Biological Carbon Sequestration and Utilization via Algal Biorefinery

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This work is concerned with process design and synthesis of an algal biorefinery for biological carbon sequestration and utilization under both economic and environmental criteria. We develop a superstructure of an algal biorefinery that consists of 11 processing sections and a plethora of state-of-the-art technology pathways, resulting in 7,800 processing routes in total. Based on the superstructure, a multi-objective mixed-integer nonlinear programming (MINLP) model is proposed to simultaneously minimize the unit carbon sequestration and utilization cost and unit global warming potential. Both unit objective functions are associated with one ton of carbon dioxide sequestered. In order to enhance the computation efficiency of solving the nonconvex MINLP, we propose a global optimization strategy that integrates a branch-and-refine algorithm based on successive piecewise linear approximations and an exact parametric algorithm based on Newton's method. The global optimal solutions of this bi-criteria MINLP problem constitute a Pareto-optimal curve that reveals the trade-offs between the two objective functions. All of the optimal points on the Pareto-optimal curve select an open pond, poly-electrolyte flocculation, pressure filtration, a storage tank, butanol extraction, sodium-methoxide-catalyzed transesterification, and anaerobic digestion. The lowest unit carbon sequestration and utilization cost obtained is 1.64 \$/t CO_2, corresponding to a unit GWP of 412.90 kg CO_2-eq/t CO_2.

1. Introduction

A variety of socioeconomic analyses based on various environmental records reach a similar conclusion that observed climate change is largely influenced by emissions of greenhouse gases (GHGs) from anthropogenic activities (Metz et al., 2005). As a result, carbon capture and sequestration (CCS) emerges as a very active research field to address the environmental challenges (Iancu et al., 2012). In this work, we focus on biotic method which takes advantage of the natural photosynthesis to convert carbon dioxide and water into renewable biomass (You et al., 2012), because biotic method is clean, safe and can be integrated with the downstream upgrading facilities to produce biofuels and reduce the carbon sequestration cost (Gong and You, 2014). Among various biomass feedstocks, microalgae are able to efficiently accumulate lipid materials (Urréjola et al., 2012), utilize non-arable land and waste water for cultivation, and be converted to hydrocarbon algal biofuels that accommodate the specifications of drop-in fuels (Yue et al., 2013a).

Despite several contributions focusing on algal processes (Gebreslassie et al., 2013b), no algae processing network that integrates comprehensive algae processing technologies from gaseous carbon source to various biofuel products, considers water and nutrients recycling, and utility generation, limits algae growth to the day, and includes the most recent technologies such as HTL has been developed (Miana et al., 2013). Therefore, our goal is to address these research gaps and develop the optimal process of an algal biorefinery for biological carbon sequestration and utilization.

In this work, we propose a superstructure of an algal biorefinery that integrates 11 processing sections, namely cultivation, harvesting, primary dewatering, secondary dewatering, storage, cell disruption & hydrothermal liquefaction, lipid extraction, upgrading, remnant treatment, electricity generation, and steam generation. Each section includes a number of state-of-the-art technology pathways, resulting in 7,800 processing routes. Based on this process superstructure, a bi-criteria mixed-integer nonlinear

programming (MINLP) model is developed to simultaneously minimize the unit carbon sequestration and utilization cost and the unit Global Warming Potential (GWP), both of which are associated with one tone of carbon dioxide sequestered. To efficiently solve the nonconvex MINLP optimization problem, we propose a global optimization strategy that integrates a branch-and-refine algorithm based on successive piecewise linear approximations and an exact parametric algorithm based on Newton's method. The optimal solutions of this multi-objective optimization problem are plotted in a Pareto-optimal curve which reveals the trade-offs between the economic and environmental objective functions.

2. Process description

As shown in Figure 1, the proposed superstructure of the algal biorefinery includes 11 sections: cultivation, harvesting, primary dewatering, secondary dewatering, storage, cell disruption & HTL, lipid extraction, upgrading, remnant treatment, electricity generation, and steam generation. The technologies considered in the superstructure are <1,1> open pond, <1,2> flat plate PBR, <1,3> bubble column PBR, <1,4> tubular PBR, <2,1> flocculation with poly-electrolyte, <2,2> flocculation with sodium hydroxide, <2,3> flocculation with poly-aluminum chloride, <2,4> flocculation with aluminum sulfate, <2,5> flocculation with chitosan, <2,6> flocculation with poly-γ-glutamic acid, <3,1> centrifugation, <3,2> pressure filtration, <3,3> blank, <4,1> freeze drying, <4,2> thermal drying, <4,3> and <4,4> blank, <5,1>, <5,2>, and <5,3> biomass storage, <6,1> bead beating, <6,2> high pressure homogenization, <6,3> bead beating, <6,4> microwaving, <6,5> sonication, <6,6> blank, <6,7> HTL, <7,1> blank, <7,2> hexane extraction for dry microalgae, <7,3> isopropanol/hexane extraction for dry microalgae, <7,4> supercritical CO2 extraction for dry microalgae, <7,5> hexane extraction for wet microalgae, <7,6> isopropanol/hexane extraction for wet microalgae, <7,7> butanol extraction for wet microalgae, <7,8> supercritical CO2 extraction for wet microalgae, <7,9> blank, <8,1> alkaline in-situ transesterification, <8,2> acidic in-situ transesterification, <8,3> enzymatic in-situ transesterification, <8,4> sodium-methoxide-catalyzed transesterification, <8,5> supercritical methanol transesterification, <8,6> enzyme-catalyzed transesterification, <8,7> heterogeneous-catalyzed transesterification, <8,8> Co/Mo-catalyzed hydroprocessing, <8,9> Ni/Mo-catalyzed hydroprocessing, <8,10> HZSM-5-catalyzed hydroprocessing, <9,1> anaerobic digestion, <10,1> electricity generation, and <11,1> steam generation.

2.1 Cultivation and dewatering
Four types of algal cultivation devices are considered in the cultivation section: open pond, flat plate photobioreactor (PBR), bubble column PBR, and tubular PBR. Open pond reactors are widely used for algae cultivation in practice, however they usually exhibit less efficient and are easily influenced by surrounding conditions. In contrast, PBRs have higher productivity, but the construction and operation cost are higher than open ponds.

The immediate mature algae slurry from the cultivation section contains too much water for downstream processing (González-Delgadoa et al., 2012). As a result, a series of technologies are employed to reduce the water content. The first section following algae cultivation is harvesting via auto-flocculation and dissolved air flotation. We consider six types of flocculants for auto-flocculation, including polyelectrolyte, sodium hydroxide, poly-aluminium chloride, aluminium sulfate, chitosan and poly γ-glutamic acid (Rizwan et al., 2013). They vary from each other with purchase price and algae yield to the next section. The harvesting technologies are able to concentrate algae slurry to 10 % by weight. Although several conversion technologies can separate lipid material from algal biomass with high water content, the qualified algal feed for most downstream technologies should contain less water. We consider two primary dewatering technologies for the product from harvesting section. Centrifugation provides an algal concentration of 32 % by weight and consumes a large quantity of energy; pressure filtration, however, saves energy in exchange for a lower product concentration of 27 %. If dry algae extraction is selected, the algal paste will be either freeze-dried or thermally dried in the secondary dewatering section so that the water content is reduced to 15 % by weight. Thus, both secondary dewatering technologies consume massive energy. Note that all of the white blocks denoted as "blank" represent bypassing of the section.

2.2 Storage, cell disruption, and extraction
As light is an essential condition during photosynthesis, algae stop growing during the night. In order to keep the downstream facilities operating continuously, we employ a storage tank to temporarily store part of the enriched algae biomass in the daily operation. Before algal biomass is sent to the extraction section, one of the five cell disruption technologies can be selected to destroy the protection layer of algae and improve lipid yields in the next section. Bead beating can be employed for both dry and wet algal biomass, while high pressure homogenization, microwaving, and sonication are utilized to specifically break the wet

algal cells. All of the above disruption technologies consume a large amount of energy. Other than the cell disruption technologies, we also include HTL to directly process dilute algae slurry.
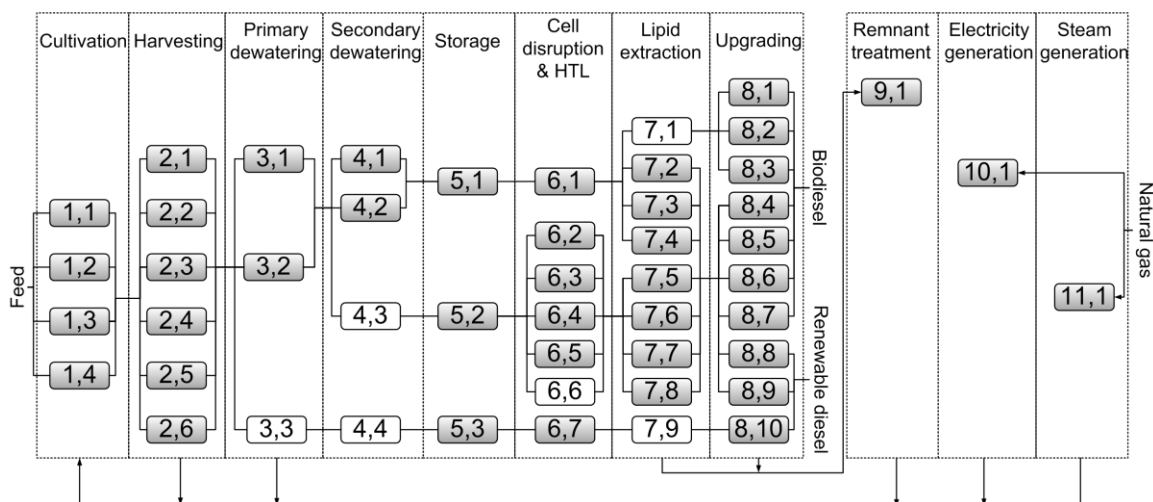

Figure 1: Superstructure of the algae processing network

In the lipid extraction section, seven technologies are designed for various upstream conditions. They are hexane extraction, isopropanol/hexane extraction, and supercritical CO_2 extraction for both dry and wet microalgae, as well as butanol extraction specifically for wet microalgae. In general, hexane extraction is the most widely accepted extraction process in conceptual algal process designs, though several experiments show very poor practical effect. As a result of "like dissolving like", alcohols with much better extraction effects are included. Supercritical carbon dioxide extraction presents the best extraction efficiency for both dry algae and wet algae at the expense of extremely high energy consumption.

2.3 Upgrading and remnant treatment

The lipid materials from the extraction section can be upgraded by the ten upgrading technologies considered in this work. Transesterification (Trans.) technologies result in fatty acid methyl esters or biodiesel, while hydroprocessing (Hyd.) pathways provide saturated hydrocarbons or renewable diesel that is capable of replacing fossil fuels directly. Hyd. technologies demand extra hydrogen and higher energy input. Specifically, we incorporate alkaline in-situ Trans., acidic in-situ Trans., enzymatic in-situ Trans., sodium-methoxide-catalyzed Trans., supercritical methanol Trans., enzyme-catalyzed Trans., heterogeneous-catalyzed Trans., Co/Mo-catalyzed Hyd., Ni/Mo-catalyzed Hyd., and HZSM-5-catalyzed Hydroprocessing. Algal remnants separated from lipid extraction and upgrading sections are utilized by anaerobic digestion (Polakovičová et al., 2012). We also couple electricity and steam generation into the superstructure to satisfy the onsite energy consumption by taking advantage of the resulting off-gas. An alternative way of meeting the energy demand is to directly purchase electricity and steam from the external market. Correspondingly, this choice could lead to lower costs but higher indirect GHG emissions.

3. Model formulation

The mathematical model of the proposed superstructure is formulated as a multi-objective MINLP problem whose objective functions are to simultaneously minimize the unit carbon sequestration and utilization cost and the unit GWP as shown in the following formulation (P1). Both unit objective functions are associated with one ton of carbon dioxide sequestered.

The model includes four types of constraints: mass balance constraints, energy balance constraints, economic evaluation constraints, and life cycle environmental impact analysis constraints. The mass balance constraints can be categorized into two groups. The first group describes the superstructure configuration using binary variables and logic constraints. The second group establishes a generic mass balance framework for each technology. The generic mass balance framework employs three sequential steps. The inlet converging step prepares the input stream by integrating the stream from the preceding section, recycling streams from downstream sections, and a makeup stream. The conversion step describes the chemical reaction occurring in the corresponding technology. Physical separation of the reaction products into a stream to the next section, a recycling stream, and an emission stream is modeled by the outlet separation step. The energy constraints define the energy consumption and production of each technology as the products of unit energy production and mass flow rates (Wang et al., 2013). The

economic constraints identify the total carbon sequestration and utilization cost to be the sum of annualized investment cost and annual operating cost, subtracted by the revenue.

$$\min \quad \frac{a + \sum_{i,j} B_{i,j} \left(m_{i,j}^{cc} \right)^{SF_{i,j}}}{m^{CO_2}} \text{(unit carbon sequestration and utilization cost)}$$

$$\min \quad \frac{gwp}{m^{CO_2}} \text{(unit GWP)}$$

$$\text{s.t.} \quad \text{mass balance constraints}$$

energy balance constraints

economic evaluation constraints

life cycle environmental impact analysis constraints

(P1)

The life cycle environmental impact analysis constraints are developed following the principles life cycle assessment (LCA). We consider a "cradle-to-gate" analysis in this study, and the system boundary include all of the 11 sections of the algal processing network, namely, cultivation, harvesting, primary dewatering, secondary dewatering, storage, cell disruption & HTL, lipid extraction, upgrading, remnant treatment, electricity generation, and steam generation. The functional unit is identified as the 1 gallon gasoline equivalent of the biofuel produced (Yue et al., 2013b). This LCA concerns the environment impact of direct GHG emissions from the cultivation, remnant treatment, and utility generation sections, and indirect GHG emissions associated with purchased electricity and steam (Gebreslassie et al., 2013a). Finally, the life cycle inventories of direct and indirect emissions are translated into their corresponding GWPs by using damage factor, and then the specific GWPs are aggregated into the total GWP.

4. Solving approaches

In order to handle the multi-objective formulation, we apply the ε-constraint method and transform the environmental objective into an additional bounding constraint, resulting in a series of single-objective optimization problems (You and Wang, 2011). In order to efficiently optimize the nonconvex single-objective MINLP problems, we propose a global optimization strategy, which integrates a branch-and-refine algorithm based on successive piecewise linear approximations and an exact parametric algorithm based on Newton's method.
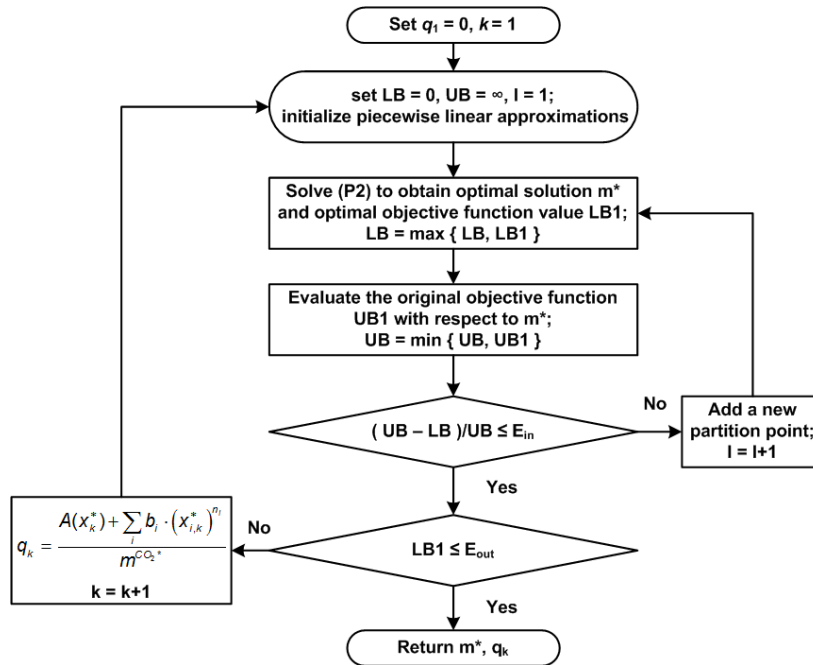

Figure 2: Flowchart of the global optimization strategy

$$\min \quad a + \sum_{i,j} B_{i,j} \cdot M_{i,j} - q \cdot gge$$

s.t.   all constraints of (P1) + piecewise linear approximation constraints   (P2)

$gwp \le \varepsilon \cdot m^{CO_2}$ (bounding constraint by ε-constraint method)

In order to implement the global optimization strategy, we introduce a parameter q and a group of piecewise linear approximation constraints to transform the fractional objective function of (P1) into a relaxed linear function as in formulation (P2). As a result of the transformation, when regarded as a function of q, the new objective function is concave, monotonic decreasing, continuous, and has bounded subgradients (Zhong and You, 2014). Thus we could utilize Newton's method to find the root of $a + \sum_{i,j} B_{i,j} \cdot M_{i,j} - q \cdot gge = 0$. Also, the separable concave terms in the economic objective function to evaluate the capital cost of each technology is relaxed by piecewise linear approximations. As a result, this relaxed model can be efficiently solved with the state-of-the-art branch-and-cut methods (You and Grossmann, 2011). The flowchart of the global optimization strategy is shown in Figure 2.

5. Results and discussion

We solve the multi-objective MINLP problem (P1) by employing the ε-constraint method and the proposed global optimization strategy and obtain 10 optimal solutions. These optimal solutions can be plotted into a Pareto-optimal curve as shown in Figure 3. The unit carbon sequestration and utilization cost decreases when unit GWP increases, explicitly demonstrating the trade-offs between the two objective functions. The Pareto-optimal curve separates the plane into a suboptimal region above the curve and an infeasible region beneath the curve. The optimal points on the curve cannot be improved simultaneously.
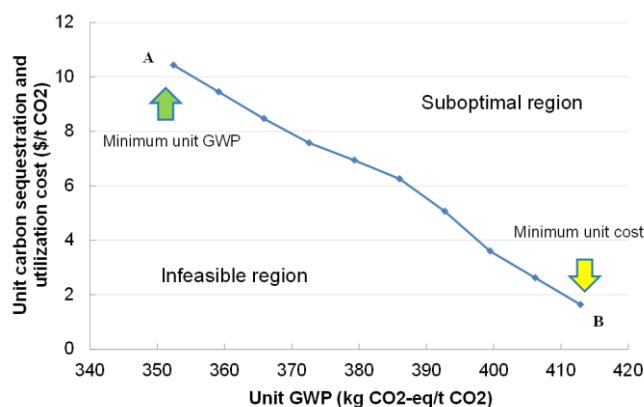

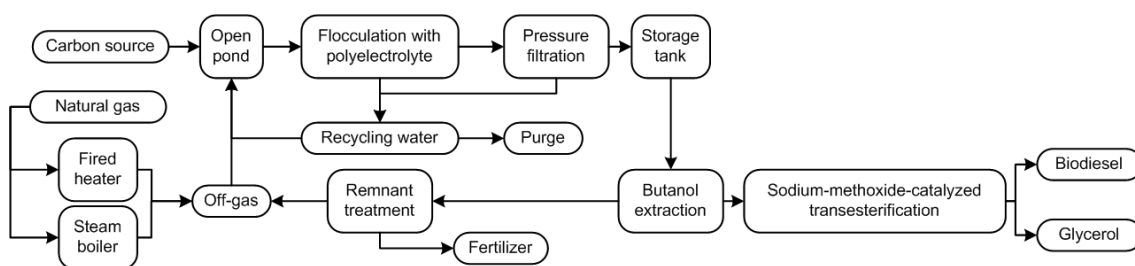Figure 3: Pareto curve of the algal biorefinery

Figure 4: Optimal process of the algal biorefinery

The optimal process designs behind the 10 optimal points select the same technologies in each section. As shown in figure 4, this process employs an open pond, poly-electrolyte flocculation, pressure filtration, a storage tank, butanol extraction, sodium-methoxide-catalyzed transesterification, and anaerobic digestion. Despite selecting the same process, the 10 differ from each other on the dependence of the electricity and steam consumption satisfied on site. Two extreme points A and B are identified with the unit carbon

sequestration and utilization costs of 10.43 \$/t of CO_2 and 1.64 \$/t of CO_2, corresponding to unit GWP's of 352.41 kg CO_2-eq/t of CO_2 and 412.90 kg CO_2-eq/t of CO_2, respectively.

6. Conclusions

We proposed a superstructure of an algal biorefinery for biological carbon sequestration and hydrocarbon biofuel production. Accordingly, we developed a multi-objective MINLP model simultaneously minimize the unit carbon sequestration and utilization cost and unit global warming potential. The problem is solve with ε-constraint method and a proposed global optimization strategy. The optimal solutions of this bi-criteria MINLP problem constitute a Pareto-optimal curve and all of the optimal solutions employ an open pond, poly-electrolyte flocculation, pressure filtration, a storage tank, butanol extraction, sodium-methoxide-catalyzed transesterification, and anaerobic digestion. The lowest unit carbon sequestration and utilization cost obtained is 1.64 \$/t of CO_2, corresponding to a unit GWP of 412.90 kg CO_2-eq/t of CO_2.

References

Gebreslassie B. H., Slivinsky M., Wang B. L., You F. Q., 2013a, Life cycle optimization for sustainable design and operations of hydrocarbon biorefinery via fast pyrolysis, hydrotreating and hydrocracking, Computers & Chemical Engineering, 50, 71-91.

Gebreslassie B. H., Waymire R., You, F., 2013b, Sustainable design and synthesis of algae-based biorefinery for simultaneous hydrocarbon biofuel production and carbon sequestration, AIChE Journal, 59, 1599-1621.

Gong, J., You, F. Q., 2014, Optimal Design and Synthesis of Algal Biorefinery Processes for Biological Carbon Sequestration and Utilization with Zero Direct Greenhouse Gas Emissions: MINLP Model and Global Optimization Algorithm, Industrial & Engineering Chemistry Research, 53, 1563-1579.

González-Delgadoa Á. D., Kafarov V., 2012, Microalgae Based Biorefinery: Evaluation of Several Routes for Joint Production of Biodiesel, Chlorophylls, Phycobiliproteins, Crude Oil and Reducing Sugars. Chemical Engineering Transactions, 29, 607-612.

Iancu P., Pleşu V., Velea S., 2012, Flue gas CO_2 capture by microalgae in photobioreactor: A sustainable technology. Chemical Engineering Transactions, 29, 799-804.

Metz B., Davison O., de Coninck H., Loos M., Meyer L., 2005, IPCC special report on carbon dioxide capture and storage. Intergovernmental Panel on Climate Change, Geneva (Switzerland).

Miana A., Ensinasa A. A., Ambrosettib G., Maréchala F., 2013, Optimal Design of Hydrothermal Gasification for Microalgae Conversion. Chemical Engineering Transactions, 35, 1009-1014.

Polakovičová G., Kušnír P., Nagyová S., Mikulec J., 2012, Process integration of algae production and anaerobic digestion. Chemical Engineering Transactions, 29, 1129-1134.

Rizwan M., Lee J. H., Gani R., 2013, Optimal processing pathway for the production of biodiesel from microalgal biomass, Computers & Chemical Engineering, 58, 305-314.

Urréjola S., Maceiras R., Pérezb L., Cancela A., Sánchezb A., 2012, Analysis of macroalgae oil transesterification for biodiesel production. Chemical Engineering Transactions, 29, 1153-1158.

Wang B., Gebreslassie B. H., You, F. Q., 2013, Sustainable design and synthesis of hydrocarbon biorefinery via gasification pathway: Integrated life cycle assessment and technoeconomic analysis with multiobjective superstructure optimization. Computers & Chemical Engineering, 52, 55-76.

You F. Q., Grossmann I. E., 2011, Stochastic Inventory Management for Tactical Process Planning Under Uncertainties: MINLP Models and Algorithms, AIChE Journal, 57, 1250-1277.

You F. Q., Tao L., Graziano D. J., Snyder S. W., 2012, Optimal design of sustainable cellulosic biofuel supply chains: Multiobjective optimization coupled with life cycle assessment and input-output analysis. AIChE Journal, 58, 1157-1180.

You F. Q., Wang B., 2011, Life Cycle Optimization of Biomass-to-Liquid Supply Chains with Distributed-Centralized Processing Networks. Industrial & Engineering Chemistry Research, 50, 10102-10127.

Yue D. J., You F., Snyder S. W., 2013a, Biomass-to-bioenergy and biofuel supply chain optimization: Overview, key issues and challenges, Computers & Chemical Engineering, 66, 36-56.

Yue D. J., Kim M. A., You F. Q., 2013b, Design of Sustainable Product Systems and Supply Chains with Life Cycle Optimization Based on Functional Unit: General Modeling Framework, Mixed-Integer Nonlinear Programming Algorithms and Case Study on Hydrocarbon Biofuels, ACS Sustainable Chemistry & Engineering, 1, 1003-1014.

Zhong Z. X., You F. Q., 2014, Globally convergent exact and inexact parametric algorithms for solving large-scale mixed-integer fractional programs and applications in process systems engineering, Computers & Chemical Engineering, 61, 90-101.