I&EC research
Industrial & Engineering Chemistry Research

Article

Cite This: Ind. Eng. Chem. Res. 2018, 57, 11342−11349

pubs.acs.org/IECR

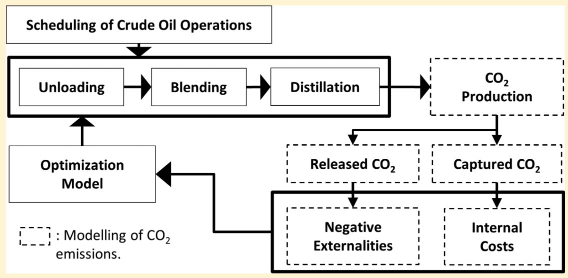
An Optimization Model To Incorporate CO_2 Emissions in the Scheduling of Crude Oil Operations

Pablo Ugalde-Salas,*[†] Felipe Díaz-Alvarado,[‡] Salvador A. Flores,[§] and Héctor Ramírez[†,§]

[†]Department of Mathematical Engineering, Universidad de Chile, Santiago 8370456, Chile
[‡]Department of Chemical Engineering, Biotechnology and Materials, Universidad de Chile, Santiago 8370456, Chile
[§]Center for Mathematical Modelling (UMI 2807, CNRS), Universidad de Chile, Santiago 8370456, Chile

Supporting Information

ABSTRACT: In previous works CO_2 emissions in oil refineries have been studied for production unit planning. In this manuscript the associated CO_2 mitigation costs are added to the scheduling of crude oil unloading and blending. Numerical simulations executed on literature cases show that the optimal scheduling may be affected, and thus CO_2 emissions may be greater than those predicted from production unit planning. Furthermore, the biobjective problem of maximizing profits and minimizing CO_2 emissions is studied; pareto-optimal solutions and the lowest carbon pricing that induces the refinery to minimize CO_2 emissions are presented for each case.



1. INTRODUCTION

Industrial activity dating from the beginning of the 19th century has been linked to the use of fossil fuels as its main energy source. As a consequence, levels of atmospheric CO_2 concentration are rising. It is a widely accepted scientific fact that the rise is due to human activity and it exceeds historical levels.[1]

There is a growing trend on regulations over green house gas emissions, such as United Nations Framework Convention on Climate change (1992), Kyoto Protocol (1997), and Paris Agreement (2015), just to name a few. Therefore, fuel dependent industries face a challenge in the upcoming years. This is the case for oil refining companies. Since these companies participate in the life cycle of many products, a reduction of CO_2 emissions produced by this sector has enormous implications in the entire global warming potential of industrial and social activity.[2]

Bengtsson[3] provides a literature review of the oil refining industry. A classical division of a refinery's supply chain is given in three subprocesses.

1. Crude oil unloading and blending.
2. Production unit planning.
3. Product blending and recipe optimization.

The purpose of this manuscript is threefold: (i) to show that an optimal scheduling of the first subprocess may vary substantially if the CO_2 mitigation costs are taken into account, (ii) to explore the Pareto frontier of emissions and profits, and (iii) to find the lowest carbon pricing that forces a refinery to minimize CO_2 emissions. To do so, the objective function of the model used for scheduling is modified. The last point is of importance since there is no consensus in the literature on which model is the best to use; therefore, the method can be adapted to other formulations if necessary.

The first subprocess consists of defining the crude oil transfers between vessels, storage tanks, charging tanks, and distillation units. The planner determines the circulation of crude oil through units in order to maximize short-term profits or minimize operational costs. This problem is solved in the literature by means of mixed integer nonlinear programming (MINLP), for a fixed time horizon, usually in the range of 1 or 2 weeks. Some aspects of the production planning are discussed later, since the second and first subprocess are interrelated.

The integer nature of the problem comes from the modeling of tasks in a temporal sequence; the nonlinearity arises from tracking the composition of mixtures in charging tanks. To solve such models a MILP−NLP decomposition strategy of MINLP can be frequently found, which consists of solving a mixed integer linear program (MILP) and then fixing the integer variables and solving a nonlinear program (NLP).[4−7] There are also global optimization solvers that can tackle this problem directly. In two studies comparing both approaches the two step decomposition strategy worked as well as the global solvers in terms of optimality and outperformed the global solvers in CPU time.[5,8] But Castro[4] shows the inverse with a different formulation.

Concerning this representation, earlier mathematical models were based on discrete time representation (e.g., refs 9−12). More recent literature focuses on continuous time formula-

Received: October 31, 2017
Revised: June 1, 2018
Accepted: July 25, 2018
Published: July 25, 2018

DOI: 10.1021/acs.iecr.7b04331
Ind. Eng. Chem. Res. 2018, 57, 11342−11349

tions because of their reduced model size.[7] However, the findings of Castro[4] show that discrete time representations may be preferable when minimizing costs.

Chen et al.[13] provide a review of three different continuous time modeling approaches: the event-based models,[14,15] the unit slot-based models,[16] and the multioperation sequence (MOS) models.[5,17] The essential difference between these is how the variables are defined. They conclude that the MOS model performed better in terms of computing time, but in a specific case the resulting scheduling returned lower profits than the other models.

A more recent approach is the resource network modeling introduced by Castro et al.[8] They compare their model with the MOS model of Mouret et al.,[5] and both models perform similarly in terms of optimality; however, that of Mouret outperforms in CPU times (Table 3). Their model has been successfully applied to real case scenarios.[18]

There is yet another approach based on Petri Nets of Zhang et al.;[19] however, as pointed out in the same article, the addition of an objective function is still under development.

Wu et al.[20] addresses sustainability in the scheduling problem by considering the energy savings in oil transportation from storage tanks to charging tanks. The relationship in energy and flow is nonlinear but avoids the nonlinearity by realizing that the number of different flow rates are limited in practice. However, as stated by Van Straelen et al.,[21] even energy-efficient refineries will continue to produce considerable amounts of CO_2, and the use of CO_2 capture technologies is a way to further diminish this impact.

In regard to the optimality and computational performance considerations mentioned before, in this work we choose to follow the model of Mouret et al.[5] The study of the pareto-optimal solutions required multiple executions of the problem, so this approach was a good compromise between global optimality and time efficiency.

The second subprocess consists of deciding which crude oils to buy and which types of products are to be produced for a time horizon of two or three months. The planner should thus determine the operation mode for the different production units to reach the most profitable configuration. Changing the operation mode of a unit is a decision that usually reduces the capacity and quality of the refinement for a short period (Elkamel et al.[22]). This subprocess is also tackled by mixed integer nonlinear programming, and the reader may refer to Neiro and Pinto,[23,24] who solved a real case in the Brazilian Petroleum industry.

In Babusiaux's work[25] linear programming techniques are used for a life cycle analysis of finished products in an oil refinery, and the authors show that the main contribution of CO_2 emissions can be traced back to the refinement process in production units rather than to combustion of finished products (Table 6 of the article). Elkamel et al.[22] developed an optimization model (also a MINLP) to take into account CO_2 emissions of an oil refinery during the planning process. Their model maximizes profits with the constraint that emissions should fulfill a reduction target. One of their main conclusions is that the use of capture technologies is necessary to achieve reductions over 30% in CO_2 emissions.

The amount of fuel used in the production units depends on the amount of crude oil to be processed in the respective unit; more precisely, it depends on the flow entering each unit (see Figure 1). At the same time, the amount of emitted CO_2 grows on the amount of burnt fuel. Since distillation units are one of the meeting points between the planning of production units and the scheduling of crude oils operations, CO_2 considerations are included in the former process.

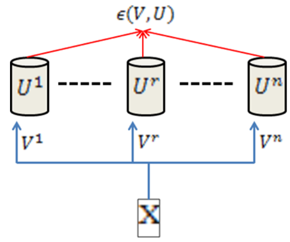


Figure 1. Schema of the CO_2 emissions from distillation units. X represents the scheduling decision, $V = (V^1, \cdots, V^n)$ are the volumes entering each distillation unit, and $U = (U^1, \cdots, U^n)$ represents if some capture technology is being used in that distillation unit. $\epsilon(V, U)$ accounts for the total emissions.

It is fairly intuitive that the objectives of minimizing emissions and maximizing profits are inherently opposed, as they have been studied in the planning of production units.[22] What is not evident is that once planning is decided, the scheduling may produce more emissions than expected.

A method is proposed to include CO_2 reduction considerations in the scheduling of crude oil operations of an oil refinery, namely unloading, blending, and distillation.

1. Mitigation costs and also a penalization term over the amount of CO_2 to be emitted is included in the objective function.
2. The trade-off between emissions and profits is done by varying the weight of the penalization term in the objective function.

This weight can be interpreted as carbon pricing over emissions; therefore, the penalization term corresponds to the negative externalities associated with CO_2 emissions.

These ideas are implemented in objective functions, and to the authors' knowledge, these changes have not been proposed previously in optimization problems in scheduling of crude oil operations to reduce emissions in refineries.

In this sense, the present work seeks to be a contribution to the reduction of emissions in the synthesis and optimization of industrial processes.The novelty lies in considering planning decisions in the scheduling process and observing that CO_2 emissions can go higher than expected by planning. Studying that problem gives insights on possible regulations for refineries.

2. METHODS

This section accounts for the mathematical optimization model (MINLP) used in the numerical experiences. It is organized in three subsections dealing with the mathematical modeling and a subsection dealing with the (MILP-NLP) decomposition strategy.

2.1. CO_2 Emissions in Oil Refineries. In this subsection the equations modeling CO_2 emissions and their associated costs are derived. The following concepts are borrowed from the model developed by Elkamel et al.[22] The authors consider three options for reducing CO_2 emissions:

1. Flow rate balancing: By increasing the flow to units that emit less CO_2 than others.
2. Fuel switching: Changing the fuel used in the production unit.

DOI: 10.1021/acs.iecr.7b04331
Ind. Eng. Chem. Res. 2018, 57, 11342−11349

3. CO_2 capture: The inclusion of CO_2 capture technologies in distillation units; this is called an "end of the pipe" solution and is the most expensive one.

The same article provides a summary of the available technologies for reducing CO_2 emissions. A current evaluation of such end of the pipe solutions in the sector is performed by Van Straelen et al.[21] They conclude that the use of such technologies is more costly than current carbon trading values, so only an increase in such values, mandatory regulations, or major technological breakthroughs are required.

The Elkamel et al.[22] model is intended to plan oil refineries whereas the model of this article is aimed at scheduling crude oil operations.

The main equations borrowed from their model are eqs 11, 19, and 20 of the article,[22] those corresponding to profits, produced CO_2, and released CO_2, respectively, which are restated to be applied in the present work.

Let R_D be the set of all distillation units and L be the set of all capture technologies. For each production unit, the emissions are proportional to a nondecreasing function f of the inlet flow rate. The emissions E_r of each unit $r \in R_D$ are of the form

$$E_r = EF_r f(FR_r)$$

where FR_r is the inlet flow rate of distillation unit r and EF_r is the emission factor. For the current work the inlet flow rate is taken as the *mean* flow rate. If the scheduling time horizon is H and the total volume that enters distillation unit r is V_r then $FR_r = V_r/H$. This is justified by the fact that distillation units should operate continuously. In the model used in this article the function f is the identity function. Since the time horizon is fixed in the scheduling problem, the emissions only depend on V_r. The emissions of each distillation unit become

$$E_r = EF_r V_r \tag{1}$$

where EF_r is an emission factor of CO_2 per unit of crude oil, measured in [tons of CO_2/bbl]. Notice that this emission factor models the carbon content of fuels used in production units.

Let $U_r^l \in \{0,1\}$ with $r \in R_D$, $l \in L$, being a parameter with value 1 if capture technology l is implemented in distillation unit r, and 0 otherwise. The cost of treating a ton of CO_2 in a distillation unit with capture technology l is denoted by c^l. The total cost associated with CO_2 capture becomes

$$\sum_{\substack{l \in L \\ r \in R_D}} c^l U_r^l E_r$$

At most one technology can be implemented in each unit; therefore, for each distillation unit r:

$$\sum_{l \in L} U_r^l \leq 1$$

U_r^l is a parameter, and then the latter inequality is not an actual constraint on the scheduling. However, it is a constraint in the planning of production units since the planner must decide which technology, if any, should be implemented in each unit.

Finally if technology l allows a fraction $q_{\text{abs}}^l \in (0, 1)$ of the emissions to be absorbed, then the total emissions released E_{rel} to the atmosphere by each distillation unit becomes

$$E_{\text{rel}} = \sum_{r \in R_D} \left(1 - \sum_{l \in L} q_{\text{abs}}^l U_r^l\right) E_r \tag{2}$$

Taking into account the previous considerations, in the next section a model for the scheduling of crude oil operations is provided. Two very important assumptions in the modeling should be highlighted. The simplest increasing function for f was chosen, and the flow rate on a given time horizon was simplified by its mean flow rate.

2.2. Scheduling of Crude Oils Operations. This subsection presents the essential elements of the model used for the optimization of the scheduling and unloading of crude oils. The original model[5] was extended by adding the CO_2 emission reduction costs. For the sake of completeness a full description of the model is included as Supporting Information.

There are four different subsets of the set resources (R).

- Vessels carrying the crude oils (R_V).
- Storage tanks for arriving crude oils (R_S).
- Charging tanks for mixing the crude oils in storage tanks (R_C).
- Distillation units which process the blends produced in charging tanks (R_D).

and three different subsets of the set **operations** W.

- Crude oil unloading from vessels to storage tanks (W_U).
- Crude oil transfers from storage tanks to charging tanks (W_T).
- Crude oil transfers from charging tanks to distillation units (W_D).

Two other relevant sets are the set of crude oil types (C) and the set of crude properties (K). The topology of the refinery is defined by the sets of input and output operations ($I_r \subset W$ and $O_r \subset W$, respectively) of the resource $r \in R$.

The goal is to maximize profits in a fixed production horizon satisfying a given demand for specified products, by acting on the following decision variables that characterize the process:

- The order in which operations take place.
- Starting times and duration of operations.
- Transferred volumes in each operation.

This model adopts the structure of priority slots[17] to address the order of operations. A brief summary of this structure is presented below.

Given $n \in \mathbb{N}$, an operation v is assigned to slot $i \in \{1, \cdots, n\}$. Let v and w be two operations that cannot occur simultaneously, assigned to priority slots i and j, respectively. If $i < j$, operation v must end before operation w begins. This mechanism is better expressed by the nonoverlapping operation constraints in the Supporting Information file. This modeling tool has the disadvantage of creating symmetric solutions and increasing the solving time exponentially on n. The same approach as in the original work is used for avoiding such symmetries.

The **variables** can be summarized as follows:

- **Assignment variables:** $Z_{iv} \in \{0,1\}$, $i \in T$, $v \in W$. It takes 1 as a value if priority slot i was assigned operation v, and 0 otherwise.
- **Starting times:** $S_{iv} \in \mathbb{R}_+$, $i \in T$, $v \in W$. Starting time of operation v if it is assigned to priority slot i, 0 otherwise. S_{iv} is measured in days.

DOI: 10.1021/acs.iecr.7b04331
Ind. Eng. Chem. Res. 2018, 57, 11342−11349

- **Duration:** $D_{iv} \in \mathbb{R}_+$, $i \in T$, $v \in W$. Duration of operation v if it is assigned to priority slot i, 0 otherwise. D_{iv} is measured in days.
- **Total volume transferred:** $V_{iv} \in \mathbb{R}_+$, $i \in T$, $v \in W$. Total crude oil volume transferred in operation v if it is assigned to priority slot i, 0 otherwise. V_{iv} is measured in [Mbbl] (1000 barrel).
- **Partial transferred volume:** $V_{\mathrm{ivc}} \in \mathbb{R}_+$, $i \in T$, $v \in W$, $c \in C$. Crude oil volume of type c transferred in operation v if it is assigned to priority slot i, 0 otherwise. V_{ivc} is measured in [Mbbl].
- **Total tank volume** $L_{ir} \in \mathbb{R}_+$, $i \in T$, $r \in R_A \cup R_M$. Total volume crude oil accumulated in tank r before the execution of operation assigned to priority slot i. Measured in [Mbbl].
- **Partial tank volume:** $L_{irc} \in \mathbb{R}_+ i \in T$, $r \in R_A \cup R_M$, $c \in C$. Volume of crude oil c accumulated in tank r before the execution of operation assigned to priority slot i. Measured in [Mbbl].

For the purposes of this subsection the relevant **parameter** of the original work is

- **Gross margin:** G_c, $c \in C$. Gross Margin per unit of crude oil of type c. Measured in dollars per barrel [$US/bbl].

In the extended model the following **parameters** are added.

- **Capture technology:** U_r^l $r \in R_D$, $l \in O$. $U_r = 1$ if capture techonolgy is implemented in distillation unit r, $U_r = 0$ otherwise.
- **Emission factor:** EF_r, $r \in R_D$. Emission factor of CO_2 per unit of crude oil of distillation unit r.
- **Cost of capture technology:** c^l represents the cost of treating a ton of CO_2 in distillation units with capture technology l. Measured in dollars per ton of CO_2 [$US/t].

The gross margins obtained from treating the different crude oil types in the distillation units are

$$\sum_{\substack{i\in T\\ r\in R_D}} \sum_{\substack{v\in I_r\\ c\in C}} G_c V_{ivc} \tag{3}$$

The capture technology costs are

$$\sum_{\substack{i\in T\\ r\in R_D}} \sum_{\substack{v\in I_r\\ l\in L}} c^l U_r^l EF_r V_{iv} \tag{4}$$

The Optimal Scheduling of Unloading and Blending (OSUB) is defined as

$$\begin{aligned} \max \quad & \sum_{\substack{i\in T\\ r\in R_D}} \sum_{\substack{v\in I_r\\ c\in C}} G_c V_{ivc} - \sum_{\substack{i\in T\\ r\in R_D}} \sum_{\substack{v\in I_r\\ l\in L}} c^l U_r^l EF_r V_{iv} \\ \text{s.t.} \quad & \text{Operational constraints} \end{aligned} \tag{OSUB}$$

where operational constraints can be found in the constraints section in the Supporting Information. The model extends the original work[5] by the inclusion of eq 4 in the objective function.

2.3. Trade-off between Emissions and Profits. Since reducing CO_2 emissions involves a cost, this section is oriented to obtain Pareto-optimal solutions, in the sense that an improvement in either emissions or profits is detrimental to the other.

$$\begin{aligned} \max \quad & \sum_{\substack{i\in T\\ r\in R_D}} \sum_{\substack{v\in I_r\\ c\in C}} G_c V_{ivc} - \sum_{\substack{i\in T\\ r\in R_D}} \sum_{\substack{v\in I_r\\ l\in L}} c^l U_r^l EF_r V_{iv} \\ & - \gamma \sum_{\substack{i\in T\\ r\in R_D}} \sum_{v\in I_r} \left(1 - \sum_{l\in L} q_{\mathrm{abs}}^l U_r^l\right) EF_r V_{iv} \\ \text{s.t.} \quad & \text{Operational Constraints} \end{aligned} \tag{P_γ}$$

Notice that γ is in [$\$/tCO_2$] units and represents the monetary cost of the negative externalities of CO_2 emissions that the refinery internalizes; this is the same unit used in several carbon pricing initiatives such as Alberta SGER ([23US $\$/tCO_2$]), Denmark carbon tax ([25US$\$/tCO_2$]), or Japan carbon tax ([3US$\$/tCO_2$]).[26] If γ is large enough, then the solution minimizes the released emissions subject to supplying the demand. By contrast, if $\gamma = 0$ the original problem (OSUB) is recovered. The emissions associated with the solution of (P_γ) are defined as ε_γ. The case where $\gamma = 0$ will be named as *Business as Usual* emissions (ε_{BAU}) because it represents an efficient oil refinery maximizing short-term profits.

An interesting problem is to find the smallest the smallest carbon pricing that forces a refinery to do its best to minimize emissions. This value will be named γ_{opt} and may be seen as a social optimum: CO_2 reduction is maximized and profits do not decrease more than necessary to achieve this. The construction of the Pareto Frontier and finding γ_{opt} is addressed by studying the following optimization problem for several values of $\gamma > 0$, as suggested in Boyd's work.[27]

2.4. Composition Constraint and Relaxation. The only nonlinear constraint of the model is the composition constraint, which expresses an equivalence between concentrations inside any tank and within their output lines. These concentrations can be followed as molar fractions. There is an underlying hypothesis that the tank contents are homogeneously mixed. In consequence, molar fractions can be estimated as volume or flow ratios: The ratio of crude type c volume over the total volume (V_{ivc}/V_{iv}) transferred in an operation leaving tank r must equal the ratio of crude type c partial tank volume over the total tank volume (L_{irc}/L_{ir}); this can be written as

$$V_{ivc} L_{ir} = L_{irc} V_{iv}$$
$$\forall\ i \in T, \forall\ r \in R, \forall\ v \in O_r, \forall\ c \in C \tag{5}$$

Notice that eq 5 is a bilinear expression and, therefore, nonconvex. This allows the existence of multiple local minima thus hindering the numerical resolution. Splitting variables and constraints may lead to loss of optimality. Although for very difficult problems like this a slightly suboptimal solution is acceptable, ignoring constraint 5 at the first step may also cause the second step problem to become infeasible for the assignment variables from the first step. Along that line, the recent work of Zhao et al.[28] proposes an algorithm which iteratively calculates MILP problems until a feasible point is always obtained; however, the solution may not be optimal.

Although the method to solve the MINLP is not the main focus of our paper, the technique two-step solution has been presented and compared with global solvers by Mouret et al.[5]

With the twofold objective of promoting overall optimality and second stage feasibility, a relaxed form of eq 5 is incorporated into the first step problem. These constraints, called McCormick relaxation,[29] consist in introducing linear inequalities that force the L_{iv}, L_{ivc}, V_{iv}, and V_{ivc} variables to lie in

DOI: 10.1021/acs.iecr.7b04331
Ind. Eng. Chem. Res. 2018, 57, 11342−11349

the convex hull of the set described by the nonlinear eq 5; the details can be found in the Supporting Information file.

Including this relaxed form of the composition constraint improves the work of Mouret et al., by diminishing the number of infeasible problems, thus increasing the applicability of the two-step strategy. In simulations, presented in Section 3, the inclusion of the McCormick relaxation played a key role in obtaining feasible problems in the second step, as can be seen in the example presented in Table 1. Notice that the same value holds for both relaxations; however, Mouret's relaxation becomes infeasible.[5]

Table 1. Case Study 1 with n = 15 Priority Slots

	value MILP	value NLP	GAP
ignoring eq 5 (Mouret et al.[5])	8380.3	unfeasible	-
McCormick relaxation	8380.3	7812.3	6.7%

Finally Kolodziej et al.[6] made a comparison of two techniques that address at the same time global optimality and feasibility, namely, piece-wise McCormick relaxation and multiparametric disaggregation. Both of them create tighter linear bounds on eq 5 than those of McCormick relaxation at the expense of computing time, thus, the choice of a two step decomposition with a simple McCormick relaxation.

3. CASE STUDIES

To account for the effects of the inclusion of the CO_2 reduction costs in the resulting scheduling and profits, the following cases were considered as case studies, and they have been recurrently used throughout the literature.[4,5,9] The general division among resources and the superstructure is representative from classic refineries (e.g., BP, Total, SK).

Case 1: The refinery's configuration consists of three vessels, three storage tanks, three charging tanks, and two distillation units (Figure 2) in a 12-day scheduling horizon.

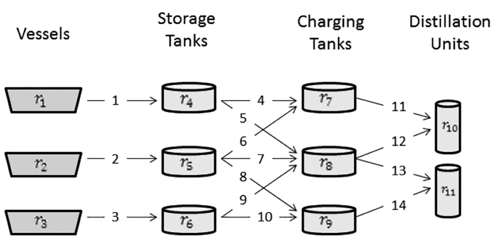


Figure 2. Case 1 configuration.

Operation sets become:

$$W_B = \{v_1, v_2, v_3\}$$

$$W_T = \{v_4, v_5, v_6, v_7, v_8, v_9, v_{10}\}$$

$$W_D = \{v_{11}, v_{12}, v_{13}, v_{14}\}$$

Case 2: The refinery's configuration for this case consists of three vessels, six storage tanks, four charging tanks, and three distillation units (Figure 3) in a 12-day scheduling horizon.

Operation sets become:

$$W_B = \{v_1, v_2, v_3\}$$

$$W_T = \{v_4, v_5, v_6, v_7, v_8, v_9, v_{10}, v_{11}, v_{12}, v_{13}\}$$

$$W_D = \{v_{14}, v_{15}, v_{16}, v_{17}, v_{18}, v_{19}\}$$

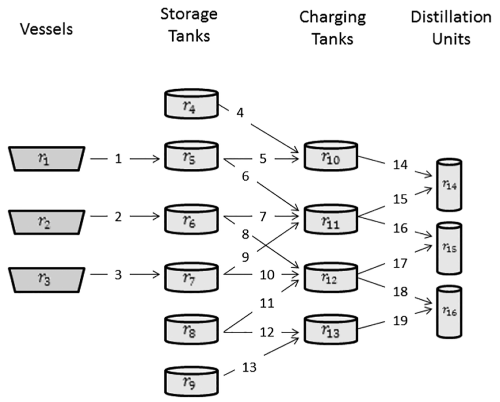


Figure 3. Case 2 configuration.

Parameters for both case studies can be found in the Data section of the Supporting Information file. The following schedules were obtained from the solution of problem (OSUB).

To highlight the effects of the costs inclusion in the scheduling, the setting $c^l = 0$ corresponding to ignoring the cost of treating the produced CO_2 emissions is presented as well for comparison.

The former represents the current state of refineries since no CO_2 costs are considered and coincides with the simulations carried out in the original work.[5] Whenever this cost is included, the optimal scheduling tends to avoid sending oil in units capturing CO_2.

For case study 1, Table 2 shows the amount of crude oil that enters each distillation unit when considering the CO_2 costs.

Table 2. Amount of Crude Oil Pumped into Distillation Units for Case 1[a]

considers CO_2 capture cost?	r_{10} [Mbbl]	r_{11} [Mbbl]
yes (Figure 4b)	844.3	655.7
no (Figure 4a)	600	900

[a]Only unit r_{11} has capture technology installed.

This result is not surprising since a cost on using unit r_{11} was added. Figure 4a,b shows how the optimal schedule is changed when the CO_2 cost is included. The most notorious change goes in distillation operations and was expected to happen; since CO_2 reduction costs are included on unit r_{11}, a new solution will try to pump crude oil to unit r_{10} rather than r_{11} as shown in Table 2. Notice that the only tank that can send crude oil to both distillation units is r_8; therefore, distillation 2 (v_{12}) should be used for a longer time instead of distillation 3 (v_{13}). Since starting and ending times of operations in a refinery are dependent on other operations, the whole scheduling is changed except for transfer 3 and the unloading operations. An analogous discussion for case study 2 can be made considering Figure 5a,b and Table 3.

In summary, an efficient profit maximizing refinery should avoid using the capture technology due to extra costs. The model predicts this behavior.

The trade-off between emissions reduction $\left(\frac{\varepsilon_{BAU} - \varepsilon_\gamma}{\varepsilon_{BAU}} \times 100\right)$ and profits is presented in Figures 6a and 7a. In both cases it can be seen that the CO_2 emissions reduction remains unchanged for several values of γ but abruptly changes at certain points. For example, in Figure 6a for $\gamma_{opt} \approx 0.59\$/tCO_2$

DOI: 10.1021/acs.iecr.7b04331
Ind. Eng. Chem. Res. 2018, 57, 11342−11349

(a) Without considering CO_2 capture costs ($c^l = 0$). $Gap = 0.08\%$.

(b) Considering CO_2 capture costs (on unit r_{11}). $Gap = 1.03\%$.

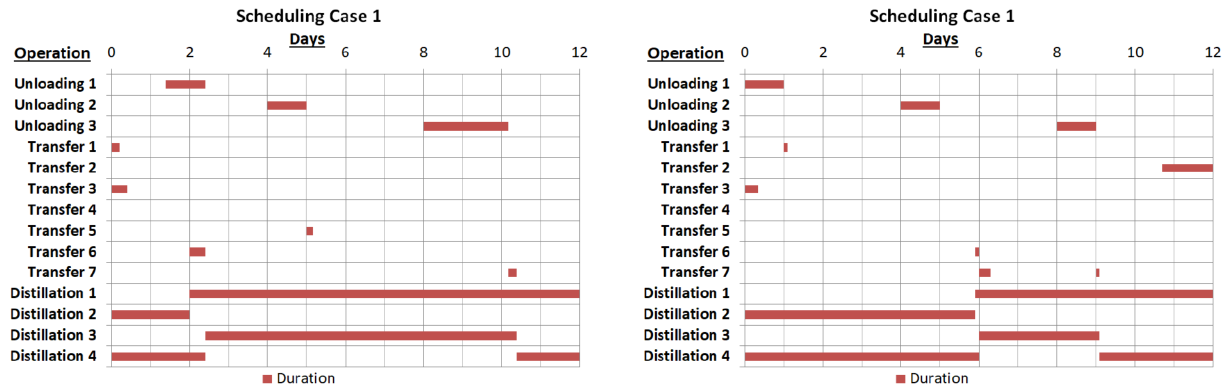


Figure 4. Case 1 scheduling.

(a) Without considering CO_2 capture costs ($c^l = 0$). $Gap = 0.07\%$.

(b) Considering CO_2 capture costs. $Gap = 2.2\%$.

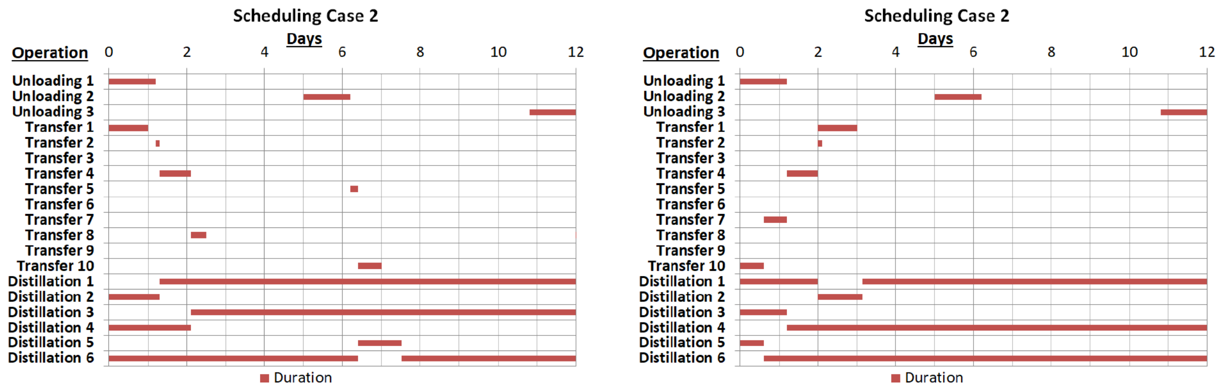


Figure 5. Case 2 scheduling.

Table 3. Amount of Crude Oil Pumped into Distillation Units for Case 2[a]

considers CO_2 capture cost?	r_{14} [Mbbl]	r_{15} [Mbbl]	r_{16} [Mbbl]
yes (Figure 5b)	1176	324	900
no (Figure 5a)	626	616	1158

[a]Units r_{15} and r_{16} have capture technology installed.

the refinery reaches the maximum possible CO_2 emissions reduction, or equivalently, the minimum level of CO_2 emissions, providing the minimum cost of the negative externalities that induces the refinery to reduce emissions as much as possible.

Since one of the stages for solving this problem is a MILP, released emissions will remain constant for several γ values: a change in γ will provide a different optimum only if a dual variable changes sign. A planner considering the cost of externalities will be faced with a finite number of Pareto-optimal solutions.

Notice that solution of model P_γ gives values of γ considerably lower than the current carbon pricing initiatives. Since the model is taken from literature examples, it gives no real insight on the pricing of CO_2 emissions. Rather, it exemplifies a way to define the pricing by finding γ_{opt}.

4. CONCLUSIONS AND FINAL REMARKS

Based on a benchmarked model and literature examples, numerical simulations of the CO_2 emissions of distillation units during the scheduling of crude oil operations were conducted. The objective function of the original model was modified to consider the cost of CO_2 capture and negative externalities of emissions in order to explore the behavior of a profit maximizing refinery.

Even though the mathematical model proposed simplifies (for the sake of resolvability) the characteristic function f of distillation units and considers the mean flow rate, the inclusion of CO_2 mitigation costs may drastically change the optimal scheduling. Both case studies show the sensitivity of the decision model to CO_2-related costs. This sensitivity is demonstrated by a change of these distillation units used in the process. Since sending more crude oil to units with some capture technologies increases the cost, the capture of CO_2 emissions can be represented into the short-term profit equation as proposed herein.

At the same time it raises the question for the trade-off between CO_2 emissions reduction and profits. To shed some light over this issue a classic multiobjective optimization approach was applied and few Pareto-optimal solutions were found. The pareto-optimal solution when emissions are

DOI: 10.1021/acs.iecr.7b04331
Ind. Eng. Chem. Res. 2018, 57, 11342−11349

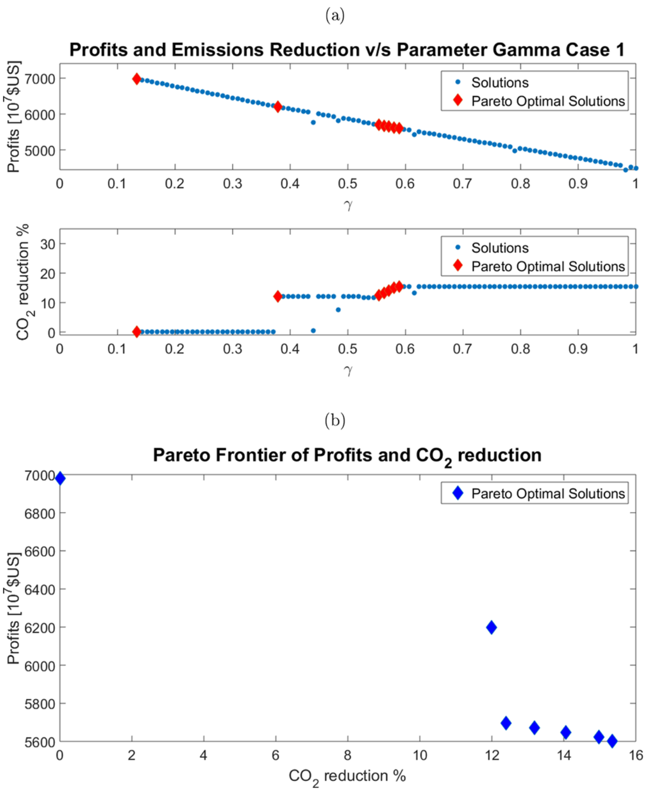


Figure 6. Case 1 profits and emissions from the solution of problem (P_γ) for different γ.

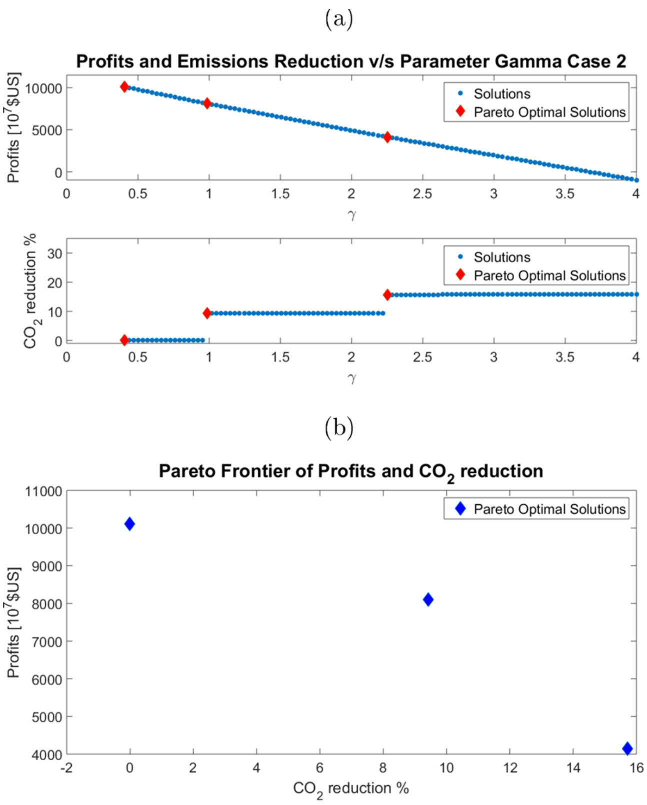


Figure 7. Case 2 profits and emissions from the solution of problem (P_γ) for different γ.

minimized is of high interest because γ_{opt} could be used to assess regulations regarding the price per ton of emitted CO_2 in each refinery. Methods to estimate such γ_{opt}, as well as its sensitivity to operational parameters, without directly calculating the scheduling problem could be further studied.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b04331.

Complete description of the model including variables, constraints, McCormick relaxation derivation, MILP and NLP used in the decomposition strategy, and parameters used for both case studies (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*(P.U.-S.) E-mail: pugalde@dim.uchile.cl.

ORCID

Pablo Ugalde-Salas: 0000-0001-9224-291X

Felipe Díaz-Alvarado: 0000-0002-2182-790X

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was financed by CONICYT (Chile) via BASAL project AFB-170001 “Centro de Modelamiento Matemático, Universidad de Chile”, FONDECYT project 1160204, and Fondecyt Iniciación 11150773. P.U.-S. thanks Juan Pablo Contreras for his help with the numerical experiences. F.D.-A. is grateful for the financial support from CONICYT/FONDECYT de Iniciación en Investigación/2017-11170042.

■ REFERENCES

(1) Karl, T. R.; Trenberth, K. E. Modern global climate change. *Science* **2003**, *302*, 1719−1723.

(2) Shine, K. P. The global warming potential−the need for an interdisciplinary retrial. *Clim. Change* **2009**, *96*, 467−472.

(3) Bengtsson, J.; Nonås, S.-L. *Energy, Natural Resources and Environmental Economics*; Springer: 2010; pp 115−130.

(4) Castro, P. M. Source-based discrete and continuous-time formulations for the crude oil pooling problem. *Comput. Chem. Eng.* **2016**, *93*, 382−401.

(5) Mouret, S.; Grossmann, I. E.; Pestiaux, P. A novel priority-slot based continuous-time formulation for crude-oil scheduling problems. *Ind. Eng. Chem. Res.* **2009**, *48*, 8515−8528.

(6) Kolodziej, S.; Castro, P. M.; Grossmann, I. E. Global optimization of bilinear programs with a multiparametric disaggregation technique. *Journal of Global Optimization* **2013**, *57*, 1039−1063.

(7) Floudas, C. A.; Lin, X. Continuous-time versus discrete-time approaches for scheduling of chemical processes: a review. *Comput. Chem. Eng.* **2004**, *28*, 2109−2129.

(8) Castro, P. M.; Grossmann, I. E. Global Optimal Scheduling of Crude Oil Blending Operations with RTN Continuous-time and Multiparametric Disaggregation. *Ind. Eng. Chem. Res.* **2014**, *53*, 15127−15145.

(9) Lee, H.; Pinto, J. M.; Grossmann, I. E.; Park, S. Mixed-integer linear programming model for refinery short-term scheduling of crude oil unloading with inventory management. *Ind. Eng. Chem. Res.* **1996**, *35*, 1630−1641.

(10) Wenkai, L.; Hui, C.-W.; Hua, B.; Tong, Z. Scheduling crude oil unloading, storage, and processing. *Ind. Eng. Chem. Res.* **2002**, *41*, 6723−6734.

(11) Moro, L. F.; Pinto, J. M. Mixed-integer programming approach for short-term crude oil scheduling. *Ind. Eng. Chem. Res.* **2004**, *43*, 85−94.

DOI: 10.1021/acs.iecr.7b04331
Ind. Eng. Chem. Res. 2018, 57, 11342−11349

(12) Reddy, P.; Karimi, I.; Srinivasan, R. Novel solution approach for optimizing crude oil operations. *AIChE J.* **2004**, *50*, 1177−1197.
(13) Chen, X.; Grossmann, I.; Zheng, L. A comparative study of continuous-time models for scheduling of crude oil operations in inland refineries. *Comput. Chem. Eng.* **2012**, *44*, 141−167.
(14) Li, J.; Misener, R.; Floudas, C. A. Continuous time modeling and global optimization approach for scheduling of crude oil operations. *AIChE J.* **2012**, *58*, 205−226.
(15) Yadav, S.; Shaik, M. A. Short-Term Scheduling of Refinery Crude Oil Operations. *Ind. Eng. Chem. Res.* **2012**, *51*, 9287−9299.
(16) Susarla, N.; Li, J.; Karimi, I. A. A novel approach to scheduling multipurpose batch plants using unit slots. *AIChE J.* **2010**, *56*, 1859−1879.
(17) Mouret, S.; Grossmann, I. E.; Pestiaux, P. Time representations and mathematical models for process scheduling problems. *Comput. Chem. Eng.* **2011**, *35*, 1038−1063.
(18) Kelly, J.; Menezes, B.; Grossmann, I.; Engineer, F. *Crude-oil Blend Scheduling Optimization of an Industrial-Sized Refinery: a Discrete-Time Benchmark*; Foundations of Computer Aided Process Operations: Tucson, AZ, U.S.A., 2017.
(19) Zhang, S.; Wu, N.; Li, Z.; Qu, T.; Li, C. Petri net-based approach to short-term scheduling of crude oil operations with less tank requirement. *Inf. Sci.* **2017**, *417*, 247−261.
(20) Wu, N.; Li, Z.; Qu, T. Energy efficiency optimization in scheduling crude oil operations of refinery based on linear programming. *J. Cleaner Prod.* **2017**, *166*, 49−57.
(21) van Straelen, J.; Geuzebroek, F.; Goodchild, N.; Protopapas, G.; Mahony, L. CO2 capture for refineries, a practical approach. *Int. J. Greenhouse Gas Control* **2010**, *4*, 316−320. (The Ninth International Conference on Greenhouse Gas Control Technologies).
(22) Elkamel, A.; Ba-Shammakh, M.; Douglas, P.; Croiset, E. An optimization approach for integrating planning and CO2 emission reduction in the petroleum refining industry. *Ind. Eng. Chem. Res.* **2008**, *47*, 760−776.
(23) Neiro, S. M.; Pinto, J. M. A general modeling framework for the operational planning of petroleum supply chains. *Comput. Chem. Eng.* **2004**, *28*, 871−896.
(24) Neiro, S. M.; Pinto, J. M. Multiperiod optimization for production planning of petroleum refineries. *Chem. Eng. Commun.* **2005**, *192*, 62−88.
(25) Babusiaux, D.; Pierru, A. Modelling and allocation of CO 2 emissions in a multiproduct industry: the case of oil refining. *Appl. Energy* **2007**, *84*, 828−841.
(26) Bank, T. W. Carbon Pricing Dashboard. 2017. http://carbonpricingdashboard.worldbank.org/map_data.
(27) Boyd, S.; Vandenberghe, L. *Convex Optimization*; Cambridge University Press: New York, NY, U.S.A., 2004.
(28) Zhao, Y.; Wu, N.; Li, Z.; Qu, T. A Novel Solution Approach to a Priority-Slot-Based Continuous-Time Mixed Integer Nonlinear Programming Formulation for a Crude-Oil Scheduling Problem. *Ind. Eng. Chem. Res.* **2016**, *55*, 10955−10967.
(29) McCormick, G. P. Computability of global solutions to factorable nonconvex programs: Part I−Convex underestimating problems. *Mathematical programming* **1976**, *10*, 147−175.

DOI: 10.1021/acs.iecr.7b04331
Ind. Eng. Chem. Res. 2018, 57, 11342−11349