and constraints. They also include carbon credits purchase as decision variables. Guillén-Gonsálbez and Grossmann (2009) develop a stochastic approach that integrates LCA principles to simultaneously account for net present value (NPV) maximization, while minimizing the environmental impact for a given probability level in chemical supply chains. They include design and operational decisions. In turn, Ramudhin et al. (2010) present a mixed integer optimization model to simultaneously account for logistic costs and environmental penalties under the emission trading system of different markets. Accounting for carbon constraints, Garcia-Alvarado et al. (2016) make use of a mixed-integer linear programming (MILP) formulation to assess the relationship between green initiatives, production and inventories strategies under carbon caps and trade policies. They show how new investments in cleaner technologies might be necessary to be profitable under certain carbon market conditions. In the same year, Shaw et al. (2016) propose a chance constraint formulation where material flows and facility location are decided. They confirm that carbon prices and caps strongly condition material flows and the design of the supply chain.

It is important to note that the optimal design and planning of sustainable supply chains is not exclusive of chemical industries. Govindan et al. (2014) propose a two-stage approach where a two-echelon location routing problem is solved to economically and environmentally optimize a perishable food supply chain network. In their work, costs associated with facilities, transportation and emissions are minimized through a tailored metaheuristic strategy. Kellner and Igl (2015) focus on food distribution logistics and propose a quantitative analysis to rearrange transport and storage flows to reduce carbon footprint. However, the research is focused on only five generic distribution alternatives. In turn, Allaoui et al. (2018) tackle the optimal design of agro-food supply chains by selecting convenient industry partners and solving a mixed-integer mathematical programming model to optimally design the supply chain network by minimizing costs, emissions, water use and accounting for job generation. Jiang et al. (2019) propose an MILP formulation that includes partner selection, production technology, type of vehicles and recovery materials flows. They address the problem of a Chinese beverage company to illustrate how carbon prices may significantly affect supply chain design.

Despite the fact that all these contributions propose optimization approaches for sustainable supply chains, they mainly focus on their design. Furthermore, there is scarce research on how to manage emissions from materials that have to be labeled and traced throughout the system. In most of these cases, emissions are quantified extensively along the value chain but without accounting for different standards imposed by different markets. On the other hand, most of these approaches are particular to specific industry supply chains, so generalization is difficult. To the best of our knowledge, there is no rigorous tool for the optimal management of supply chain operations that allows accurate tracking and administration of carbon intensity indicators at every stage of the value chain.

1.3 Problem motivation

In supply chains of global scale, materials and components enter the network through diverse sources, often overseas, with different carbon intensity properties. Along the value chain, the activities carried out on these materials tend to increase the carbon intensity of the products according to how they are performed (e.g., depending on the energy source being used). In this context, an important trade-off arises when deciding how to plan and execute operations in order to meet demand under CI specification at minimum total cost. More specifically, tasks can be performed in different ways affecting not only costs and yield rates (among other productivity measures) but also through the magnitude of their carbon impact, often being *greener* at the expense of higher costs (e.g., transporting products by electric trucks instead of diesel trucks). In fact, determining which tasks should change operating conditions to reduce either emissions or costs (seeking to meet specifications or improve the overall economic performance) is also an important goal. For instance, it might be necessary to anticipate the reduction of emissions in the value chain (e.g., at the level of feedstocks) in order to obtain a better economic performance towards the final end of the network (e.g., final distribution).

Figure 2 illustrates a simple example of a chemical industry mixing different streams of the same feedstock coming from different locations into a common tank. Without loss of generality, it is assumed that a single feedstock A can be indistinctly supplied from two sources and is converted to a final product B by a sequence of two processes. One of the feedstock streams comes from the main facility (S1), whose production has a relatively high carbon emission rate. By contrast, the other stream comes from a *cleaner* source (S2), but needs a transportation task to get to the processing facility and mix with the feedstock coming from S1. An important assumption is that materials of different CI can be mixed to obtain a blend of materials with a different CI, resulting from the mass average of their original properties. From the production perspective, feedstocks from any source and blends are equivalent and interchangeable. After that, two sequential processes are performed. Each of them can be executed in alternative modes, thus yielding different carbon emissions. If a maximum CI is imposed on the final product, it might be required to increase the proportion of feedstock from S2 or to reduce emissions at the transportation or processing stages. Generally speaking, tasks across the supply chain can reduce their emissions by increasing their execution times, incurring in higher costs and/or reducing production yields. That is the case of maritime transportation for which shipping material at lower speeds reduces emissions due to lower drags. Similarly, certain processes can manage CI by adopting different operation settings.

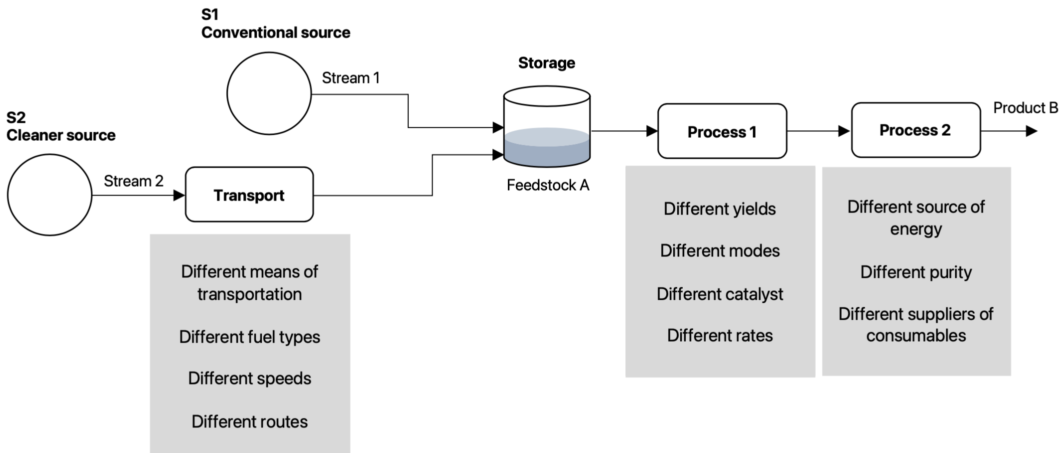

Figure 2 – Illustrative example for carbon intensity management

2. Problem statement

Consider a supply chain whose nodes are connected through material transfer paths that rely on logistics and transportation resources. To keep operations running, several tasks might be required, such as onshore and offshore transportation, storage and material processing stages. Each of these operations can be performed in alternative ways (i.e., using different means of transportation, fuels, speeds, catalyst, yields, energy sourcing or type of feedstocks, among others), giving operators the chance to reduce carbon dioxide emissions but directly impacting costs. In particular, in this work we address a global supply chain including maritime transportation, packing, processing and unpacking stages, onshore transportation and storage tasks, as illustrated in Figure 1. More specifically, the supply chain planning problem under carbon intensity constraints can be stated as follows.

Given: (a) a set of source nodes producing feedstocks at known rates and carbon intensity levels; (b) storage nodes with tanks of known capacity; (c) customer nodes/markets with known demand rates and carbon intensity requirements; (d) a set of transportation maritime resources that can move at different speeds; (e) a set of processing tasks to be performed over feedstocks to transform them into final products; and (f) a fleet of vehicles using alternative fuels/energy sources to carry out ground transportation tasks.

We seek to determine: (i) the optimal planning of offshore shipments and their corresponding speed; (ii) the optimal operations plan of packing and unpacking operations; (iii) the optimal planning of processing operations; and (iv) the optimal number of daily onshore shipments to meet customers' demands using different trucks. The optimization model will seek to minimize the total cost of supply chain operations, while meeting demands under CI constraints.

2.1 Model Assumptions

1. We assume a given supply chain network structure where connections between sourcing, storage points and end customers are predefined (see Figure 1).
2. Without loss of generality, we consider a single feedstock A that is supplied from different sources and converted into the final product B.
3. The total time horizon is specified and discretized into daily periods.

4. Daily production rates of feedstocks at different sources, with different carbon intensities, are given data.
5. Material flows are combined instantaneously at storage points, resulting in a homogeneous mixture with mass-averaged carbon intensity.
6. For the maritime transportation, it is assumed that direct trips and milk-runs of up to two destinations can be carried out. In any case, every ship returns to its assigned source node.
7. No ship can remain loaded by the end the time horizon.
8. All emissions (CI) from transportation tasks sharing two delivery points are distributed on a mass-basis among the destination nodes, according to the material delivered to each of them.
9. To simplify the CI calculations, ship speeds for maritime transportation are selected from a discrete set of alternatives.
10. For safety reasons, no vessel can carry less than 30% of its capacity on any of the forward voyages.
11. All trips that have started within the current planning horizon must deliver the material before the end of the horizon. However, ships are not required to return to their sources within the planning horizon.
12. For processing stages, energy can be acquired from renewable sources (typically wind and solar) or from non-renewable sources (typically coal and natural gas). Energy sources can be combined on a continuous basis and the energy mix can be adjusted day by day.
13. There is a finite set of modes of operation for batch processing steps that can be changed on a daily basis.
14. Economic penalties are assumed for delivering material out-of-specification to end customers.
15. Demand that is not met at any period of time incurs in an economic loss for the supply chain.

3. Mathematical Formulation

When using mathematical programming techniques to plan supply chain operations, several logistic and production activities have to be modeled and specified. In addition, managing carbon intensity along the chain means that each of these tasks may perform differently in terms of carbon dioxide emissions according to operational decisions. If those tasks have different ways of being carried out, which might be tuned in order to properly manage carbon intensity indicators, such alternatives should be included in the optimization model. In this section, we present a discrete-time State-Task-Network (STN) representation (Kondili et al., 1993) for the optimization of daily tasks across global supply chains, under carbon intensity constraints. First, we address feedstock production and model maritime transportation tasks accounting for different ship speeds and emissions rates, as well as direct and "milk-run" shipments. Second, we present the selection of discrete operating modes for certain processing tasks like packing, unpacking and daily batch handling. Third, we develop a simplified set of equations to manage finishing tasks for chemical products before delivery (e.g., dehydration, compression, liquefaction) consuming energy from alternative sources. On a first block of equations (Section 3.1) we present basic physical relations like material balances and inventory tracking at each storage point based on incoming and outgoing flows at each time period. On a second block (Section 3.2) we present logical conditions to manage the ship transportation schedule. Finally, constraints computing carbon emissions for all stages and overall carbon intensity tracking are presented in Section 3.3, which together with the objective function in Section 3.4 defines the MINLP optimization model.

3.1 Material Balances and Inventory Tracking

Stage 1: Feedstocks production and packing

The structure of the value chain addressed in this work begins with the production of feedstocks at source nodes. We assume that these feedstocks are produced with a time varying pattern, but at known yield rates and with given carbon intensities, according to the operating conditions at the production stages. Feedstocks enter the source tanks with given carbon intensity measures and merge with existing inventories, yielding a new carbon intensity for the total amount of feedstock stored and/or sent to downstream processes. Consider a generic feedstock *A* stored in source *s*. Equation (1) shows how feedstock tanks are loaded at a given feed rate $ss_{s,t}^{A}$ during period *t*, and discharged by further transportation through the variable $QF_{s,t}^{A,out}$. This inventory balance equation establishes the inventory level $IS_{s,t}^{A}$ of feedstock *A* at each time period *t* in source *s*. Note that, for clarity, continuous variables are presented in capital letters while parameters are given in lower case.

$$IS_{s,t}^{A} = IS_{s,t-1}^{A} + ss_{s,t}^{A} - QF_{s,t}^{A,out} \qquad \forall\, s \in S, \forall\, t \in T \tag{1}$$

Inventory of carbon emissions in source tanks is also tracked in order to keep control of the environmental measures of the products that will be later obtained from these feedstocks. Furthermore, in our network structure we assume that feedstocks leave the sources by maritime overseas transportation that also adds carbon intensity to product streams. Modelling for tracking CI properties over feedstocks and products is presented in later sections.

Stage 2: Maritime transportation

Maritime shipping is an essential part of the logistics operations in global supply chains of chemicals products. Optimizing overseas transportation implies coordinating multiple ships and vessels to make an efficient use of their capacities. In our model, the amount of feedstock *A* taken by ships from tanks of *A* at *s* during period *t* is represented by the variable $QS_{v,s,rp,sp,t}^{A,out}$. More specifically, variable $QS_{v,s,rp,sp,t}^{A,out}$ in Equation (2) denotes the amount of feedstock *A* discharged into ship *v* during time period *t*, which will then move at the speed *sp*, from source *s* to port *rp*.

$$QF_{s,t}^{A,out} = \sum_{v \in V(s)} \sum_{rp \in RP(s)} \sum_{sp \in SP(v)} QS_{v,s,rp,sp,t}^{A,out} \qquad \forall\, s \in S, \forall\, t \in T \tag{2}$$

Besides single-source, single-destination trips, the so-called “milk run” deliveries refer to shipments where partial discharges from the ship to two ports visited in a row are made. Both direct voyages and milk-run deliveries require the ships to depart fully loaded. However, the milk-run strategy allows the cargoes to be split into two destinations. Equations (3) to (6) account for ship loads at each departure node and define the amount that is withdrawn from the source tanks at each time period. Equations (4) to (6) include 0-1 decision variables to restrict the size of the cargo when a direct trip of ship *v* goes from source *s* to receiving port *rp* at speed *sp* starting at time *t* ($xv_{v,s,rp,sp,t}$=1), or a milk-run to visit *rp* and *rp'* in a row is selected ($xmr_{v,s,rp,rp',sp,t}$=1). Continuous variables $QMR1_{v,s,rp,rp',sp,t}$ and $QMR2_{v,s,rp,rp',sp,t}$ determine the amount that should be discharged at ports *rp* and *rp'*, in that order. On the other hand, variable $QD_{v,s,rp,sp,t}$ represents the amount of feedstock that is taken through a direct trip from source *s* with destination to port *rp*, departing at time *t*. Vessels are not allowed to split the load in fractions of less than ρ % of their total capacity (usually fixed at 30% for safety reasons).

$$QS^{A,out}_{v,s,rp,\,sp,\,t} = QD_{v,s,rp,sp,t} + \sum_{rp' \in MR_{s,rp}} (QMR1_{v,s,rp,rp',sp,t} + QMR2_{v,s,rp',rp,sp,t}) \qquad \forall s \in S, \forall\, rp \in RP(s), \forall sp \in SP(v), \forall v \in V, \forall t \in T \tag{3}$$

$$QMR1_{v,s,rp,rp',sp,t} \geq \rho_v\ s^{CAP}_v\ xmr_{v,s,rp,rp',sp,t} \qquad \forall s \in S, \forall\, rp \in RP(s), \forall\, rp' \in RP(s), \forall sp \in SP(v), \forall v \in V, \forall t \in T \tag{4}$$

$$QMR2_{v,s,rp,rp',sp,t} \geq \rho_v\ s^{CAP}_v xmr_{v,s,rp,rp',sp,t} \qquad \forall s \in S, \forall\, rp \in RP(s), \forall\, rp' \in RP(s), \forall sp \in SP(v), \forall v \in V, \forall t \in T \tag{5}$$

$$QD_{v,s,rp,sp,t} = s^{CAP} xv_{v,s,rp,sp,t} \qquad \forall s \in S, \forall\, rp \in RP(s), \forall sp \in SP(v), \forall v \in V, \forall t \in T \tag{6}$$

Once ships have reached receiving ports, material is added to tank inventories after a few days of dwelling and docking times. Equation (7) tracks the inventory at the receiving ports using variable $IRP_{rp,t}$. Notice that incoming flows are defined by the amounts that have been delivered by the sources Δt periods before time *t*, as stated in Equation (8). Also note that Δt depends on the type of trip (direct or milk run) and the corresponding speed. Variable $QRP^{A,in}_{v,s,rp,t}$ refers to the amount of feedstock A that is discharged into the port *rp* in period *t* with material coming from source *s* carried by vessel *v*. Moreover, $QU_{rp,t}$ indicates the amount of material that is sent from *rp* tanks for unpacking operations during period *t*.

$$IRP^{A}_{rp,t} = IRP^{A}_{rp,t-1} + \sum_{v \in V_s} \sum_{s \in S_{rp}} QRP^{A,in}_{v,s,rp,t} - QU^{A}_{rp,t} \qquad \forall\, rp \in RP, \forall\, t \in T \tag{7}$$

$$QRP^{A,in}_{v,s,rp,\,t} = \sum_{sp \in SP_v} QD_{v,s,rp,sp,t-\Delta t^{d}_{s,rp,sp}} + \sum_{rp' \in MR_{s,rp}} (QMR1_{v,s,rp,rp',sp,t-\Delta t^{mr1}_{s,rp,rp',sp}} + QMR2_{v,s,rp',rp,sp,t-\Delta t^{mr2}_{s,rp',rp,sp}}) \qquad \forall s \in S, \forall\, rp \in RP(s), \forall v \in V, \forall t \in T \tag{8}$$

Stage 3: Unpacking and processing

This section presents the modelling of inland processing steps in the supply chain. Processing is used here in the broad meaning capturing all activities that produce transformations on a product. These stages usually account for unpacking operations (e.g., discharging material from a carrier), involving chemical reactions or changes of state (Bontron et al., 2023; Riera et al., 2023). These operations can be usually carried out in different ways based on operational targets such as increasing performance, reducing emissions or reducing waste. To achieve this, decision makers can resort to different catalysts, energy sources, additives or technologies. At extreme conditions, an operation can be performed prioritizing yields regardless of emissions, or vice versa.

In order to track the carbon intensity on these tasks, and without loss of generality, we assume that after the material reaches the port from maritime transportation, processing stages need to be performed in site. First, we consider the case in which an endothermic chemical reaction is required to unpack material *A*. Depending on the catalyst and fuel used, the operation provides different yields and different emissions rates. Typically, the yield is higher when the operation is performed using catalysts or energy requirements that produce higher emissions. Equation (9) shows that part of the material received in the port is sent to unpacking operations. The binary variable $xrp_{rp,m,t}$ is used for the selection of the reactor operating mode m. This modeling approach assumes that operation mode may be modified every single day. On the other hand, Equations (10) and (11) relate the continuous variables accounting for the amount of material that is processed with the 0-1 decisions on the mode. Variable $QU^{in}_{rp,m,\ t}$ represents the amount of material coming into the reactor using mode *m* during day *t*, while α_m limits the amount of product *A* that can be processed according to the selected mode.

$$\sum_{m\in M(rp)} xrp_{rp,m,t} \le 1 \qquad \forall\, rp \in RP, \forall\, t \in T \tag{9}$$

$$QU^{A}_{rp,t} = \sum_{m\in M(rp)} QU^{A,in}_{rp,m,t} \qquad \forall\, rp \in RP, \forall\, t \in T \tag{10}$$

$$\underline{\alpha}_m\, xrp_{rp,m,t} \le QU^{A,in}_{rp,m,t} \le \bar{\alpha}_m\, xrp_{rp,m,t} \qquad \forall\, rp \in RP, \forall\, t \in T, \forall m \in M \tag{11}$$

Following the proposed structure for the supply chain, assume that the material becomes product of type *B* after reaction, and requires changing its aggregation state. The latter process may need large amounts of energy to be performed. Depending on carbon footprint attributed to the material so far, the supply chain manager may decide for convenience in buying green energy to carry out these processes, use grid energy, or combine energy sources. This kind of processes can be modeled with continuous variables, since companies may buy energy from any source in the required amounts. Equations (12) and (13) impose that all material flows coming from the reactor need to be processed at this stage. Note that parameter γ_m stands for the yield of the previous process (chemical reaction) depending on the operating mode. Variable $QU^{B,in}_{rp,t}$ indicates the amount of product *B* produced by the chemical reaction stage. In turn, variables $QS^{e/g}_{rp,\ t}$ represent the amount of product *B* that is processed using energy coming from the electrical grid (*e*) and/or a green energy source (*g*), respectively.

$$\sum_{m\in M(rp)} QU_{rp,m,t}^{A,in}\ \gamma_m = QU_{rp,t}^{B,in} \qquad \forall\ rp \in RP, \forall\ t \in T \tag{12}$$

$$QU_{rp,t}^{B,in} = QS_{rp,t}^{e} + QS_{rp,t}^{g} \qquad \forall\ rp \in RP, \forall\ t \in T \tag{13}$$

A different set of dedicated tanks is assumed to be available at ports that store resulting product B. Equation (14) defines the inventory balance for these tanks, accounting for incoming product flows and outgoing material via onshore transportation. Variable $QRP_{f,\,rp,\,c,\ t}^{B,out}$ stands for the amount of product *B* that is sent from port *rp* to destination node *c* using trucks of fuel *f* at time period t.

$$IRP_{rp,t}^{B} = IRP_{rp,t-1}^{B} + QU_{rp,t}^{B,in} - \sum_{f\in F(rp)} \sum_{c\in C(rp)} QRP_{f,rp,c,t}^{B,out} \qquad \forall\ rp \in RP, \forall\ t \in T \tag{14}$$

Stage 4: Onshore transportation

Once the material is available at the port, trucks are used to deliver orders to customers' nodes. Land transportation must not add more emissions than allowed to reach the destination on specification regarding carbon intensity limits. We assume that different types of vehicles are available for the company (e.g., electric and diesel trucks). The optimization procedure will determine how many deliveries should be made with each of those vehicles in a way that the material reaches its destination on spec.

Let $nt_{f,rp}$ be the number of trucks of type *f* available at receiving port *rp* and λ_f be the number of hours per day that a truck of type *f* is available. Service availability will typically depend on the autonomy of electric vehicles and the work shifts for combustion vehicles. Since a large number of daily trips are often required to meet demand, a continuous variable can be used to account for them. Equation (15) relates the outflow of product *B* with the total number of trips $NTR_{f,rp,c,t}$ based on the truck capacities μ_f. In turn, Equation (16) ensures that the number of trips does not exceed the availability of vehicle hours by accounting for the travel time $\tau_{rp,c}$ (including backhaul) from port *rp* to customer node *c*.

$$QRP_{f,\,rp,\,c,\ t}^{B,out} = \mu_f\ NTR_{f,rp,c,t} \qquad \forall f \in F(rp), \forall\ rp \in RP, \forall c \in C(rp), \forall\ t \in T \tag{15}$$

$$\sum_{c\in C(rp)} NTR_{f,rp,c,t}\, \tau_{rp,c} \le \lambda_f\ nt_{f,rp} \qquad \forall f \in F(rp), \forall\ rp \in RP, \forall\ t \in T \tag{16}$$

Since storage tanks for product *B* are available at customers nodes, inventory balance is also required at the destinations, as stated by Equation (17). Variable $IC_{c,t}^{B}$ accounts for the inventory level of product *B* at customer tanks, while parameter $\omega_{c,t}$ indicates the demand of product *B* at time t for node c (given data) Variable $UD_{c,t}$ refers to unmet demand and is weighted by penalty values in the objective function, as will be shown later in this work.

$$IC^{B}_{c,t} = IC^{B}_{c,t-1} + \sum_{f\in F(rp,c)} \sum_{rp\in RP(c)} QRP^{B,out}_{f,rp,c,\ t} - \omega_{c,t} + UD_{c,t} \qquad \forall c \in C, \forall\, t \in T \tag{17}$$

3.2 Logical Constraints for Maritime Transportation Scheduling

Equation (18) makes use of binary variables to allocate resources to maritime transportation tasks and set the STN, non-overlapping constraints over the duration of the travelling times. Binary variable $xv_{v,s,rp,sp,t'}$ takes value 1 if ship *v* is sent from source *s* to port *rp* at speed *sp* starting in day *t'*, and equals 0 otherwise. In turn, the binary variable $xmr_{v,s,rp,rps,sp,t'}$ indicates the starting day *t'* of a milk-run of ship *v* at speed *sp* departing from source *s* and visiting ports *rp* and *rp'*, respectively, in an ordered sequence of partial discharges. Notice that $\Delta t^{dt}_{s,rp,sp}$ and $\Delta t^{mrt}_{s,rp,rp',sp}$ are parameters accounting for the total duration of the trips depending on the speed *sp* of the ship *v* (see Figure 3). By assumption 7, variables accounting for trips that cannot deliver the material by the end of the time horizon are omitted.

$$\sum_{s\in S(v)} \sum_{rp\in RP(s)} \sum_{sp\in SP} \sum_{t'=t-\Delta t^{dt}_{s,rp,sp}+1}^{t'=t} xv_{v,s,rp,sp,t'} + \sum_{s\in S(v)} \sum_{rp\in RP(s)} \sum_{rps\in RP(s)} \sum_{sp\in SP} \sum_{t'=t-\Delta t^{mrt}_{s,rp,rp',sp}+1}^{t'=t} xmr_{v,s,rp,rps,sp,t'} \leq 1 \qquad \forall v \in V, \forall\, t \in T \tag{18}$$

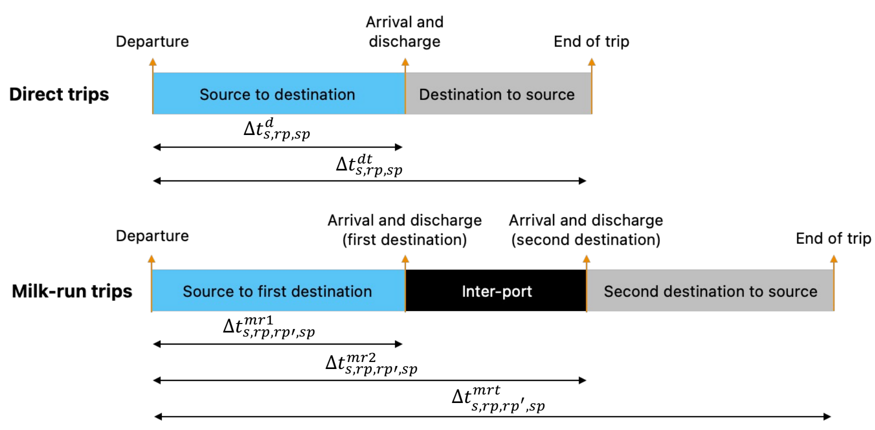

Figure 3 – Parameters for transportation task durations

The latter integer constraints are usually called *backward aggregation* inequalities in the STN discrete-time model, whose relaxation has proved to be very tight (Shah et al., 1993) especially when compared to the initial big-M constraint. For more details on the STN discrete-time representation for scheduling problems we refer the reader to the works by Kondili et al. (1993) and Shah et al. (1993). For a general review on this topic, see Maravelias (2021).

3.3 Carbon Inventory Balances and Carbon Intensity Tracking

In parallel to planning operations, monitoring carbon intensity indicators requires quantifying emissions from every task. If the carbon footprint of the feedstocks at the sources is tracked over time, adding the emissions from maritime transportation leads to the CI of the material unloaded at the receiving ports. Figure 4 shows an illustrative example where a ship delivers material from a source to a port. The ship transports 25,000 tons of feedstock *A* whose CI at the origin is 0.1 ton of CO_2 per ton of *A*. During the trip (from time t-Δt to t), the vessel emits 2,000 tons of CO_2, which are added as CI to the transported material. Upon delivery, the material is mixed with 10,000 tons of *A* already stored in the tank, with a CI of 0.5 tons of CO_2 per ton of *A*. The blending process yields a final amount of 35,000 tons, from which 5,000 tons are sent to downstream processing stages. Note that the stored material (30,000 tons) and the 5,000 tons sent to production share the same CI value of 0.27 tons of CO_2 per ton of feedstock.

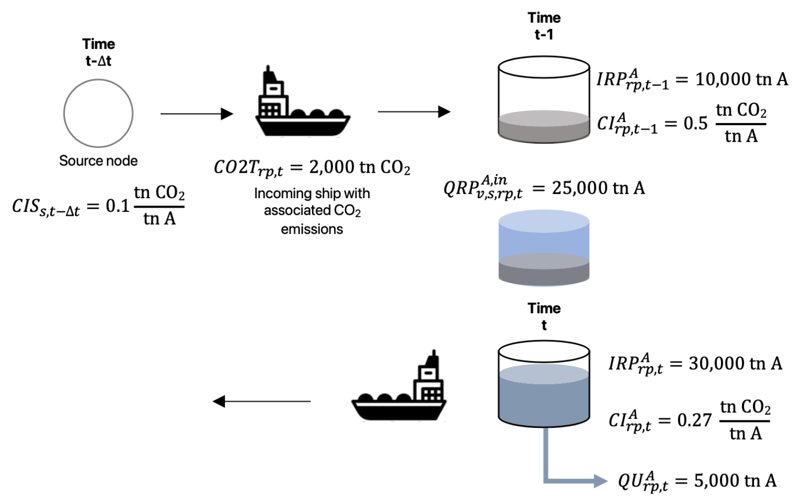

Figure 4 – Illustrative example of CI calculation at receiving ports

Following a similar procedure, carbon intensity tracking must be carried out from the origin to the final destination, at every storage tank. Parameter $cf_{s,t}$ in Equation (19) indicates the carbon footprint of the feedstock produced by source s in period t (given data) while variable $CIS_{s,t}$ define the carbon intensity of the material that is stored in source s at period t. Equations (20) and (21) compute extensive carbon dioxide emissions (tons of CO_2) coming with the feedstock and added by transportation, respectively. Note that the inherent emissions associated with the feedstock must be backdated to the time when the ship loads and departs from the source (see parameters Δt in Eqs. 20 and 21, also depicted in Figure 3). The variable $CO2S_{rp,\,t}$ in Equation (20) represents the emissions associated with the product received at the port in period t. In turn, $ce_{v,sp}$ in Equation (21) is a parameter representing emissions from ship v per nautical mile while moving a cargo at speed *sp*, whereas $cr_{v,sp}$ stands for unit emissions of empty ship movements. Note that the latter are evenly distributed among the ports visited in the trip.

$$CIS_{s,t}\left(IS_{s,t}^{A}+\sum_{sp\in SP(v)}\sum_{v\in V(s)}\sum_{rp\in RP(s)}QS_{v,s,rp,sp,\,t}^{out}\right)=cf_{s,\,t}ss_{s,t}^{A}+CIS_{s,t-1}IS_{s,t-1}^{A} \qquad \forall s\in S,\forall\,t\in T \tag{19}$$

$$\begin{aligned}CO2S_{rp,t}=&\sum_{sp\in SP(v)}\sum_{v\in V(s)}\sum_{s\in S(rp)}CIS_{s,t-\Delta t_{s,rp,sp}}\;QD_{v,s,rp,sp,t-\Delta t_{s,rp,sp}^{d}}\\&+CIS_{s,t-\Delta t_{s,rp,rp',sp}^{mr1}}\sum_{rp'\in MR_{s,rp}}QMR1_{v,s,rp,rp',sp,t-\Delta t_{s,rp',rp,sp}^{mr1}}\\&+\;CIS_{s,\,t-\Delta t_{s,rp',rp,sp}^{mr2}}\sum_{rp'\in MR_{s,rp}}QMR2_{v,s,rp',rp,sp,t-\Delta t_{s,rp',rp,sp}^{mr2}}\end{aligned} \qquad \forall\,rp\in RP,\forall\,t\in T \tag{20}$$

$$\begin{aligned}CO2T_{rp,\,t}=&\sum_{s\in S}\sum_{v\in V(s)}\sum_{sp\in SP(v)}xv_{v,\,s,\,rp,\,sp,\,t-\Delta t_{s,rp,sp}^{d}}\left(ce_{v,sp}\;d_{s,rp}+cr_{v,sp}\;d_{s,rp}\right)\\&+\sum_{rp'\in MR_{s,rp}}xmr_{v,s,rp,rp',sp,t-\Delta t_{s,rp,rp',sp}^{mr1}}\left(ce_{v,sp}\;d_{s,rp}+0.5\;cr_{v,sp}\;d_{s,rp'}\right)\\&+\sum_{rp'\in MR_{s,rp}}xmr_{v,s,rp',rp,sp,t-\Delta t_{s,rp',rp,sp}^{mr2}}\left(ce_{v,sp}\;d_{rp,rp'}+0.5\;cr_{v,sp}\;d_{s,rp}\right)\end{aligned} \qquad \forall\,rp\in RP,\forall\,t\in T \tag{21}$$

In addition, variable $CO2T_{rp,\,t}$ computes carbon dioxide emissions of direct trips and milk-runs and assigns them to the corresponding discharged material. As new material is received at the port, it is combined with the product stored from previous periods. Rigorously computing their carbon content requires the use of bilinear terms. This is also the case when the company receives material flows from other companies or activities in the value chain. Equation (22) shows how the extensive emissions and the carbon content in the stored material are used to obtain the intensive carbon properties of the material that is kept in storage tanks and/or derived for downstream processing at time period *t* (see Figure 4). Note that variable $CI_{rp,t}^{A}$ represents emissions per unit mass of feedstock *A* stored and dispatched from port *rp* at time period *t*, while $QU_{rp,t}^{A}$ stands for the amount of *A* sent for production at the port. If a product can also be derived to a second stream, the flow has to be included in the right-hand side of the equation.

$$CO2S_{rp,t}+CO2T_{rp,t}+CI_{rp,t-1}^{A}\,IRP_{rp,t-1}^{A}=CI_{rp,t}^{A}\left(QU_{rp,t}^{A}+IRP_{rp,t}^{A}\right) \qquad \forall\,rp\in RP,\forall\,t\in T \tag{22}$$

The emissions produced by processing stages are computed in Equation (23), where θ_m and ε stand for chemical reaction emissions in mode *m* per unit of product *A* and emissions from grid energy consumption per unit of product *B*, respectively. Variable $CO2P_{rp,\,t}$ collects all the emissions generated during one day of processing. In addition, accurate tracking of the carbon footprint of product *B* in the tanks at receiving ports also requires the use of bilinear equations. An extensive carbon dioxide emissions balance (tons of CO_2) attributed to product *B* in the tanks is proposed in Equation (24). Variable $CI_{rp,t}^{B}$ in the right-hand side of Eq. (24) conveys the carbon intensity of material *B* stored and discharged into trucks at day *t*.

$$CO2P_{rp,t} = \sum_{m \in M} QU^{A,in}_{rp,m,t}\, \theta_m + QS^{e}_{rp,t}\ \varepsilon_e + QS^{g}_{rp,t}\, \varepsilon_g \qquad \forall\, rp \in RP, \forall\, t \in T \tag{23}$$

$$CI^{A}_{rp,t}\, QU_{rp,t} + CO2P_{rp,t} + CI^{B}_{rp,t-1}\, IRP^{B}_{rp,t-1} = CI^{B}_{rp,t} \left(\sum_{f \in F(rp,c)} \sum_{c \in C(rp)} QRP^{B,out}_{f,rp,c,t} + IRP^{B}_{rp,t} \right) \qquad \forall\, rp \in RP, \forall\, t \in T \tag{24}$$

As already discussed, monitoring the carbon footprint of the product at customer nodes is required to meet the demand on specification. Emissions added by ground transportation must be accounted for to determine these values. Equation (25) aggregates the total amount of carbon dioxide emissions that should be attributed to the material in customer node *c* by day *t*. Truck emissions from incoming flows are then added to the carbon dioxide balance in Equation (26) to determine the carbon footprint of product *B* stored at destination tanks and further delivered.

$$CO2TT_{c,t} = \sum_{f \in F(rp,c)} \sum_{rp \in RP(c)} NTR_{f,rp,c,t}\, \sigma_f\, d_{rp,c} \qquad \forall\, c \in C, \forall\, t \in T \tag{25}$$

$$CIC^{B}_{c,t} \left(\omega_{c,\,t} + IC^{B}_{c,t} \right) = \sum_{f \in F(rp,c)} \sum_{rp \in RP(c)} CI^{B}_{rp,t}\, QRP^{B,out}_{f,rp,c,t} + CO2TT_{c,t} + CIC^{B}_{c,t-1}\, IC^{B}_{c,t-1} \qquad \forall\, c \in C, \forall\, t \in T \tag{26}$$

Finally, product specifications in terms of carbon footprint are imposed on the final product. All operations along the value chain have to be coordinated in order to meet these emissions constraints. Equation (27) establishes the carbon intensity bounds on product *B* for every destination node depending on market regulations.

$$CIC^{B}_{c,t} \leq ci^{max}_{c} + CI^{s}_{c,t} \qquad \forall\, c \in C, \forall\, t \in T \tag{27}$$

3.4 Objective function

The economic performance of operations may vary significantly according to their nature. Moving ships at lower speeds may provide lower costs and emissions per trip, but may also require a larger fleet of ships to keep inventories under control. Lack of ships to remove material from the sources may block the feedstock production, while the receiving ports may also fall short. Further down the supply chain, processing stages may provide lower yields and/or consume more expensive energy when attempting to reduce emissions. That is also the case of truck transportation, where moving material with diesel vehicles is usually the cheapest option but more emissions are generated. An important trade-off arises when planning operations. On the one hand, companies try to reduce emissions to deliver the product on specification. On the other hand, profitably meeting demand often requires faster shipments, efficient processes and lower costs along the chain. We present the economic terms in the objective function following stages along the supply chain.

Maritime shipping costs are modeled in the first term of the RHS of Equation (28) and include sailing cost per day (fxc_v), fuel cost per nautical mile (vc_v), cost of return trip (c_v^{ret}), port admission fees ($c_{v,rp}^{port}$) and cost of entry at source ports ($c_{v,s}^{src}$).

$$MSC_t = \sum_{s\in S}\sum_{v\in V(s)}\sum_{rp\in RP(s)}\sum_{sp\epsilon SP(v)} xv_{v,s,rp,sp,t}\,(fxc_v\,\Delta t_{s,rp,sp}^{dt} + 2\,vc_v\,d_{s,rp} + c_v^{ret} + c_{v,rp}^{port} + c_{v,s}^{src}) + \sum_{s\in S}\sum_{v\in V(s)}\sum_{rp\in RP(s)}\sum_{rp'\in MR(s,rp)}\sum_{sp\epsilon SP(v)} xmr_{v,s,rp,rp',sp,t}\Big[fxc_v\,\Delta t_{s,rp,rp',sp}^{mrt} + vc_v\big(d_{s,rp} + d_{rp,rp'} + d_{s,rp'}\big) + c_v^{ret} + c_{v,rp}^{port} + c_{v,rp'}^{port} + c_{v,s}^{src}\Big] \quad \forall\, t\in T \tag{28}$$

On the other hand, unpacking and processing stages include costs for yielding product *B,* and converting its aggregation state by consuming energy. Equations (29) and (30) calculate these costs according to the selected operating strategy. Within these equations, c_m^{cr} represents the unit cost of operating the chemical reactor under mode *m*, c_{rp}^{e} indicates the unit cost of processing product *B* with energy coming from the electrical grid, and c_{rp}^{g} stands for the unit cost of doing so with green energy.

$$CRC_t = \sum_{m\in M(rp)}\sum_{rp\in RP} QU_{rp,m,t}^{A,in}\,c_m^{cr} \qquad \forall\, t\in T \tag{29}$$

$$PC_t = \sum_{rp\in RP}\left(c_{rp}^{e}\,QS_{rp,t}^{e} + c_{rp}^{g}\,QS_{rp,t}^{g}\right) \qquad \forall\, t\in T \tag{30}$$

For truck transportation we need to multiply the number of trips to each destination by the distance traveled, times the unit transportation cost according to the type of vehicle used (see Equation 31). Parameter χ_f represents the cost per unit of distance delivered by vehicles of type *f*.

$$TC_t = \sum_{f\in F}\sum_{rp\in RP}\sum_{c\in C(rp)} NTR_{f,rp,c,t}\,\chi_f\,d_{rp,c} \qquad \forall\, t\in T \tag{31}$$

Since storing products in any node may require the use of electrical power to maintain pressure and/or temperature conditions, we add Equation (32) to account for the storage costs of product *B*. Parameter ζ_{rp} indicates the cost of keeping one unit of material *B* in a tank of port *rp* or customer node *c* during one day.

$$SC_t = \zeta_{rp}\left(\sum_{c\in C(rp)} IC_{c,t}^{B} + \sum_{rp\in RP} IRP_{rp,t}^{B}\right) \qquad \forall\, t\in T \tag{32}$$

Economic penalties are imposed for not meeting the demand of the delivery points or delivering the product out of specification. Equation (33) establishes the corresponding overall penalty cost. Note that φ_c represents a cost per mass unit of CO_2 in excess at delivery market c.

$$EPC_t = \sum_{c \in C(rp)} (\psi_{c,t}\, UD_{c,t} + \varphi_c\, CI^s_{c,t}\, \omega_{c,t}) \qquad \forall\, t \in T \tag{33}$$

Finally, Equation (34) establishes the objective function for the optimization model. In summary, the MINLP formulation seeks to minimize Equation (34) subject to constraints (1) to (33).

$$\text{Min}\, z = \sum_{t \in T} (MSC_t + CRC_t + PC_t + TC_t + SC_t + EPC_t) \tag{34}$$

4. Solution approach

The formulation presented in this work is a non-convex mixed-integer non-linear program (MINLP), specifically a mixed-integer quadratically constrained programming (MIQCP) model given the bilinear equations for tracking carbon intensity properties along the value chain (see Equations 19, 20, 22, 24 and 26). Indeed, solving such a system of non-linear equations can introduce serious numerical issues and make the solver fail or produce suboptimal solutions. Moreover, addressing large MINLPs monolithically can be intractable even if they have the special structure of MIQCP. This section introduces a decomposition strategy aimed at obtaining good quality solutions in reasonable computational times. The decomposition approach illustrated in Figure 5 seeks to solve an MILP formulation that first addresses the combinatorically intensive part of the problem (i.e., the maritime transportation planning) by approximating the carbon intensity measures in an aggregate fashion. Then, accurate CI values are adjusted by fixing ship schedules and deciding on successive stages of the supply chain through a reduced MINLP formulation. These two models overlap in inland stages in order to improve the quality of the solution when solving the MINLPs. The decomposition framework is also coupled to a receding horizon strategy that proves to be useful to tackle large instances of the problem.

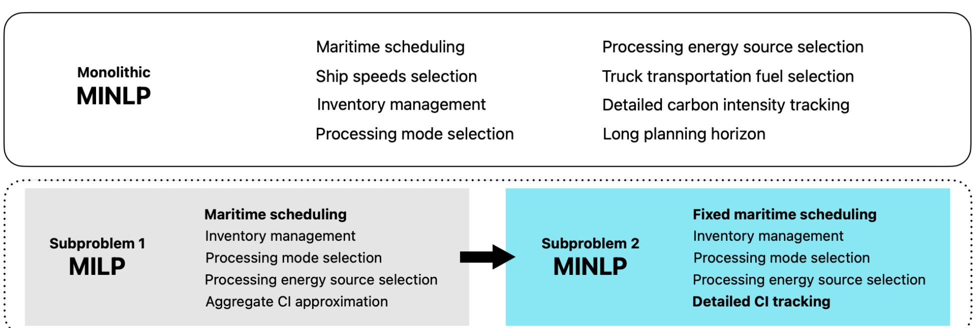

Figure 5 – Sequential decomposition strategy to avoid solving a single large MINLP

4.1 Carbon intensity approximation

The first stage of the decomposition strategy seeks to solve the ship scheduling problem efficiently using a mixed integer-linear programming (MILP) model. For this purpose, equations accounting for detailed tracking of carbon intensity along the supply chain are replaced with an overall linear approximation of this property at the final nodes. The approximation is made assuming that all emissions produced in the different stages of the chain are evenly distributed in the product *B* produced so far. This is performed by averaging the total supply chain emissions over the delivered and stored amount of product B up to day t. Equation (35) accounts for all the emissions from transportation and production tasks, as shown in Equations (20), (21) and (23). In turn, Equation (36) assesses the total amount of product B stored and delivered up to time t. In the latter equation, $\Omega_{rp,\,t}$ represents the overall demand of product B at time t to be delivered from the receiving port rp.

$$GHGT_{rp,t} = \sum_{t' \leq t} (CO2T_{rp,t} + CO2P_{rp,t}) \qquad \forall\, rp \in RP, \forall\, t \in T \tag{35}$$

$$TPB_{rp,t} = \sum_{t' \leq t} \Omega_{rp,t'} + IRP^{B}_{rp,t} - irp^{B,init}_{rp,t} \qquad \forall\, rp \in RP, \forall\, t \in T \tag{36}$$

By using Equations (35) and (36), a rough estimation of the carbon footprint of product B can be obtained. This may imply that even if the material has been produced by processes that generate large emissions, the carbon footprint of the material may be lower, by offsetting emissions with material produced in other sources or at an earlier time. To rectify this effect, decisions are then revisited in the reduced MINLP (second step). Note that, due to the combinatorial nature of the ship scheduling problem, a significant reduction in the complexity of the second model is obtained by fixing the solution of the maritime transportation problem (first step).

Besides that, to reduce the decision instances of the MILP approximation, a backward calculation of the required emissions is performed to eliminate client nodes from the network. This allows the setting of bounds for the CI indicators at the ports, just after the processing stages. To this end, it is assumed that all the material in the port will be transported by diesel trucks to the destinations. Thus, carbon dioxide emissions are maximized in the last mile delivery and conservative constraints are imposed on the estimated carbon footprint that the product must have after arriving at the port and being processed. This is captured by Equation (37)

$$GHGT_{rp,\,t} \leq \min_{c \in C(rp)} (ci^{max}_{c} - \sigma_{diesel}\, d_{rp,c}/\mu_{diesel})\, TPB_{rp,t} \qquad \forall\, rp \in RP, \forall\, t \in T \tag{37}$$

In summary, the MILP subproblem formulation replaces Equations (19), (20), (22), (24) and (26) by linear Equations (35), (36) and (37) to solve the combinatorial part of the problem, i.e., the maritime transportation. After solving that, offshore ship scheduling decisions (through 0-1 variables $xv_{v,s,rp,sp,t}$ and $xmr_{v,s,rp,rps,sp,t}$) are fixed in the MINLP formulation, and the reduced MINLP is solved to optimality by using outer approximation algorithms.

4.2 The receding horizon strategy

The decomposition approach presented in the previous section is embedded into a receding horizon solution strategy, where several shorter-term instances are solved in order to tackle a 1-year term problem (see Figure 6). This is done by iteratively solving the MILP-MINLP steps over shorter time horizons. At every iteration, the time horizon is rolled over the next 30 days, and the MILP-MINLP sequence is solved for the next 60 days. The operating plan for the first 30 days of the current time horizon is fixed and a new iteration follows. The strategy allows solving long-term instances of the problem in reasonable CPU times.

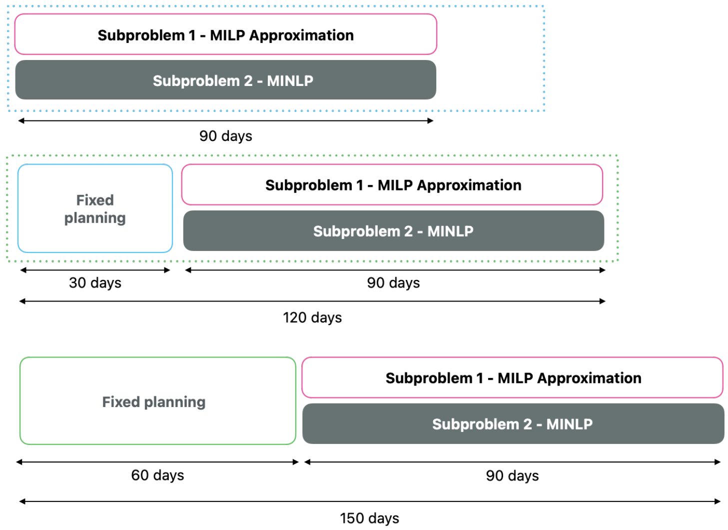

Figure 6 – Receding horizon strategy to solve over long planning timeframes

5. Results

In this section two case studies are presented to illustrate the capabilities of the proposed solution approach and to outline conclusions. First, a small case is addressed to assess the combinatorial and nonconvex nature of the problem and to establish guidelines regarding its computational complexity. For this, we propose an example with two sources and a single receiving port for feedstock *A* that is then converted through operations into product B, which is afterwards distributed to different markets (see Figure 7). Second, the model is used to solve a generalized global supply chain network over an extended horizon of one year. A decomposition strategy is proposed and analyzed in the extended example to reach quality solutions for real-sized cases.

5.1 Case study 1

A simple case study involving two sources, one intermediate receiving port and ten final destinations is presented in this section (see Figure 7). The sources are located far from consumption and require overseas shipping to supply the intermediate point. In addition, one of these sources provides greener material than the other. Once on land, the material is converted into another product, conditioned and transported by trucks to destination nodes. Meeting the demand while managing carbon intensity requires to plan operations and selecting among a discrete set of three possible speeds for ships (slow, medium and high), three operation modes for process 1 (catalyst 1, 2 or 3), two possible energy sources (from the grid or from renewable electricity generation) for process 2 and two types of fuel (electric or diesel) for onshore transportation. Each of these activities adds carbon emissions to the product according to the way in which they are performed. As expected, carbon intensity constraints are imposed at delivery nodes as stated in Equation (27). Figure 7 also includes model variables that are relevant for CI calculation.

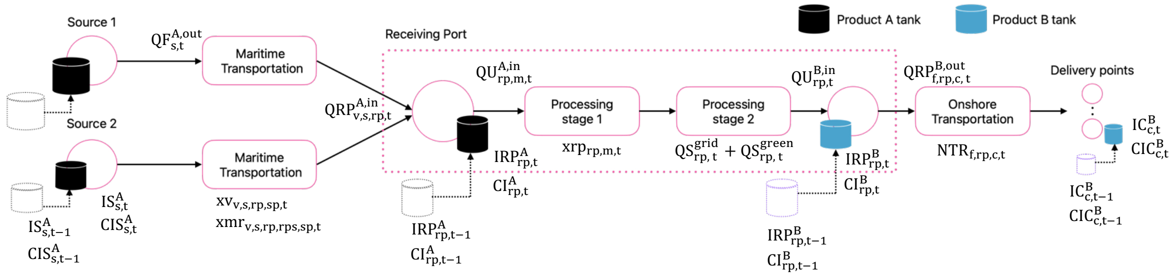

Figure 7 – Network representation for case study 1

The production rates of feedstock *A* are variable over time, as are their daily carbon intensity levels. The demand at delivery nodes is constant over time and noncompliance (due to lack of material or excess of CI) is admitted under a given economic penalty. For this example, the planning horizon is discretized into days and set to 45 days length. The main parameters of the problem such as tank sizes, production and demand rates, production yields in each mode, ship speeds, emissions per speed, mode, energy and fuel source, initial conditions and distances between nodes are given in the supplementary material. The MINLP model is coded in software GAMS and yields a formulation with 4,282 linear equations, 667 bilinear equations, 5,583 continuous variables and 352 discrete variables (see Table 1).

The model is solved both monolithically and by means of the decomposition approach proposed in Section 4, combining GUROBI for MILP subproblems and DICOPT for MINLPs. The monolithic instance of the problem is solved using the GUROBI MIQCP solver for non-convex problems. After 10,000 seconds of computation on an Intel Core i7 CPU (8 cores at 3.5 GHz) with 16 GB RAM, the solver yields a solution of 19.12 M$ with 1.10% of optimality gap. This objective value is 0.6% below the best solution found by the decomposition approach, which reports its best feasible solution after 15 seconds of CPU time. More specifically, the solution from the decomposition approach yields a total cost of 19.22 M$ and, interestingly, both approaches manage to deliver all the required amounts of product *B* under specification. Similar results are obtained when SBB solver is used for the MINLP subproblems. Although branch and bound algorithms like SBB are less likely to get trapped in local solutions, most of the discrete variables in the second subproblem are fixed from the solution of the MILP approximation in the first step, thus making outer approximation solvers like DICOPT also competitive. It is important to highlight that the solution from the monolithic approach shows small changes in the way that ships are operated, which yield savings in the first processing stage by allowing the use of mode 1 during a few periods. In addition, operating the chain unrestricted in terms of CI results in a reduction of 1.82 M$ in total costs, delivering the product with almost twice the required carbon intensity (i.e., 6.61 vs 3.38 ton of CO_2 per ton of product *B*).

Table 1 – Summary of computational results

	Description	**Solution approach**	**Linear Equations**	**Bilinear equations**	**Cont. Variables**	**Binary variables**	**Solver**	**CPU Time (s)**	**Optimality gap**	**Objective (M$)**
Case study 1	2 sources 1 Receiving port 45 days planning horizon	Monolithic	4,282	667	5,583	352	GUROBI MIQCP Non-convex	10,000	1.10 %	19.12
		Decomposition strategy *	4,282	667	5,583	135	GUROBI + DICOPT	15	0 %	19.23
		Unconstrained CI	2,867	-	3,865	352	GUROBI	12	0 %	17.39

Case study 2	2 sources 6 receiving ports 360 days planning horizon	Monolithic	314,343	60,070	183,147	62,805	GUROBI MIQCP Non-convex	15,000	>100 %	2897.45
		Decomposition strategy (+ receding horizon) *	44,120	8,014	44,927	13,614	GUROBI + DICOPT	12,600	7.6 %**	522.09

* Model size corresponding to MINLP instances

** Optimality gap relative to GUROBI MIQCP non-convex best bound

Figure 8 illustrates the maritime transportation schedule proposed by the best solution found with the decomposition strategy. Note that while shipping speeds are a tool for managing emissions, keeping inventory levels under control can constrain these strategies. The push and pull effects of sources (offer) and markets (demand) reduce the degrees of freedom of the optimization problem. However, the model is able to control emissions once the inventories have been stabilized in the first part of the planning horizon. The use of a medium speed at the end of the program is mainly driven from tightly coordinating inventory levels between sources and port, without much concern for carbon intensity due to an end-of-horizon effect. Figure 9 shows inventory levels, as well as carbon intensity values at sources and port. Note that a high-speed trip, even coming from the cleaner source, produces a substantial rise in carbon intensity levels, which is then reduced by the arrival of new material from a low-speed ship on day 29.

Regarding the first processing stage, operation mode 1 is the most economical and offers a maximum yield, but emissions are significantly higher than the other modes. Those emissions must be compensated downstream in the chain in order to avoid off-spec product. That is why the solution obtained suggests the use of mode 2 for the first 10 days and production under mode 3 from the arrival of the first vessel. Mode 3 significantly reduces the yield of product *B* obtained from *A*, but also diminishes emissions substantially. In turn, the second processing stage is an energy-intensive task, whose emissions can be regulated through the purchase of electricity from renewable or conventional sources. The energy source used in processing stage 2 appears to be an important, albeit costly, emissions adjustment variable (see Figure 10). Reaching this point with a high carbon intensity value would produce too expensive energy costs. From that, using cleaner modes in stage 1 appears as a better strategy. Final deliveries are made by diesel trucks in virtually all cases, due to their cost efficiency in comparison with cleaner fuels. This shows that it would not be convenient to manage emissions by means of greener ground transportation modes. Only the farthest destination (250 km far from port) requires cleaner transportation in 2 days to make product *B* arrive under specification. Figure 9 shows the inventory profile and carbon intensity over the sources, receiving port and a reference customer. Finally, Figure 11 illustrates the economic performance of the three solution strategies.

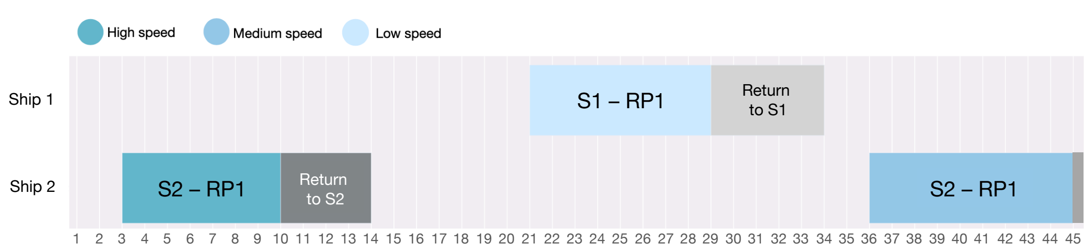

Figure 8 – Optimal maritime transportation schedule

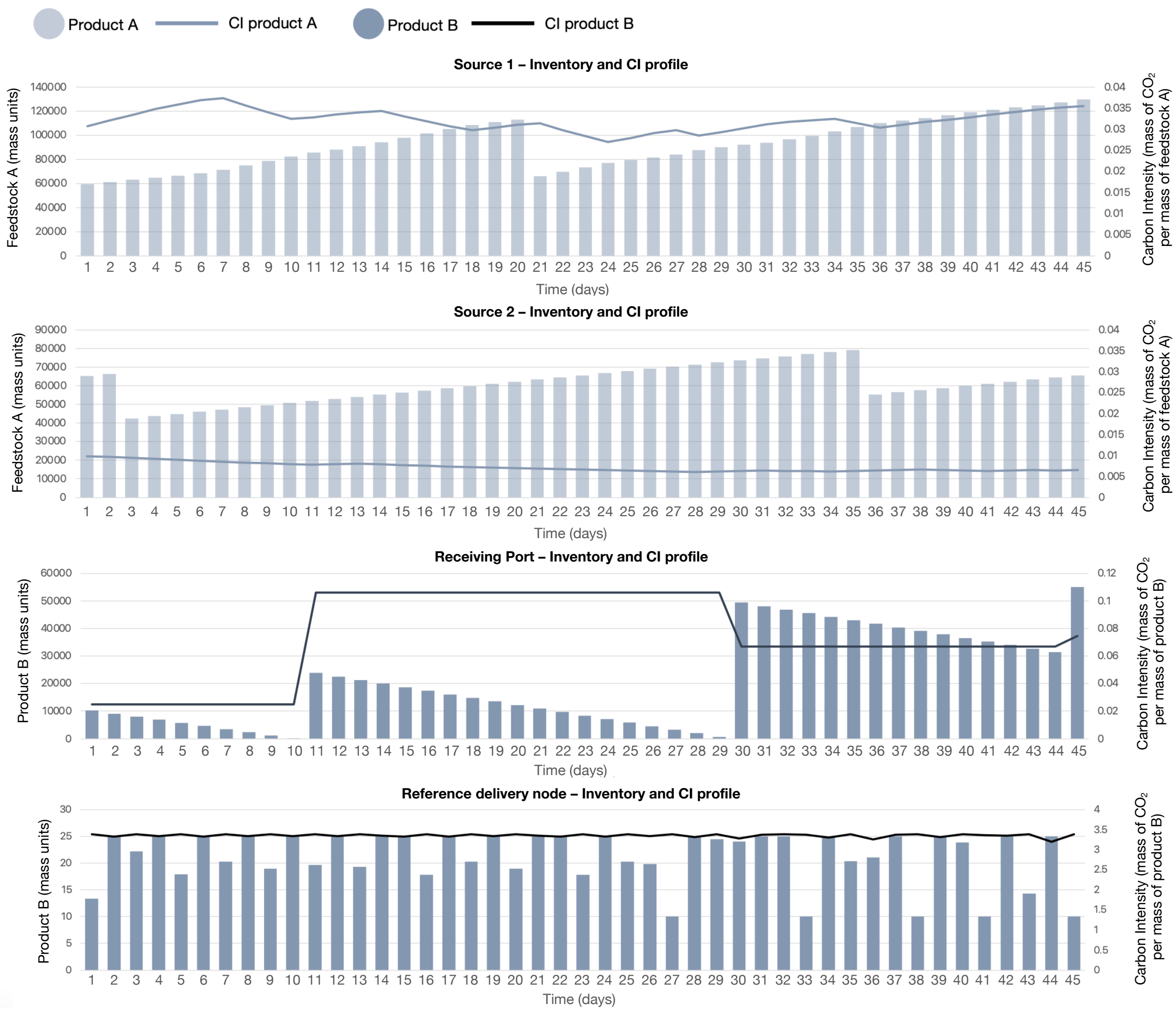

Figure 9 – Inventory profiles at storage tanks of sources, receiving port and reference customer

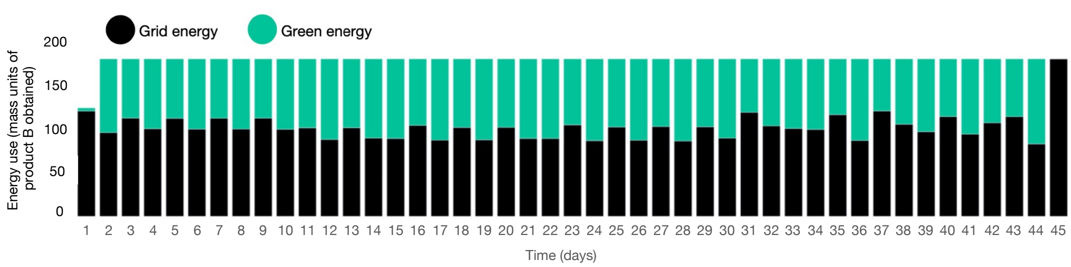

Figure 10 – Energy source selection for processing stage 2

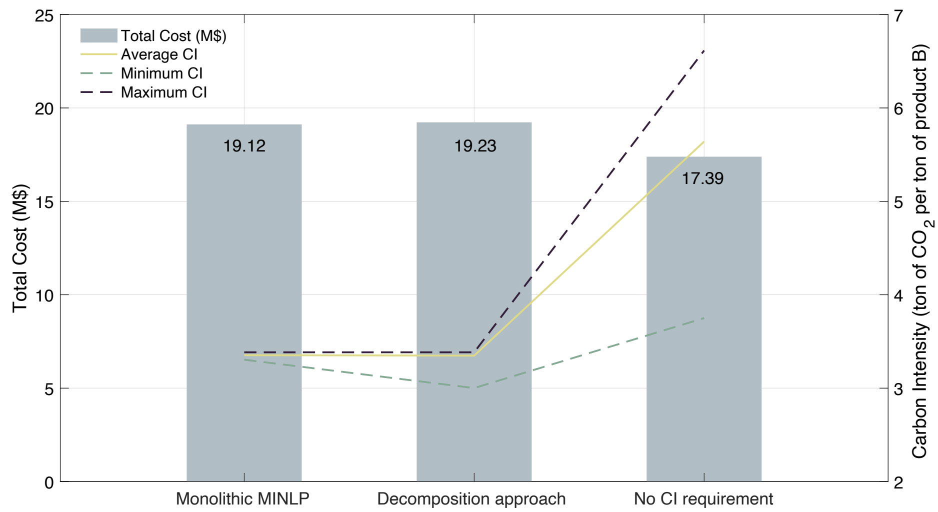

Figure 11 – Comparison of total cost and CI management for the three solutions approaches

5.2 Case study 2

In this section a real size case study is proposed, involving two sources of production and six ports of reception and unpacking of the material. An illustrative representation of this case is shown in Figure 1. The nodes are distributed around the world assuming that there are two production sources in two different continents. Receiving ports are located in pairs in other continents, namely (RP1 and RP2), (RP3 and RP4) and (RP5 and RP6) respectively. Each of these pairs supports delivery through partial discharge (also known as milk-runs). Nevertheless, a minimum amount of 30% of the ships' capacity is imposed for partial deliveries of the cargoes. Demand, CI requirements, electricity prices and storage costs also vary by market, as do the penalties for failure to meet the delivery specification. As in the previous case, production source 2 is cleaner than source 1, delivering feedstock with lower CI, albeit at a lower production rate. Ship speeds, modes of operation for processing stages, emissions and shipping costs are not disclosed for confidentiality reasons. An industrial planning horizon of one year is established in order to size and validate the ship fleet, also ensuring a proper response to time-varying supply and demand patterns.

Using a monolithic approach, the formulation yields an intractable optimization model with 374,413 equations, 60,070 of which are bilinear, 62,805 discrete variables and 183,147 continuous variables (see Table 1). The GUROBI MIQCP solver leads to an optimality gap of more than 100% (2897.45 with a lower bound of 485.1 economic units) after 10,000 seconds of computation in the same PC specs used for Case Study 1. Therefore, the decomposition approach presented in this work is coupled to a receding horizon strategy as proposed in Section 4 and used to solve the problem in an MILP-MINLP sequence (see Figure 6). The problem has been solved within a wall time of 3.5 hours with the breakdown between MILPs and MINLPs of 10,260 seconds and 2,088 seconds, respectively.

The solution strategy delivers a solution of 522.1 economic units for the entire year with an optimality gap relative to global solver bounds of 7.6%. The maritime schedule obtained is shown in Figure 12 accounting for deliveries from sources 1 and 2 to each of the receiving ports, as well as inventory and CI profiles at the tank of receiving port 5, for reference. Note that color intensity in the Gantt chart represent ship speed. Figure 12 shows how CI is optimally managed (reaching the bound of 5.776 mass units of CO_2 per unit of product B) to meet requirements while overall costs are reduced. We note that units in Figure 12 have been modified from actual values and are just reported for illustrative purposes.

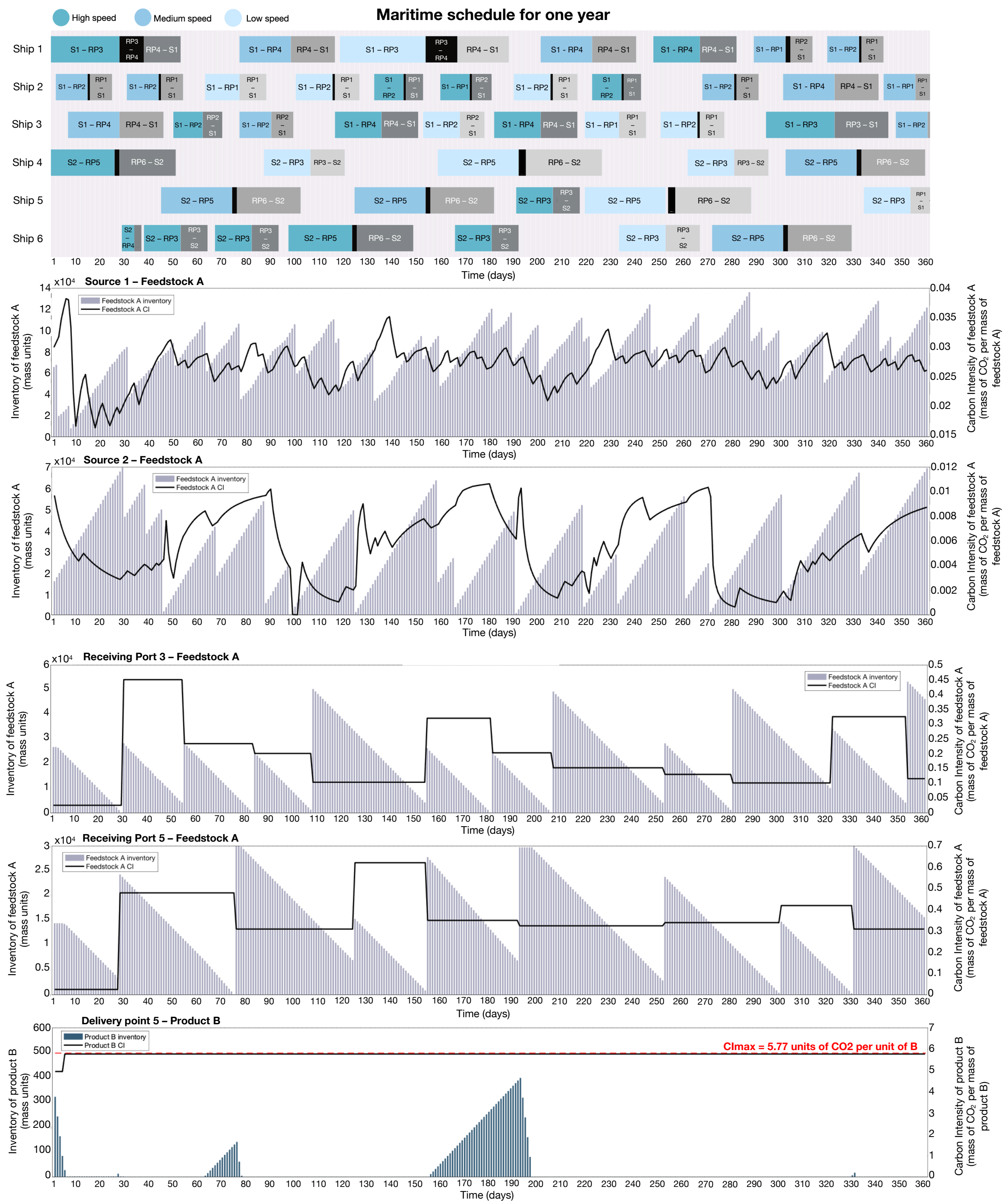

Figure 12 – Maritime schedule, inventories and carbon intensity for a subset of nodes

6. Environmental discussion

Some important findings from an environmental viewpoint can be derived from the results obtained by the optimization framework. If no limits on carbon emissions are imposed by the markets, the carbon intensity of the final products shows an average increase of almost 100%. For the reference case study that holds an overall demand of 8,019 tons of the final product B along the timeframe of 45 days, CO2 emissions increase by 25,901 tons with respect to the CI-constrained case. This can be economically valued using the expected cost per ton of CO2 emitted based on its damage potential, also known as the social cost of CO2 (Rennert et al., 2022). Currently, this value is estimated at 51 $/ton, from which it can be stated that the CI limits in the reference case (i.e., using industry data) provides an economic reduction in the environmental impact of 1.32 M$. The counterpart of this reduction is an increase in the operation costs of the supply chain of 1.82 M$ for the assessed timeframe, mainly coming from the need of using cleaner energy in the Processing Stage 2.

Figure 13 shows the evolution of total costs comprising charges from supply chain operations and damage potential of carbon emissions for different CI requirements. With no CI constraints, total emissions are valued at 2.7 M$ in the optimal solution, yielding the minimum point in the total cost curve. This means that in a context of carbon-trade regulatory framework with a penalty of 51 $ per emitted ton, it would be convenient for the company to minimize logistic costs paying for the corresponding penalties for carbon emissions. Furthermore, from simple calculations it follows that a minimum penalty cost of 93 $ per ton of CO2 is required to match the logistic savings. Nevertheless, the effects of adding a new term in the objective function accounting for the social cost of overall CO2 emissions might not be the same as setting CI constraints. The latter regulatory framework imposes that each unit of delivered product embodies a certain amount of emissions at most, and does not allow compensating emissions coming from different regions across the value chain.

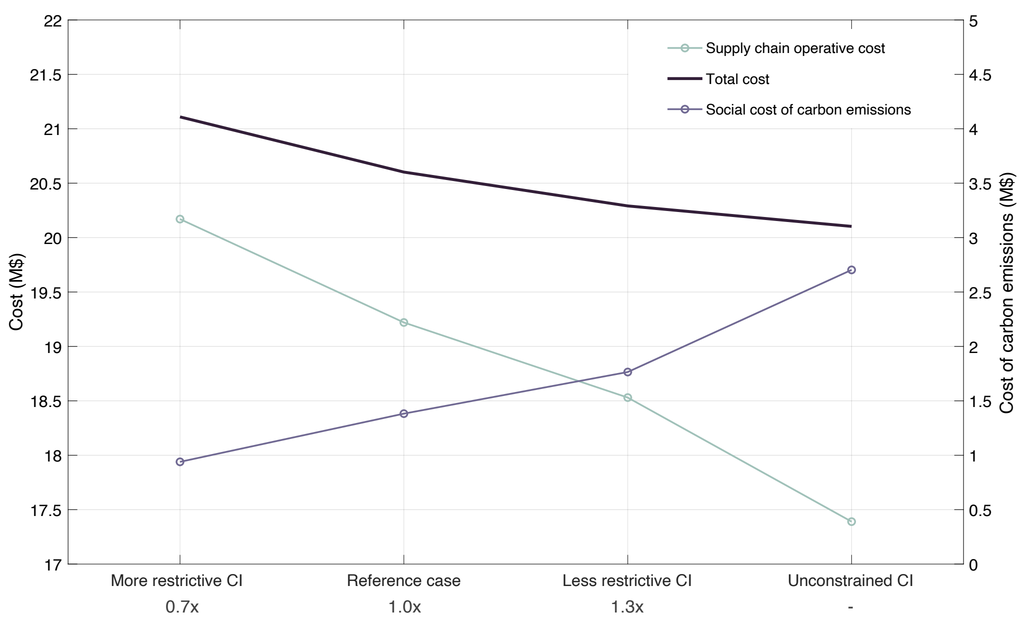

Figure 13 – Comparison of total cost for scenarios with different CI limits

Table 2 shows the contribution of each stage to the average carbon intensity embodied per unit of delivered product and to the total cost of the supply chain in the optimal solution. From this breakdown, Process 2 is clearly the most important contributor to carbon emissions. However, this process also adds 44.2% to the supply chain operating cost. Reducing emissions in this stage implies purchasing cleaner energy to mitigate emissions. In turn, transportation activities may use different technologies such as electric vehicles charged by renewables energies, hydrogen-fueled units or simply rely on speed reductions in order to lower emissions. The latter strategy, however, can hinder the timely meeting of customer demands because lead times are longer. Similarly, Process 1 can make use of different discrete modes to reduce carbon emissions but with a reduction in production yields that might also impact the performance of the supply chain. Despite this fact, the optimal solution to the illustrative example with the specified CI constraints suggests to operate Process 1 at the cleanest mode over most of the time due to the relative lower cost per unit of avoided emission. Since emissions contributed by this stage cannot be further reduced, CI targets are met by partially procuring energy from green sources at the most expensive stage, namely Process 2. Finally, storage of products under specific conditions seems not to be a spot to mitigate emissions, since its contribution to carbon intensity is quite low.

Table 2 – Contribution to carbon intensity and total costs of each stage in the supply chain for the optimal solution of the Case Study 1.

Stage	Contribution to CI	Contribution to supply chain cost
Transportation	20.5%	11.4%
Process 1	3.2%	43.6%
Process 2	76.0%	44.2%
Storage	<1%	<1%

Note that, in contrast to previous contributions where total emissions are minimized along with costs (Guillén-Gosálbez et al., 2009), our optimization framework makes use of rigorous calculations to accurately attribute emissions to feedstocks, intermediates and products. As shown in this work, proper calculations to support CI certification schemes is especially important. Nevertheless, discussion on how to proceed is still open. Integrated methodologies that combine accurate computation of emissions per unit of product through digital supply chains and digital certificate management technologies (e.g., blockchain) seems to be the key for the implementation of reliable regulatory systems. The model presented in this work can provide important insights on how to compute and manage these indicators in a systematic way.

7. Conclusions

We have presented a novel MINLP model that corresponds to a MIQCP that allows planning logistic, production and storage operations at minimum cost, to supply markets imposing different requirements on the carbon intensity (CI) of the final products. The need of tracking the CI of bulk products results in a large-scale, multi-period pooling problem that includes a set of challenging bilinear equations.

The capabilities of the MINLP formulation proposed in this work have been illustrated by addressing global supply chain structures including several types of tasks that can be executed in different modes to manage costs and emissions. We show that meeting CI requirements is not always much more costly than meeting demand at minimum total cost under unrestricted CI conditions. This follows from the fact that there are several stages along the value chain, and some of them can meet emission regulations at relatively low cost. However, critical stages like maritime shipping are more constrained. While speeds are adjustable to reduce emissions, the need of coordinating large loads along with product availability and room for storage at sources and destinations reduces the capabilities of managing CI by means of the transportation schedule. As an illustrative case, average reductions of 51.1% in the carbon intensity can be achieved by increasing the operating costs only 9.5%. In absolute terms, however, the reduction in the carbon emissions can be translated to an economic value of 1.32 million USD (from current social cost of CO_2) which is still insufficient to compensate extra costs.

The optimization framework proves to be a useful tool for identifying critical operations, prioritizing sources and markets, or determining key points for the development of clean technologies. Nevertheless, the computational challenges are evident. Monolithic models for real size problems comprise more than 62,000 discrete variables and 60,000 bilinear constraints not reaching even a good feasible solution after 3 hours of computation. Indeed, the non-convex nature of the problem requires complex relaxations to assess the global optimality gap, as well as the development of decomposition techniques to obtain good quality solutions in reasonable times.

The solution strategy proposed in this work approximates product CI using a linear formulation that is then refined by a detailed MINLP model. The MILP approximation can be solved to optimality in less than an hour of computation for a time horizon of 90 days. Although this approach does not represent a rigorous relaxation, it allows to recognize in a first step those activities that contribute the most to carbon emissions and to reduce the combinatorial complexity resulting from maritime transportation. The algorithm yields solutions that are close to those provided by global optimizers on small problems (only 2.6% more costly) and allows solving large-scale problems over long-term planning horizons.

Future research will be focused on the development of more detailed approaches such as continuous-time formulations for shipping scheduling, including more transportation modes, deriving more accurate emission functions, integrating LCA and addressing uncertainties surrounding the emissions data. We also aim to improve decomposition strategies by exploiting key aspects of multi-period pooling formulations.

Acknowledgments

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Nomenclature

Sets

C Delivery nodes

$C(rp)$ Delivery nodes that can be supplied from receiving port *rp*

F Fuel types for truck transportation

$F(rp, c)$ Fuel types for truck transportation available in the route from receiving port *rp* to customer *c*

M Operation modes for processing stage 1

$M(rp)$ Operation modes for processing stage 1 available at receiving port *rp*

MR (s, rp) Additional destinations that are visited through a milk-run when a trip is made from source *s* to receiving port *rp*

RP Receiving ports

RP(s) Receiving ports that can be supplied from source *s*

S Sources of feedstocks

SP Available speeds for ships

$SP(v)$ Available speeds for ship type *v*

T Time periods in the planning horizon

V Available ships

$V(s)$ Ships operating from source *s*

Parameters

c_m^{cr} Operation cost of Processing stage 1 when mode *m* is used (\$ per unit of feedstock *A*)

$cf_{s,\,t}$ Carbon intensity of feedstock *A* from production at source *s* in time period *t* (mass of CO_2 per unit of feedstock *A*)

c_{rp}^{e} Green energy cost at receiving port *rp* (\$ per unit of product)

c_{rp}^{e} Grid energy cost at receiving port *rp* (\$ per unit of product)

ci_c^{max} Carbon intensity of product *B* required at delivery node *c* (mass of CO_2 per unit of product *B*)

$ce_{v,sp}$ Carbon emissions of vessel *v* when traveling loaded at speed *sp* (mass of CO_2 per unit of distance)

$cr_{v,sp}$ Carbon emissions of vessel *v* when traveling empty at speed *sp* (mass of CO_2 per unit of distance)

$c_{v,rp}^{port}$ Cost for admitting ship *v* in receiving port *rp* (\$)

c_v^{ret} Return maintenance cost for ship *v* (\$)

$c_{v,s}^{src}$ Cost for admitting ship *v* in source *s* (\$)

$d_{rp,\,c}$ Distance between receiving port *rp* and delivery node *c* (distance)

$d_{s,\,rp}$ Distance between source *s* and receiving port *rp* (distance)

$d_{rp,\,rp'}$ Distance between receiving port *rp* and *rp'* (distance)

fxc_v Sailing cost of ship *v* (\$ per time period)

$nt_{f,rp}$ Number of available trucks of fuel type *f* at receiving port *rp* (-)

s_v^{CAP} Load capacity of the ship *v* (mass)

$ss_{s,t}^{A}$ Rate of supply of feedstock *A* to source *s* during period *t* from production (mass per time period)

vc_v Fuel cost of ship *v* (\$ per unit of distance)

$\bar{\alpha}_m$ Maximum processing amount for operation mode *m* in processing stage 1 in a time period (mass of product *A* per time period)

$\underline{\alpha}_m$ Minimum processing amount for operation mode *m* in processing stage 1 in a time period (mass of product *A* per time period)

γ_m Processing yield from product *A* to *B* of operation mode *m* (unit mass of *A* per unit mass of *B*)

$\Delta t^{d}_{s,rp,sp}$ Traveling time from source *s* to receiving port *rp* at speed *sp* (number of periods)

$\Delta t^{dt}_{s,rp,sp}$ Traveling time from source *s* to receiving port *rp* at speed *sp,* including backhaul (periods)

$\Delta t^{mr1}_{s,rp,rp',sp}$ Traveling time from source *s* to the first destination *rp* in a milk-run also visiting *rp'* at speed *sp* (number of periods)

$\Delta t^{mr2}_{s,rp',rp,sp}$ Traveling time from source *s* to the second destination *rp* in a milk-run previously visiting *rp'* at speed *sp* (number of periods)

$\Delta t^{mrt}_{s,rp,rp',sp}$ Traveling time from source *s* to destination *rp* and second destination *rp'* at speed *sp*, including backhaul (number of periods)

$\varepsilon_{e/g}$ Carbon emissions from grid/green energy consumption (mass of CO_2 per unit of product *B*)

ζ_{rp} Cost of storing product *B* at receiving port *rp* (\$ per unit of product *B*)

θ_m Carbon emissions from processing stage 1 operating at mode *m* (mass of CO_2 per unit of product *A*)

λ_f Truck availability (time per time period)

μ_f Load capacity of trucks using fuel type *f* (mass)

ρ_v Minimum cargo ratio in the ship *v* (-)

σ_f Carbon emissions from truck transportation when using fuel type *f* (mass of CO_2 per unit of distance)

$\tau_{rp,c}$ Travel time from receiving port *rp* to delivery node *c* including backhaul (time)

φ_c Unit cost for exceeding the required CI in the delivery point *c* (\$ per mass unit of CO_2)

χ_f Cost of truck transportation for fuel type *f* (\$ per unit of distance)

$\psi_{c,t}$ Cost for not meeting demand of the delivery point *c* (\$ per unit of product *B*)

$\Omega_{rp,\,t'}$ Aggregated customer demand of receiving port *rp* in time period *t* (mass of product *B*)

$\omega_{c,t}$ Demand of delivery node *c* in time period *t* (mass per time period)

Variables

$CI^{A}_{rp,t}$ Carbon intensity of *A* stored at receiving port *rp* in time period *t* (mass of CO_2 per unit of *A*)

$CI^{B}_{rp,t}$ Carbon intensity of *B* stored at receiving port *rp* in time period *t* (mass of CO_2 per unit of *B*)

$CIS_{s,\,t}$ Carbon intensity of *A* stored at source *s* in time period *t* (mass of CO_2 per unit of *A*)

$CO2P_{rp,\,t}$ Carbon emissions from production tasks performed at *rp* in time period *t* (mass of CO_2)

$CO2S_{rp,\,t}$ Carbon emissions attributed to material unloaded in *rp* in time period *t* (mass of CO_2)

$CO2T_{rp,\,t}$ Carbon emissions from maritime transportation to *rp* in time period *t* (mass of CO_2)

$CO2TT_{c,\,t}$ Carbon emissions from truck transportation to c in time period t (mass of CO_2)

CRC_t Processing stage 1 associated cost in time period t ($)

EPC_t Economic penalty costs in time period t ($)

$GHGT_{rp,t}$ Total amount of carbon emissions attributable to receiving port rp up to time t (mass of CO_2)

$IC_{c,t}^{B}$ Inventory of product B at delivery node c in period t (mass of product B)

$IRP_{rp,t}^{A}$ Inventory of feedstock A at receiving port rp in period t (mass of feedstock A)

$IRP_{rp,t}^{B}$ Inventory of product B at receiving port rp in period t (mass of product B)

$IS_{s,t}^{A}$ Inventory of feedstock A at source s in period t (mass of feedstock A)

MSC_t Maritime transportation costs in time period t ($)

$NTR_{f,rp,c,t}$ Number of trips from rp to c using trucks of fuel type f in period t (-)

PC_t Cost of processing stage 2 in time period t ($)

$QD_{v,s,rp,sp,t}$ Amount of feedstock A that is sent from source s to port rp by ship v at speed sp in period t through direct trip (mass of feedstock A)

$QF_{s,t}^{A,out}$ Amount of feedstock A withdrawn from source s in period t (mass of feedstock A)

$QMR1_{v,s,rp,rp',sp,t}$ Amount of feedstock A that is sent from source s to first destination rp by ship v at speed sp in period t through milk-run trip (mass of feedstock A)

$QMR2_{v,s,rp',rp,sp,t}$ Amount of feedstock A that is sent from source s to second destination rp by ship v at speed sp in period t through milk-run trip (mass of feedstock A)

$QRP_{v,s,rp,t}^{A,in}$ Amount of feedstock A that is loaded into receiving port rp from source s by ship v in period t (mass of feedstock A)

$QRP_{f,\,rp,\,c,\;\;t}^{B,out}$ Amount of product B sent from receiving port rp to delivery point c with trucks using fuel type f in period t (mass of product B)

$QS_{v,s,rp,\,sp,\,t}^{A,out}$ Amount of A that is sent from s to rp by ship v at speed sp in period t (mass of feedstock A)

$QS_{rp,\;\;t}^{g}$ Amount of product B processed in stage 2 using green (renewable) energy at receiving port rp in period t (mass of product B)

$QS_{rp,\;\;t}^{e}$ Amount of product B processed in stage 2 using grid (non-renewable) energy at receiving port rp in period t (mass of product B)

$QU_{rp,t}^{A}$ Amount of feedstock A that is sent to processing stage 1 in rp in period t (mass of feedstock A)

$QU_{rp,m,\;t}^{A,in}$ Amount of A processed through mode m at receiving port rp in period t (mass of feedstock A)

$QU_{rp,t}^{B,in}$ Amount of B that is sent to processing stage 2 at receiving port rp in period t (mass of product B)

SC_t Product B storage cost in time period t ($)

TC_t Truck transportation cost in time period t ($)

$TPB_{rp,\,t}$ Total amount of B delivered and stored up to time t from receiving port rp (mass of product B)

$UD_{c,t}$ Unmet demand at delivery node *c* in time period *t* (mass of product *B*)

$xmr_{v,s,rp,rp',sp,t}$ Binary variable telling if ship *v* is performing a milk-run from source *s* to receiving ports *rp* and *rp'* at speed *sp* starting at period *t* (-)

$xv_{v,s,rp,sp,t}$ Binary variable telling if ship *v* is performing a direct trip from source *s* to receiving port *rp* at speed *sp* starting at period *t* (-)

$xrp_{rp,m,t}$ Binary variable telling if processing stage 1 at receiving port *rp* performs under operation mode *m* in period *t* (-)

References

1. Adhya, N., Tawarmalani, M., Sahinidis, N.V., 1999. A Lagrangian approach to the pooling problem. Ind. Eng. Chem. Res. 38, 1956–1972. https://doi.org/10.1021/ie980666q

2. Allaoui, H., Guo, Y., Choudhary, A., Bloemhof-Ruwaard, J.M., 2018. Sustainable agro-food supply chain design using two-stage hybrid multi-objective decision-making approach. Comput. Oper. Res. 89, 369–384. https://doi.org/10.1016/j.cor.2016.10.012

3. Azapagic, A., Clift, R., 1999. The application of life cycle assessment to process optimisation. Comput. Chem. Eng. 23, 1509–1526. https://doi.org/10.1016/s0098-1354(99)00308-7

4. Benjaafar, S., Li, Y., Daskin, M., 2013. Carbon footprint and the management of supply chains: insights from simple models. IEEE Trans. Autom. Sci. Eng. 10, 99–116. https://doi.org/10.1109/TASE.2012.2203304

5. Bontron, C., Rodrigues, D., Braz, C.G., Matos, H.A., 2023. Life cycle assessment of two liquid organic hydrogen carriers. Comput. Aided Chem. Eng. 52, 3381–3386. https://doi.org/10.1016/b978-0-443-15274-0.50539-4

6. Burgess, J., Nye, M., 2008. Re-materialising energy use through transparent monitoring systems. Energy Policy 36, 4454–4459. https://doi.org/10.1016/j.enpol.2008.09.039

7. Caritte, V., Acha, S., Shah, N., 2015. Enhancing corporate environmental performance through reporting and roadmaps. Bus. Strategy Environ. 24, 289–308. https://doi.org/10.1002/bse.1818

8. Carter, C.R., Easton, P.L., 2011. Sustainable supply chain management: evolution and future directions. Int. J. Phys. Distr. Log. Manag. 41, 46–62. https://doi.org/10.1108/09600031111101420

9. Castro, P.M., 2016. Source-based discrete and continuous-time formulations for the crude oil pooling problem. Comput. Chem. Eng. 93, 382–401. https://doi.org/10.1016/j.compchemeng.2016.06.016

10. Foulds, L.R., Haugland, D., Jörnsten, K., 1992. A bilinear approach to the pooling problem. Optimization 24, 165–180. https://doi.org/10.1080/02331939208843786

11. Garcia-Alvarado, M., Paquet, M., Chaabane, A., 2016. Joint strategic and tactical planning under the dynamics of a cap-and-trade scheme. IFAC-Pap. 49, 622–627.

12. Ghosh, P., Jha, A.K., Sharma, R., 2020. Managing carbon footprint for a sustainable supply chain: a systematic literature review. Mod. Supply Chain Res. Appl. 2, 123–141. https://doi.org/10.1108/mscra-06-2020-0016

13. Govindan, K., Jafarian, A., Khodaverdi, R., Devika, K., 2014. Two-echelon multiple-vehicle location–routing problem with time windows for optimization of sustainable supply chain network of perishable food. Int. J. Prod. Econ. 152, 9–28. https://doi.org/10.1016/j.ijpe.2013.12.028

14. Guillén-Gosálbez, G., Grossmann, I.E., 2009. Optimal design and planning of sustainable chemical supply chains under uncertainty. AIChE J. 55, 99–121. https://doi.org/10.1002/aic.11662

15. Guillén-Gosálbez, G., Mele, F. D., Grossmann, I. E., 2009. A bi-criterion optimization approach for the design and planning of hydrogen supply chains for vehicle use. AIChE J., 56, 650–667. https://doi.org/10.1002/aic.12024

16. Hervani, A., Helms, M., Sarkis, J., 2005. Performance measurement for green supply chain management. Benchmarking: An International J. 12, 330–353.

17. Hugo, A., Pistikopoulos, E.N., 2005. Environmentally conscious long-range planning and design of supply chain networks. J. Clean. Prod. 13, 1471–1491. https://doi.org/10.1016/j.jclepro.2005.04.011

18. Jiang, Y., Zhao, Y., Dong, M., Han, S., 2019. Sustainable supply chain network design with carbon footprint consideration: A case study in China. Math. Probl. Eng. 2019, 1–19. https://doi.org/10.1155/2019/3162471

19. Joshi, S., 2022. A review on sustainable supply chain network design: Dimensions, paradigms, concepts, framework and future directions. Sustainable Operations and Computers, 3, 136–148. https://doi.org/10.1016/j.susoc.2022.01.001

20. Kellner, F., Igl, J., 2015. Greenhouse gas reduction in transport: Analyzing the carbon dioxide performance of different freight forwarder networks. J. Clean. Prod. 99, 177–191. https://doi.org/10.1016/j.jclepro.2015.03.026

21. Kondili, E., Pantelides, C.C., Sargent, R.W.H., 1993. A general algorithm for short-term scheduling of batch operations—I. MILP formulation. Comput. Chem. Eng. 17, 211–227. https://doi.org/10.1016/0098-1354(93)80015-F

22. Majer, J.M., Henscher, H.A., Reuber, P., Fischer, D., Fischer, D.A., 2022. The effects of visual sustainability labels on consumer perception and behavior: A systematic review of the empirical literature. Sustain. Prod. Consum. 33, 1–14. https://doi.org/10.1016/j.spc.2022.06.012

23. Mala, P., Palanivel, M., Priyan, S., Jirawattanapanit, A., Rajchakit, G., Kaewmesri, P., 2022. Sustainable supply chain system for defective products with different carbon emission strategies. Sustainability 14, 16082. https://doi.org/10.3390/su142316082

24. Maravelias, C.T., 2021. Chemical Production Scheduling: Mixed-Integer Programming Models and Methods. First ed. Cambridge University Press, New York.

25. Martí, J.M.B., Tancrez, J., Seifert, R.W., 2015. Carbon footprint and responsiveness trade-offs in supply chain network design. Int. J. Prod. Econ. 166, 129–142. https://doi.org/10.1016/j.ijpe.2015.04.016

26. Ramudhin, A., Chaabane, A., Paquet, M., 2010. Carbon market sensitive sustainable supply chain network design. Int. J. Manag. Sci. Eng. Manag., 5, 30–38. https://doi.org/10.1080/17509653.2010.10671088

27. Rennert, K., Errickson, F., Prest, B.C. et al., 2022. Comprehensive evidence implies a higher social cost of CO2. Nature 610, 687–692. https://doi.org/10.1038/s41586-022-05224-9

28. Riera, J.A., Lima, R.M., Knio, O.M., 2023. A review of hydrogen production and supply chain modeling and optimization. Int. J. Hydrog. Energy. 48, 13731–13755. https://doi.org/10.1016/j.ijhydene.2022.12.242

29. Shah, N., Pantelides, C.C., Sargent, R.W.H., 1993. A general algorithm for short-term scheduling of batch operations—II. Computational issues. Comput. Chem. Eng. 17, 229–244. https://doi.org/10.1016/0098-1354(93)80016-g

30. Shaw, K., Irfan, M., Shankar, R., Yadav, S.S., 2016. Low carbon chance constrained supply chain network design problem: a Benders decomposition based approach. Comput. Ind. Eng. 98, 483–497. https://doi.org/10.1016/j.cie.2016.06.011

31. Subramanian, R., Talbot, F.B., Gupta, S., 2010. An approach to integrating environmental considerations within managerial decision-making. J. Ind. Ecol. 14, 378–398. https://doi.org/10.1111/j.1530-9290.2010.00243.x

32. Sundarakani, B., de Souza, R., Goh, M., Wagner, S., Manikandan, S., 2010. Modeling carbon footprints across the supply chain. Int. J. Prod. Econ. 128, 43–50. https://doi.org/10.1016/j.ijpe.2010.01.018

33. Taufique, K.M.R., Nielsen, K.S., Dietz, T., 2022. Revisiting the promise of carbon labelling. Nature Climate Change 12, 132–140. https://doi.org/10.1038/s41558-021-01271-8

34. Xu, M., Lin, B., 2021. Leveraging carbon label to achieve low-carbon economy: Evidence from a survey in Chinese first-tier cities. J. Environ. Manag. 286, 112201. https://doi.org/10.1016/j.jenvman.2021.112201

35. Younis, H., Sundarakani, B. and Vel, P., 2016. The impact of implementing green supply chain management practices on corporate performance. Competitiveness Review 26, 216–245. https://doi.org/10.1108/CR-04-2015-0024