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PROCESS SYSTEMS ENGINEERING

Process Synthesis for Addressing the Sustainable Energy Systems and Environmental Issues

Zhihong Yuan and Bingzhen Chen
Dept. of Chemical Engineering, Tsinghua University, Beijing 100084, China

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Diminishing petroleum reserves and oscillations of the global petroleum market, together with the influence on the environment in terms of greenhouse gas emissions have accelerated the needs to explore renewable feedstocks and to seek novel sustainable production systems. Process synthesis, the core of process systems engineering, can be predicted to be the powerful tool to construct an environmental-friendly, cost-effective sustainable energy system. Following the brief descriptions of the main methodologies for process synthesis, the present article reviews current activities on the optimal synthesis of biorenewables conversion processes, polygeneration processes, as well as carbon capture processes. Set in the context of exist achievements and future energy and environment requirements, we further elucidate the potential research vistas on optimal synthesis of novel energy systems, specifically, (a) novel biorenewable conversion process; (b) innovative materials-based carbon capture process; (c) solar/wind driven energy conversion system; (d) integrated biorenewable conversion process for the production of chemicals. Finally, challenges about the above aspects are concisely discussed.
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Introduction

Since the beginning of last century, fuels and chemicals for our daily requirements have been mainly derived from fossil carbon-based sources (i.e., petroleum, coal, and natural gas), and these fossil fuels will continue to constitute the backbone of current energy resource in the foreseeable future.[1] However, the growth of the worldwide population will eventually exhaust the world's supplies of easily exploitable fossil carbon-based sources. Moreover, green house gas (GHG) emissions, especially CO2 emissions associated with the use of fossil carbon-based fuels have been linked to global climate changes such as ice melting at the poles and rising of ocean levels. The above issues are presently driving the whole society to seek renewable sources for replacing coal, natural gas, and petroleum and to develop the innovative and sustainable technologies for the production of energy, fuels and chemicals.

From Figure 1 which shows the trends on the United States and World energy demand contributions, it can be easily found that the account of renewable sources will increase largely in the next two decades. Plenty of interlinked research activities for the sustainable technology development have been the main focus of the worldwide research. Generally, these activities depicted by Figure 2 include: the increased utilization of renewables such as wind/biomass/solar energy,[2] the hydrogen economy,[3] and CO2 capture/sequestration.[4,5]

Accordingly, various routes for the production of energy, transportation fuels and chemicals with high efficiency and sustainable manner have been proposed, and these routes can be divided into four categories: (a) Integration of wind and solar power for the production of fuels and chemicals.[6–9] (b) Biorenewable resources conversion (i.e., lignocellulose and starch) through thermochemical,[10,11] biochemical,[12–15] and catalytic pathways.[16–22] (c) Polygeneration process for the simultaneously production of transportation fuels, energy and fine chemicals from coal, biomass, or natural gas feedstocks.[23,24] (d) Combination of hydrogen production and syngas methanation for the production of chemicals.[25]

A series of exist research reports have proclaimed that the integrated framework including multiple conversion routes would be the best solution to the sustainable cost-efficient renewable energy system development. However, process efficiency is actually the central point of the aforementioned production pathways.[26] For example, biorenewables conversion process based on biological or thermochemical approach only transfers a small portion of energy in the original biorenewable resources to final products with very low overall thermal conversion efficiency.[27] Obviously, chemical reaction engineering and process systems engineering (PSE) will play very crucial roles in the improvement of the process efficiency.[28] As known, PSE, which systematically considers the relationship between the ''behavior'' of the system and that of the components,[29,30] encompasses the activities involved in the engineering of systems involving physical/

Correspondence concerning this article should be addressed to B. Chen at dcecbz@tsinghua.edu.cn.

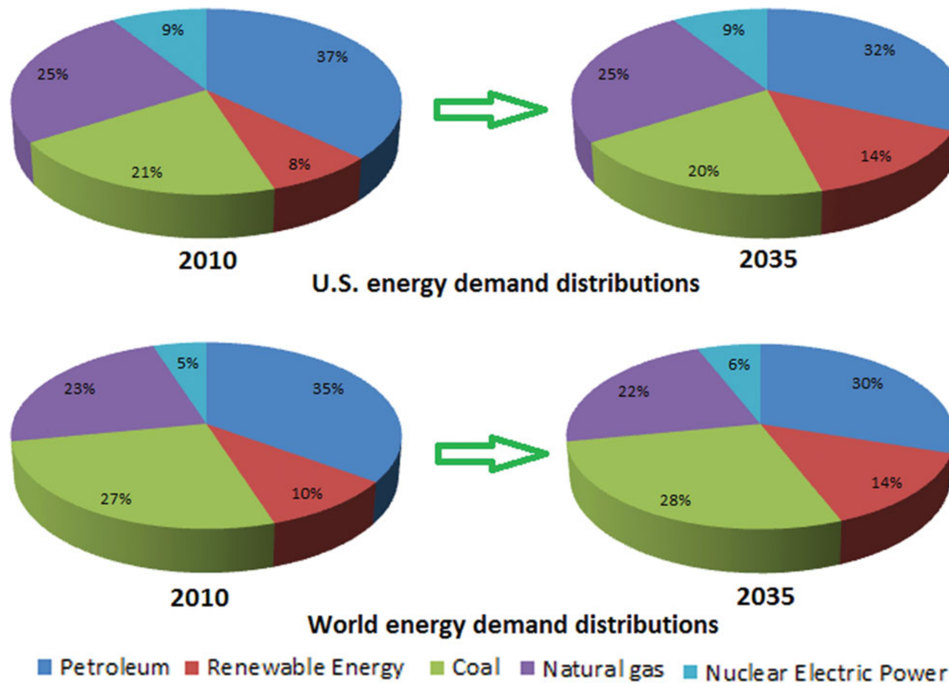

Figure 1. Trends of United States and World energy demand contributions.[1]

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chemical/biological processing operations. During the past several decades, as one of the most significant accomplishments in PSE era, process synthesis has demonstrated its conspicuous influence on the creative design, operation and control of (petro) chemical processes,[31] without any doubt it is envisioned to play an extremely vital role in tackling the energy and environmental crisis and offering the significant outcomes during the search of the environmental-friendly, high-efficiency renewable energy systems.

This perspective article aims principally at highlighting the role that the optimal synthesis plays in the design/operation of the sustainable and cost-efficiency energy systems, mainly through the selection of optimal reaction pathway, optimal process topology structure, optimal design/operation parameter level as well as the implementation of various uncertainties into consideration. It is written to facilitate the advances in this novel research area worldwide. Topics of this article touched upon include brief description of process

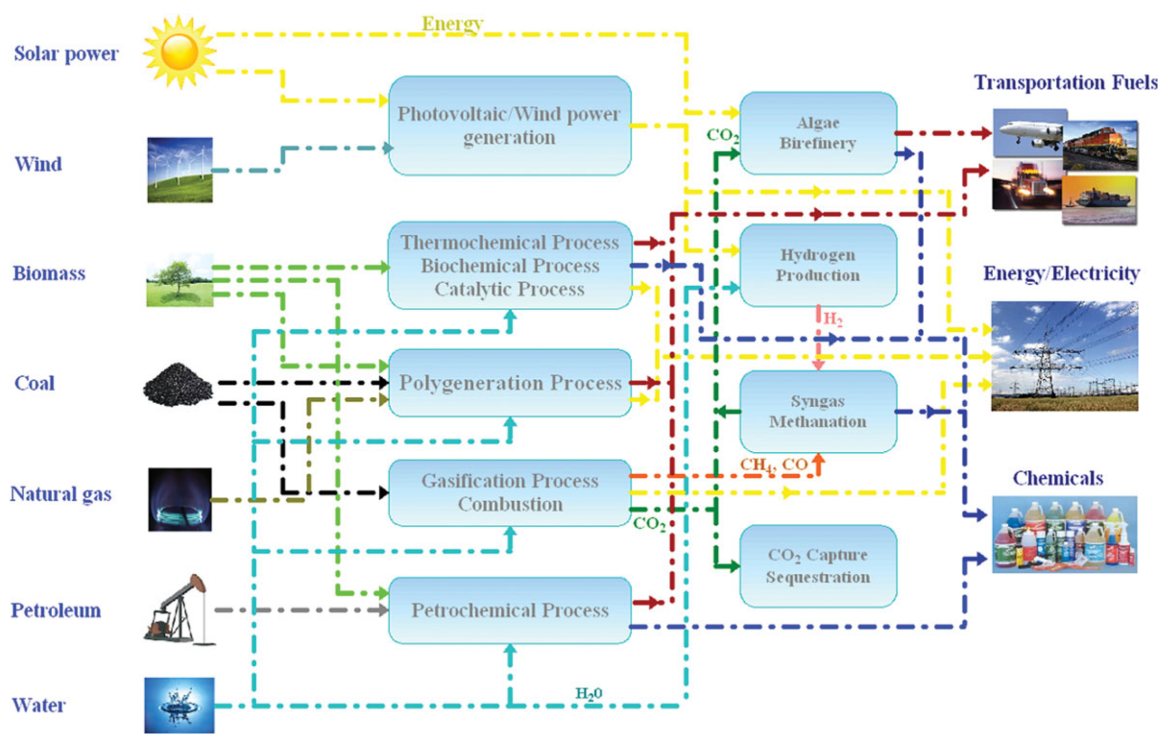

Figure 2. Activities on the development of sustainable energy systems.

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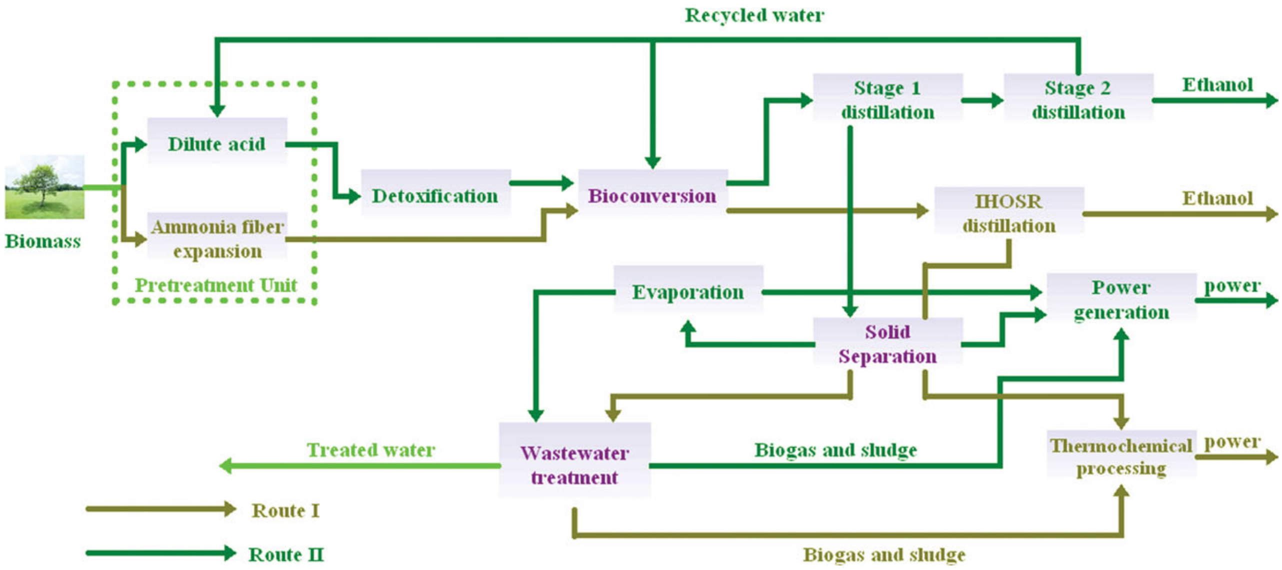

Figure 3. Biochemical route alternatives for the production of ethanol from biomass.

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synthesis, optimal synthesis of polygeneration process, optimal synthesis of biorenewables conversion process, and optimal synthesis of CO2 capture process. Furthermore, further directions and challenges are given.

Motivations for Optimal Synthesis of Sustainable Energy Systems

The optimal synthesis problem can be described as follows: given a set of feedstocks and desired final products with specifications, it is desirable to generate a systematic framework with various objectives for the extraction of the best configuration and unit operation among an astronomically large number of promising alternatives.[32]

Building upon the petroleum depletion and environmental challenges, various innovative sustainable systems have been developed for the production of cost-competitive fuels and chemicals from renewable sources. The following three issues are promoting both the industry and academia toward the application of optimal synthesis to the proposed sustainable energy systems.

Optimal technology and type of operation unit selection from candidates

For a given set of feedstocks, several promising technologies can be utilized to convert them to final products. For the device level of a given energy system, there are probably multiple alternatives for each operating unit, as an example, fluidized bed reactor, moving bed reactor, and fixed bed reactor can be selected for the solid sorbent based carbon capture process, of course, different unit will generate various capital costs. Apparently, the decision on the operating unit selection will significantly affect the whole flowsheet, for instance, Figure 3 depicts two possible biochemical conversion routes for producing ethanol from biomass,[33] and from the Figure, we can find that the pretreatment technology will determine the selection of the follow-up operation units and eventually affect the overall process cost. All of the above aspects demonstrate that the selection of the optimal technology and corresponding operating unit to formulate a high efficiency energy system requires a systematic design methodology.

Process efficiency improvement

As aforementioned, efficiency is the core issue of the sustainable energy system. To complete with conventional petrochemical processes, renewable energy systems should do their best to achieve maximum efficiency. Unfortunately, till now, many energy systems such as coal-based stationary power plants and biochemical conversion processes exhibit low energy conversion efficiency. As known, higher process efficiencies will lead to lower cost capital, how to improve the efficiency of the energy system especially the renewable energy system has attracted more and more attentions. From the viewpoint of PSE, for the generation of an integrated renewable energy system with better control performance and higher conversion efficiency, optimal synthesis through the selection of the optimal flowsheet and the decision on the corresponding operation level offers some promises and clues to this challenge.[34]

Multiobjectives trade-offs

For a given energy system, there usually exist several conflict objectives such as environmental requirement and overall process cost. As an example, for a coal-based power plant with CO2 capture system, adding the CO2 capture device will improve the capital cost and reduce the efficiency of the power plant. In addition, the process flowsheet will vary with the changes in multiobjectives trade-offs. Hence, optimal synthesis is needed to systematically deal with the above conflicts based on the system engineering viewpoint.

Viewed from the above perspectives, the following definition of optimal synthesis activities for sustainable energy system can thus be extracted from Westerberg's one[32]:

Optimal synthesis for sustainable energy systems is the automatic generation of design candidates and the multiobjective selection of the better ones based on the creative postulation of the cost-efficiency, environmental-friendly, and social beneficially alternatives that can convert a broad of range of feedstocks into affordable transportation fuels,

Figure 4. Framework of hierarchical decomposition approach.

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high value chemicals and heat/electricity with high energy conversion efficiency.

Brief Overview on Methodologies for Process Synthesis

For the optimal synthesis of chemical processes, a great number of contributions have proposed the following systematic approaches[35]: total enumeration of an explicit space, tree search in the space of design decisions, evolutionary methods, superstructure optimization, targeting, problem abstraction, and combinations of these. Among these technologies, hierarchical decomposition-based approach[36] and mathematical programming-based approach[37] are the two most widely used approaches for the optimal synthesis of both specific subsystems and total process flowsheets. Figure 4 shows the hierarchical decomposition framework which contains five sequential steps. Figure 5 demonstrates the brief flowsheet of the mathematical programming-based approach. Li and Kraslawski[38] discussed the detailed merits and defects of these two approaches.

As efficient optimization techniques, solution algorithms, and strategies are available and enable us to solve various optimization problems arising from chemical process,[39] the mathematical programming-based approach is recognized as the most successful used approach to the synthesis of discrete-continuous problems.[40] The original discrete-continuous optimization problems arising from process synthesis can be described as follows[41]:

$$\begin{aligned} & \min Z = c^T y + f(x) \\ s.t.\quad & Ay + h(x) = 0 \\ & By + g(x) \leq 0 \\ & Cy + Dx \leq b \\ & x \in X = \{x | x \in R^n, x^L \leq x \leq x^U\} \\ & y \in Y = \{y | y \in \{0,1\}^m\} \end{aligned} \tag{P}$$

where $f(x)$, $h(x)$, and $g(x)$ are continuous differentiable nonlinear functions. $x \in X$ are continuous variables associated with operating and design variables such as temperatures, pressures, flowrates, and equipment sizing characteristics. $y \in \{0,1\}$ denote the binary variables which correspond to the discrete decisions linking to the selection of equipment and the decision of the flowsheet configuration. Z means the objective function subjected to mass/heat balances, physical/thermodynamic equations, and design equations that describe the system performance. Various algorithms have been proposed for the solution of mixed integer nonlinear programming (MINLP) problems shown as (P), Grossmann recently summarized the recent advances on these algorithms.[42]

As a large number of integer variables and nonlinear/nonconvex equations will prevent not only in seeking the

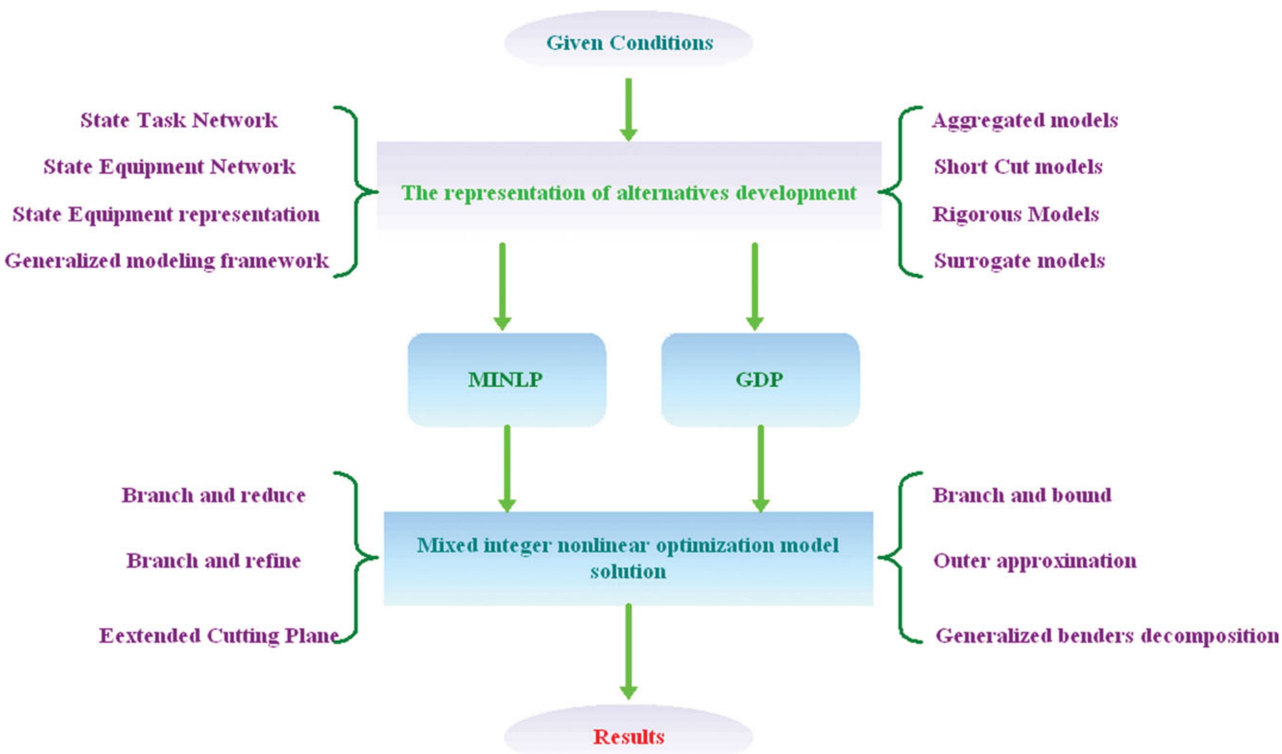

Figure 5. Framework of mathematical programming-based approach.

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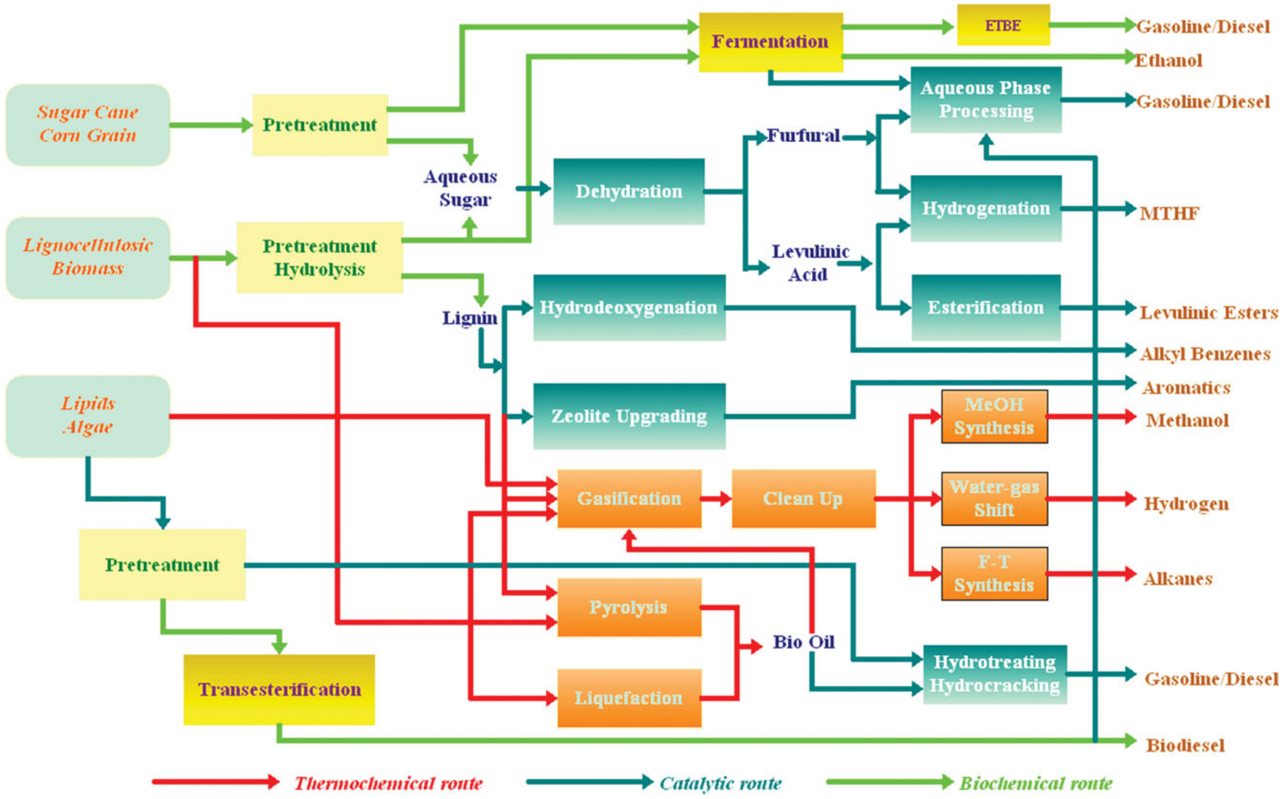

Figure 6. Routes for the conversion of biorenewable sources into liquid fuels.

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optimal solution but even in obtaining a feasible point, conversely, to improve the combinatorial search efficiency, a novel mathematical programming,[43,44] namely generalized disjunctive programming (GDP) shown as (P1), has been proposed for nonlinear chemical process synthesis problems.

$$\begin{aligned} &\min Z = \sum_k c_k + f(x) \\ s.t.\quad & r(x) \leq 0 \\ &\bigvee_{j \in J_k} \begin{bmatrix} Y_{jk} \\ g_{jk}(x) \leq 0 \\ c_k = \gamma_{jk} \end{bmatrix}, \; k \in K \\ &\Omega(Y) = true \\ &x \in R^n, c_k \in R^m \\ &Y_{jk} \in \{true, false\}^m \end{aligned} \tag{P1}$$

Y_{ij} are the Boolean variables that decide whether a given term j in a disjunction $k \in K$ is true or false, and x are the continuous variables. The objective function includes the term $f(x)$ for the continuous variables and charges c_k that depend on the discrete selection in each disjunction $k \in K$. The constraints $r(x) \leq 0$ must hold regardless of the discrete choice, and $g_{jk}(x \leq 0)$ is the conditional constraints when Y_{jk} is true in the jth term of the kth disjunction. $\Omega(Y)$ are logical relations for the Boolean variables expressed as propositional logical. Although MINLP model is based entirely on algebraic equations and inequalities for discrete/continuous optimization problem, the GDP model facilities a combination of algebraic and logical equations. The extensive way to solve a GDP problem is to reformulate it as a mixed integer programming, using either a big-M reformulation or a hull relaxation formulation.[45]

The above approaches have been applied successfully to the optimal synthesis of homogeneous processes such as heat/mass exchanger networks, reactor networks, separation sequences, and utility systems as well as the whole plants.[46] The above successful stories have accommodated an excellent basis for penetrating the application of optimal synthesis into novel sustainable energy systems such as biorenewables conversion process, polygeneration process as well as carbon capture process.

Optimal Synthesis for Biorenewable Conversion Process

Plant biomass, whose energy is stored as chemical bonds,[47] is the only accessible non-fossil source of carbon. Hence, it is a promising alternative source for the production of organic fuels, chemicals, and materials. Biorenewable derived carbohydrates have the form of large polymer chains with thousands of sugar units, and each unit includes six carbon atoms and a similar number of oxygen atoms.[48] The aim of the biorenewables processing, through complex multiple chemical/physical processing steps, is to remove the oxygen from the biomass and convert it into biopower, value-added chemicals and transportation liquid fuels with the appropriate combustion and thermochemical properties.[49]

Various conversion routes have been developed to enable the cost-competitive removing of oxygen while minimize the loss of energy value of the original biomass-derived carbohydrates. Figure 6 delineates multiple pathways for the conversion of biorenewable sources into liquid fuels, and these routes can be categorized under three categories[22]: biochemical routes, thermochemical routes, and catalytic routes. Because of the complexity of the biorenewables structure, multiple routes between the feedstocks, intermediate, and final products may exist, each route will require special pretreatment technology, operation units, and relevant operating conditions. For the fixed technology, various solvents and catalysts can be selected, as an example, alkylphenol and butylacetate can be used as solvent in the catalytic process for the production of levulinic acid. Therefore, to fix an economically viable, environmentally benign, and socially beneficial innovative biorenewable conversion process, from the viewpoint of PSE, systematic efforts on optimal synthesis should focus on the following issues:

- Select the functional molecules based on the product properties prediction;
- Extract the optimal reaction pathway with the maximum biorenewable carbon conversion efficiency;
- Generate the optimal flowsheet topology structure with minimum capital cost coupled with the minimum impact on the environment;
- Consider the water/heat integration simultaneously to minimize the fresh water and energy consumption;
- Establish the robust conversion process that can yield desired value-added products under uncertainties including regional and seasonal availability as well as density and energy demand-supply balance.

In general, the above five issues result into three topics including: reaction pathway synthesis, separation process synthesis, robust process flowsheet synthesis. Thanks to the advances on the methodologies for process synthesis, substantial achievements on these topics have been published. Recently, a perspective paper briefly discussed the opportunities and main challenges during the shift of applications of optimal synthesis from conventional chemical process to biorefinery process (Yuan et al., submitted for publication). Based on this perspective, the rest of this section will comprehensively review the progress in the biomass conversion process synthesis from different aspects.

Biomass conversion pathway synthesis

Biorenewable resources with a carbon-to-oxygen ratio of 1:1, which are significantly different from the petroleum driven feedstocks, have complex reaction networks. New chemistries including various biochemical/thermochemical/catalytic routes are essential to refunctionalize complex molecules, and in turn, a large number of reaction pathways which are defined as the sequence of all the required reaction steps connecting the starting and target molecules may exist.[50] Therefore, based on the given targets, the first application of optimal synthesis is to provide a systematic way to analyze and rank a large amount of reaction routes and, subsequently, decide the most attractive one. During the past 2 years, several excellent contributions have focused on the biorenewables conversion pathways synthesis.

First, instead of breaking biorenewables into C1 building blocks and subsequently reassembling them into desired functional molecules,[51] Marquardt[51] convincingly argued that a simultaneous approach which integrates product design and process synthesis should be set up to exploit the "rich molecular structure of biorenewables" without any degradation. Inspired by the methods for metabolic pathway analysis,[52] Marquardt and coworkers recently proposed a novel optimization based screening tool, namely reaction network flux analysis, to systematically identify and select promising and attractive reaction pathways of the biorefinery from a given reaction network.[53–55] The first step of this methodology is the construction of reaction networks where all possible reactions linking raw biorenewable feedstocks, intermediates and final products are summarized; the second step is to model the reaction networks through the graph theory such as nodes and arcs; the third step is the mixed integer programming formulation and solution with the target of maximum carbon conversion efficiency; the last step is the evaluation of the identified reaction pathways generated from the third step. They applied this methodology to the classification of the optimal reaction pathway for the production of the biofuel 3-methyl-tetrahydrofuran from the platform chemical itaconic acid. The results demonstrate that promising pathways of biomass conversion can be classified from the set of solution provided by mixed integer programming which is based on a variety of economic, ecological indicators. Of course, the outcome from this approach heavily depends on the completeness of the reaction network. Hence, an automatic generation of the biorenewables reaction network should be integrated with this approach.[56]

Bao et al.[57] proposed a shortcut method for the synthesis and screening of reaction pathways for the integrated biorefineries, an optimization approach was also developed to determine the optimum network configuration for various technology pathways based on the simple data. Pham and EI-Halwagi[58] proposed a two-stage approach which includes the "forward-backward" formulation and the optimization stage to optimize the reaction route for the production of bioalcohols from lignocellulosic biomass, and they recently gave a disjunctive programming based synthesis approach to solve the above question.[59] Ng and coworkers proposed a fuzzy mathematical programming-based automated targeting approach to determine the optimal pathway of a gasification-based integrated biorefinery aiming at the maximum economic performance and minimal environmental impact, based on this approach, the design parameters can be generated simultaneously through the solution of the optimization problem.[60–62]

Apparently, these preliminary research works only focus on classification of the limited thermochemical and biochemical-based conversion routes. More and more novel conversion routes especially the catalytic routes are being explored,[63] future significant research efforts on pathway synthesis are required to classify potential of various biomass reaction routes which should effectively cope with competing economic and environmental objectives.[64]

Separation process synthesis

Multiple desired and undesired side reactions in the biorenewable conversion process will lead to very complex and even azeotropic multicomponent mixtures, together with insolubility of biorenewables in conventional solvents require novel organic solvents for the pretreatment, molecular transformations and separation. As an example, ionic liquids are extensively used for biorenewable pretreatments[65] and separation units.[66,67] As known, costs of separation units which are often energy extensive operations will be the dominating factor in the overall cost of a biorenewable conversion process. Besides, biorenewable conversion process will call for novel purification/separation units and special operating conditions,[68] for instance, as a result of the nonvolatile nature of biorenewable components, lower temperature separation units such as vacuum evaporation and vacuum distillation are utilized for the 2,5-dimethylfuran production.[69] Clearly, systematic methodologies for synthesizing a novel

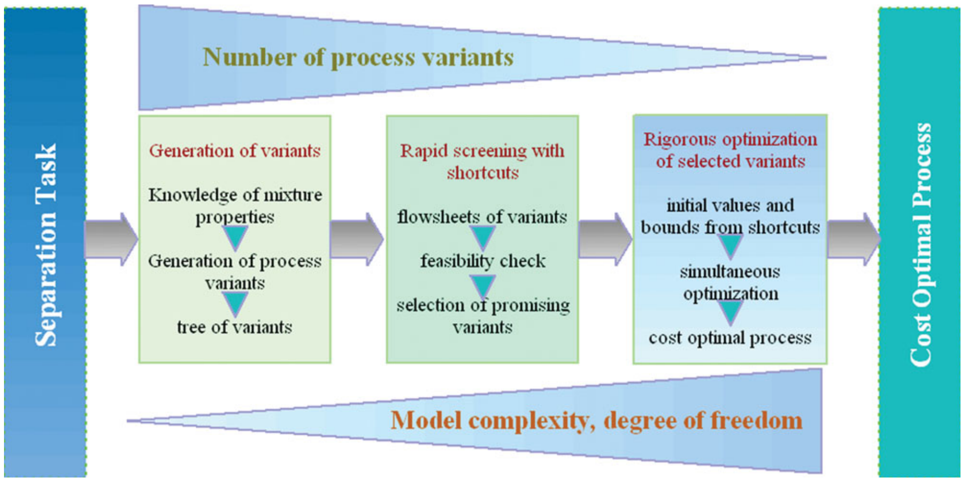

Figure 7. Framework for the optimal synthesis of separation process (revised from Ref. 72).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cost-effective, energy-efficient separation process are highly required.

Roughton et al. proposed an integrated framework for the simultaneously optimal synthesis of the energy efficient azeotropic separation and ionic liquid design.[70] In this framework, an ionic liquid is firstly constructed using a computer-aided molecular design method-based on the given azeotropic mixture; then candidates are evaluated and screened by the UNIFAC model with the aim of minimum ionic liquid concentration to break the azeotrope; finally, the extractive distillation column is decided through the driving force method. The simultaneous optimal design of ionic liquid and extractive distillation column will reduce materials and energy requirements through the demonstration of acetone-methanol separation process design. Valencia-Marquez et al.[71] formulated a steady-state disjunctive MINLP to simultaneously synthesize the extractive column and ionic liquid, where physical and thermodynamic properties of ionic liquid are computed by group contribution methods. The properties of ionic liquid and all topology candidates of extractive column are included in the MINLP formulation to minimize the investment and operating costs. Through solving the MINLP problem, all design/operating levels such as ionic liquid feedtray location, reflux ratio, and column diameter can be selected.

Marquardt et al. presented a three-step framework shown as Figure 7 for the optimal synthesis of hybrid separation flowsheets.[72] The first step, namely generation of variants, generates possible flowsheet alternatives based on the knowledge of mixture properties; the second step, namely rapid screening, is responsible for the evaluation of candidates based on shortcut models; the third step, namely rigorous optimization of selected variants, rigorously optimizes the best remaining alternatives by using MINLP optimization, Kraemer et al. then extended this systematic methodology to the synthesis of a hybrid extraction-distillation system which is used for separating butanol from acetone–butanol–ethanol fermentation[73] and to the synthesis of a pressure swing process for the separation an azeotropic four-component mixture,[74] respectively. The results demonstrate that the proposed methodology can considerably save the total annualized cost of the downstream separation process.

Recently, Harwardt and Marquardt proposed a MINLP based synthesis method for the optimal design of a butyl-levulinate production process from biorenewables,[75] in this article, a favorable successive initialization strategy and continuous reformulation policy is used to overcome the challenging optimization problem due to highly nonlinear behavior of the thermodynamic and kinetic representations. The outcomes illustrate that the optimal separation process has the potential to produce a renewable liquid fuel at reasonable cost.

Innovative unit operations, hybrid separation systems, novel solvents are recognized as three significant contributions to energy and emission reduction.[76] For future biorenewable conversion process, aside from the above discussed extractive distillation technology, membrane separation technologies such as membrane pervaporation and vacuum membrane distillation are recognized as the most effective and energy-saving process for separation of azeotropic mixtures from the biorenewable feedstocks.[77,78] Hence, future endeavors toward the optimal synthesis of novel separation processes (including the separation technology selection and combination as well as the relevant design/operation parameters such as location of feeds, number of trays, energy recycle and heat integration policies) are extremely required. A sustainable, economical, and energy-efficient downstream separation process will not only considerably reduce the total capital cost and the negative impacts on environment but also improve the competitiveness of biorenewable driven products with petroleum-based products.

Flowsheet synthesis

An optimal flowsheet of a biorenewable conversion process shown as Figure 8 involves pretreatment, multiple reaction steps in various reactors, downstream processing units, and recycles. Different pretreatment technologies will need different types of reactor; moreover, each type of the reactor will have different product distribution which exerts different requirements on the downstream units.[79,80] Conversely, results from the techno-economic analysis demonstrate that the high mass/energy transfer efficiency is the key factor in the design of biorenewable conversion process.[81–83] Hence, the whole flowsheet design should be explored in an integrated manner. Optimal flowsheet synthesis of the biorenewable conversion process for liquid transportation fuels production has been the focus of several contributions.

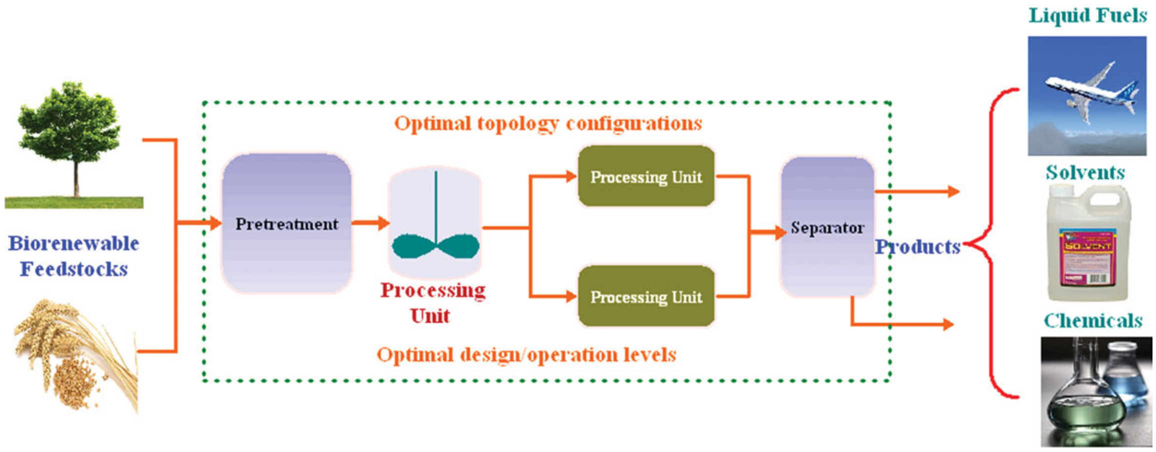

Figure 8. Illustrative of an optimal flowsheet for biorenewable processing.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Cardona and Sanchez investigated the optimal design and synthesis for the fuel ethanol production process,[84] they compared different structures of flowsheet involving reaction–separation, reaction–reaction, and separation–separation, the comparison shows that optimal synthesis will offer the most significant outcome for the search of the high-efficiency production process. Upadhye et al. used the five-step hierarchical decomposition approach shown as Figure 4 to synthesize an optimal biorenewable conversion process for producing tridecane from aqueous hemicellulose,[85] the final process is economically attractive as the significant reduction of utilities costs due to energy integration. Typically, when refer to a mathematical programming-based optimal synthesis, a superstructure will represent the biomass conversion network configuration which includes all possible pretreatment/reactor/separator alternatives, in the superstructure formulation, binary variable is used to limit to only one selection from alternatives to meet the optimal topology structure requirements. Following the above idea, Zondervan and coworkers[86,87] considered a superstructure optimization formulation resulting in a MINLP to seek the optimal multiproduct biorefinery network for the production of ethanol, butanol, succinic acid and blends from biomass, in their formulation, different pretreatment steps, reaction technologies and separation operations are included, with the respective aim of maximum yield, minimum costs, minimum waste, the corresponding optimal system can be obtained through the solution of MINLP problem correspondingly.

Biorenewable conversion process is the water and energy extensive consuming process,[88,89] where freshwater is used for washing operations, steam, and power generation, as well as separation process and cooling systems. Karuppiah et al.[90] addressed the optimal synthesis of a corn-based bioethanol plants using heat integration and mathematical programming techniques, a limited superstructure of alternative designs including various units and utility streams is first proposed, through solving the formulated MINLP problem where mass and energy balances for all the units are denoted by shortcut models, the optimal connections between units with minimum capital cost and energy usage are determined, heat integration is performed finally for the optimal flowsheet, the final-synthesized flowsheet can reduce the energy consumption by 40% compared with the initial basic design. Similarly, Martin et al.[91–95] extended the above method to the optimal synthesis of the bioethanol production from various biorenewable feedstocks via different conversion technologies as well as the hydrogen production from biomass. Recently, Martin et al.[96] gave a detailed overview of the above applications.

Based on the generalized superstructure of the integrated water networks[97] and its relevant solving algorithm,[98] Martin et al.[99] proposed a three-step approach for the optimal synthesis of second generation bioethanol plants, the first step is to optimize the energy consumption, in the second step, the optimal reaction route are selected from various candidates such as thermochemical and thermobiochemical routes, the third step determines the water consumption, resue, and recycle together with the required treatment through the superstructure optimization approach.

The exist research works have demonstrated that water consumption can be reduced by energy optimization together with the recycle and reuse of process and cooling water and steam. It is worth pointing out that the total process flowsheet synthesis, heat integration minimizing energy consumption, and water integration minimizing freshwater consumption and wastewater discharge should be investigated simultaneously for biorenewables conversion processes. Conversely, addressing the optimal synthesis of biorenewable energy systems not only requires research on the high carbon conversion efficiency and low production cost but also address social and environmental challenges such as GHG emission, air quality, soil quality, biodiversity, and land use in parallel.[100] In face with uncertainties in regional and seasonal availability as well as biorenewables properties and energy demand-supply balance, further optimal synthesis of total biorenewable conversion process flowsheet should be coupled with biomass feedstocks supply chain optimization[100–107] to make the production process can tackle multiple biorenewable feedstocks at environmental-friendly, economically viable and energy-save operation mode.

Optimal Synthesis of Polygeneration Process

The above section mainly discussed the optimal synthesis of biorenewable conversion process which produces liquid fuels such as bioethanol and biofuels. In this section, we will

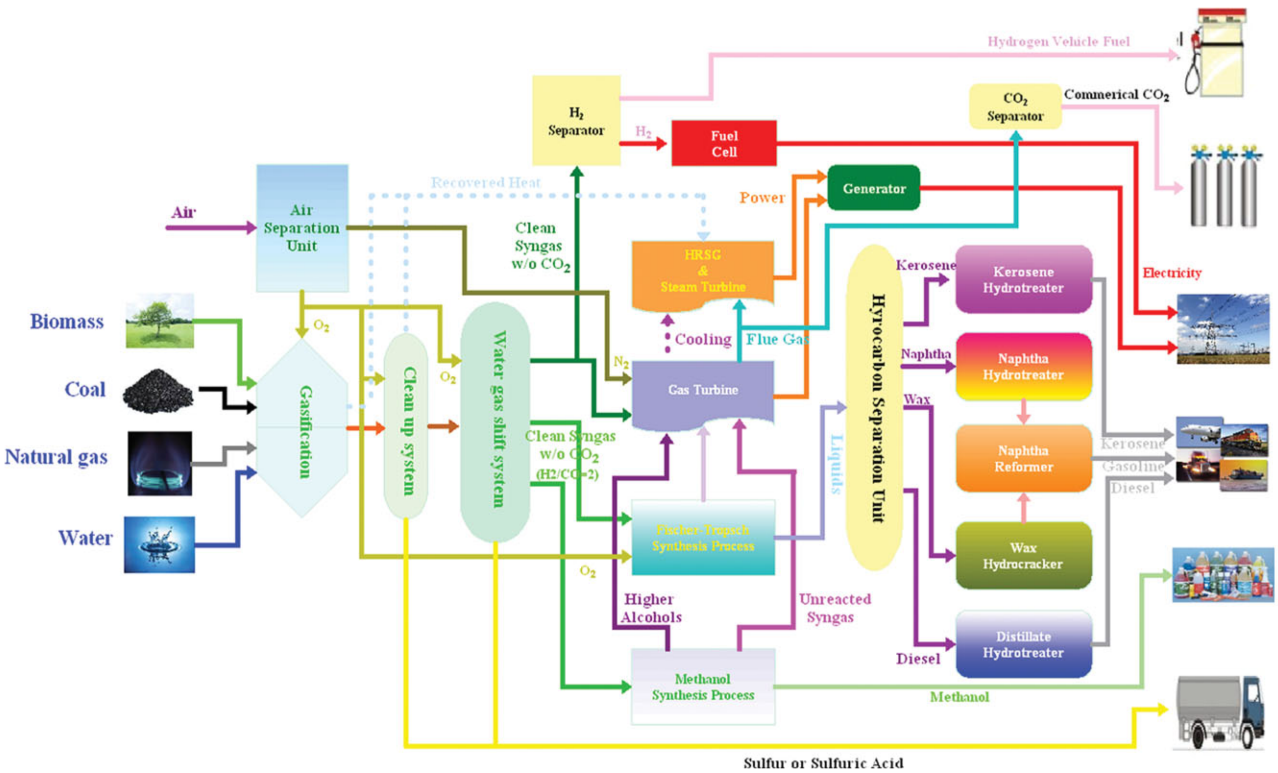

Figure 9. Summaries on the polygeneration process flowsheets.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

investigate the application of optimal synthesis to the polygeneration process which generates chemicals, liquid fuels and electricity simultaneously.

Brief introduction of polygeneration processes

Coal with abundant known reserve is a promising energy source for the generation of chemicals, liquid fuel, and electricity. Several coal-based conversion processes such as integrated gasification combined cycle (IGCC) and coal-to-liquid have been developed.[108–110]

The main drawback of the coal conversion process with single product is its lower adaptability to the oscillation of market prices. Polygeneration, a multioutput energy conversion process which involves the coproduction of electricity, chemicals, and liquid fuels, becomes an attractive alternative which exhibits much higher energy efficiency as the tight heat integration[111,112] and lower GHG emissions. Furthermore, lower economic risks and potentially higher profits of polygeneration can be achieved by diversification of product portfolios. During the past 5 years, numerous contributions have explored different polygeneration processes for thermochemical liquid fuels and chemicals production from coal, natural gas, and biorenewables through the Fischer–Tropsch reaction and methanol synthesis where the syngas is the intermediate.[10,113,114] Figure 9 gives the overall schematic flowsheet that summaries the exist polygeneration processes, detailed flowsheet for polygeneration process can be found elsewhere.[114,115]

The majority part of studies that were mentioned in Floudas et al.[10] focus on the limited process designs with specific operating condition; however, whether the fixed design topology with specific operating condition can produce liquid fuels at the lowest cost is not clear. Hence, optimal synthesis, which can systematically evaluate a large feasible set of process flowsheet alternatives to extract the optimal one that yields a minimal fuel cost, will unquestionably play a key role on the building of cost-efficiency and sustainable polygeneration processes, it involves the following typical six issues:

(a) Select the optimal technology and correct type of each piece of equipment from alternatives;

(b) Balance the economic objective and environmental objective with the aim of high energy efficiency and reduction of GHG emissions;

(c) Design the robust conversion system under inevitable and unpredictable uncertainties as the several decade-long operating horizon of a polygeneration energy system;

(d) Consider the water/heat integration simultaneously to minimize the fresh water consumption and wastewater discharge;

(e) Decide the optimal design and operation parameters for each unit;

(f) Formulate the optimal flowsheet topology structure-based on the above five aspects.

Optimal synthesis of coal-based polygeneration process

Coal can be converted into liquid fuels via direct or indirect liquefaction. As known, the latter one, through specific gasification and Fischer–Tropsch conversion, has been widely studied due to the superior economic performance when the electricity and chemicals (e.g., methanol, dimethyl ether) are simultaneously generated. Floudas et al.[10] gave a comprehensive list of exist activities on conceptual design, simulation, economic analysis, and heat/power integration for the coal based polygeneration process. Compared with the above aspects, there are not so abundant research contributions that have focused on the optimal synthesis of coal-based polygeneration process.

Based on their previous proposed system for converting coal to methanol and electricity,[110] Liu et al.[116] introduced a superstructure framework, formulated as a MINLP model with an economic objective function, to determine the optimal polygeneration plant. In their study, the whole polygeneration system is divided into four blocks including gasification, methanol synthesis, gas turbine, heat recovery steam generator, and steam turbine. For each functional block, all potential alternatives of technology and kinds of each unit are included in the superstructure representation, hence, all possible combinations of the technologies and connections between blocks are captured. Through solving the formulated MINLP problem with the aim at maximizing the profit, the optimal total flowsheet together with the optimal design/operation levels can be decided.

As the above discussion, the formulation only considered the economic objective, subsequently, Liu et al.[117] proposed a multiobjective optimization approach for synthesizing a polygeneration system producing methanol and power, the objective contains both economic issue denoted by net present value (NPV) and environmental issue represented by a cradle-to-gate GHG emissions. Therefore, the mathematical formulation is as follows.

$$
\begin{aligned}
&\max_{y,d,x} \quad U\begin{cases} f_1(y,d,x) = -NPV \\ f_2(y,d,x) = -GHG \end{cases} \\
&\quad Ay + h(d,x) = 0 \\
s.t. &\quad By + g(d,x) \leq 0 \\
&\quad Cy + Dx \leq b \\
&\quad x \in X = \{x | x \in R^n, x^L \leq x \leq x^U\} \\
&\quad x \in Y = \{y | y \in \{0,1\}^m\}
\end{aligned}
$$

In this formulation, aggregated models are set up to describe input–output relationships for each functional block, and the methanol synthesis block is described by the first principle models to capture the chemical kinetics and phase equilibrium relationships. By solving the multiobjective MINLP problem, the optimal Pareto curve is generated. Under different environmental requirement, the technological and connection combination can be decided based on the optimal Pareto curve. For example,[116] the combination of quench gasification, cold gas cleanup, and liquid phase methanol synthesis selections is the most viable design for the very tight environmental constraints, while under the comfortable environment requirements, the combination of radiative gasification, cold gas cleanup, and gas phase methanol synthesis decisions is the suitable design.

Till now, their mentioned works are mainly focused on the optimal synthesis of a polygeneration system under deterministic conditions. However, due to the long-term operation horizon, implementation of various inevitable uncertainties into consideration can significantly improve the robustness of the synthesized system. Liu et al.[118] continued to incorporate the probability distribution functions based uncertainties such as market conditions and stream composition into the optimal synthesis framework which is then formulated as a two-stage stochastic programming problem, and a decomposition algorithm[119] is used to get the optimal solution. Compared with the results of optimal synthesis under the stochastic and deterministic conditions, the outcome demonstrates that a process design obtained from the stochastic condition provides a much larger envelope of feasible operation than that from the deterministic one, obviously, the former one properly balanced the economic and risk.

When synthesizing an optimal coal polygeneration system, research works usually consider a superstructure of technologies and conversion pathway of coal to products, and identify the optimal overall plant topology based on an optimization framework. Exist contributions have shown that the amount of carbon converted from coal feedstock into final liquid product, whose range is currently from 20 to 35%, would be heavily dependent upon the flowsheet topology and technology of the conversion system,[23,24,120] higher conversion rate of carbon comes at a higher cost capital for the process. A cost-efficiency polygeneration process with higher carbon conversion rate will attract more and more attentions from public and industry. Optimal synthesis through the selection of the optimal units and configurations further reduce the production cost which will accelerate the speed for achieving this goal.

Optimal synthesis of biomass-based polygeneration process

Many researchers have investigated various routes of biorenewables conversion to liquid fuels.[10] However, many of the existing conversion technologies for the production of fuel and power require relatively dry and clean feedstock.[121] To relax this condition, Gassner and Marechal proposed a promising conversion process to produce synthetic natural gas (SNG) through the hydrothermal gasification of biorenewables in the supercritical water.[122]

Following the presented framework for the conceptual design of hydrothermal gasification processes,[123] Gassner et al.[124–126] investigated the optimal synthesis of hydrothermal gasification process in supercritical water for the production of SNG, power, and heat simultaneously. In their framework, the suitable candidate of unit operations and energy recovery policies, which are inserted into the process superstructure, is first identified based on biorenewables characteristics, product specifications and feasible pathways; the flowsheet candidates can then be systematically developed through a decomposition-based modeling approach; here, the combined mass/energy integration is formulated as a mixed integer linear programming where both material flows and heat cascades are included as constraints.[123] To trade-off conflicts between efficiency, cost, and environmental impact, a multiobjective optimization technique is also introduced, relationships between catalyst alternatives, feedstock properties and optimal flowsheet topology configurations as well as the accomplished operating conditions can be rapidly figured out. According to these relationships, the optimal process flowsheet and operating condition will be eventually determined under the given scenario and scale.[127] Through the integration of life cycle assessment (LCA)[128] into optimal synthesis framework, impacts of process flowsheet, efficiency, and scale on the environment can be further highlighted.[129]

Optimal synthesis for coal and biomass-based polygeneration process

Coal and biomass, as their abundant reserves and wide distributions across the world, are two welcoming source for co-producing power/electricity, liquid fuels, and chemicals. As the flexibility in converting multiple types of feedstock inputs into a wide range of products, hybrid feedstock-based polygeneration system shows several advantages over the coal-based polygeneration process, for instance, the CO2 emission from the hybrid coal/biomass conversion process is less than the coal-based one. Hence, a number of proposals have been offered to hybrid coal/biomass conversion systems.[130–132] However, these contributions mainly provided potential feasible polygeneration process designs from the economic performance and CO2 emission and did not consider the influences of process structural and design/operation parameters.

Chen et al.[115] carried out the optimal synthesis of a polygeneration process that produces power, naphtha, diesel, and methanol from coal and biomass. On the first step work, the authors synthesized the static optimal plant under different scenarios of markets and carbon policy conditions. Their MINLP formulation contains mass/energy balance of each unit, enthalpy calculations, capital cost calculations, and CO2 emission rates. Optimal product portfolios can be obtained via the solution of MINLP problem, and results can demonstrate the relationship between CO2 emission and the level of carbon tax.

As known, the product prices vary from season to season, the static optimal polygeneration system would fail to deal with the price fluctuations. Therefore, on their subsequent work, Chen et al.[133] synthesized a flexible polygeneration system to tackle the changes in prices and fluctuations throughout the plant lifetime. Similarly, a two-stage programming formulation is built to decide the long-term design issue and the short-term operational problem simultaneously in all scenarios. At the cost of higher capital investments, the NPV of the optimal flexible polygeneration plant is higher than the static counterpart under the same carbon tax. To seek the global optimal solution in a finite time, they proposed an enhanced decomposition algorithm which could find a ε-optimal solution of the large scale nonconvex MINLP problem representing the optimal synthesis of flexible polygeneration systems.[134]

Optimal synthesis for coal/biomass/natural gas-based polygeneration process

The aforementioned developments on polygeneration process based on single feedstock or two hybrid feedstocks open up opportunities to explore the energy system with hybrid coal/biomass/natural gas feedstocks. For example, Kim et al.[135] developed a superstructure optimization framework for the optimal synthesis of polygeneration process, where coal and biomass as well as natural gas are included in the superstructure as feedstock options. From 2010, Floudas and coworkers[10,136–141] have pursued considerable works to the exploration of the hybrid coal, biorenewable, and natural gas to liquid (CBGTL) polygeneration process, and their contributions range from process modeling/simulation to economic analysis, from optimal synthesis to enterprise supply chain optimization. In this section, only the part of optimal synthesis of this novel CBGTL polygeneration process will be highlighted.

The CBGTL superstructure contains multiple conversion routes from coal, biomass, and natural gas to gasoline, diesel, and kerosene products in ratios consistent with the United States transportation demands.[112,114] Of course, different conversion routes exhibit different economic and environmental performances. To balance the conflicts between various objectives, Baliban used mixed integer nonlinear optimization technology to address the optimal synthesis of CBGTL process.[137] The components in the comprehensive thermochemical superstructure include: fixed process units, variable process units, fixed stream connections, variable stream connections, fixed unit operating conditions, and variable unit operating conditions. The cost of the process is comprised by capital cost, feedstock cost, electricity cost, CO2 sequestration cost, and cooling utility cost. The above aspects are modeled mathematically, heat/power integration[142,143] that utilizes heat engines to recover waste heat from the process and produces steam and electricity is incorporated into the formulation simultaneously.

Based on the formulated MINLP problem, optimal flowsheet topology for the CBGTL under different scenarios can be conducted. For instance, influences of CO2 sequestration and GHG reduction targets (50% and 100% emission reduction) on the optimal topology have been investigated,[137] results show that the pressure swing adsorption (PSA) will be activated to produce hydrogen when the CO2 sequestration unit is added to the flowsheet, otherwise, the electrolyzers must be used to generate hydrogen. Additionally, the optimal topology with CO2 sequestration unit will achieve higher amounts of electricity recovered. Basically, the simultaneous heat/power integration can provide the operating condition, working fluid flowrate and the needed amount of cooling water for heat engines. Through the optimal synthesis, how the other factors such as electricity and biorenewable price affect the final optimal flowsheet as well as the operating condition can be illustrated.

In their follow-up works, Baliban and coworkers[138] incorporated the efficient wastewater treatment network into the proposed superstructure formulations to minimize the freshwater consumption and wastewater discharge. They postulated a superstructure of the wastewater network including a biological digester, a sour stripper and reverse osmosis system, the wastewater treatment network would take the charge of treating and recycling wastewater and freshwater from various process units. Hence, the process synthesis problem with simultaneous heat, power, and water integration has been fully formulated. With the adding of the wastewater treatment topology into the CBGTL superstructure, the economic and environmental benefits as well as the optimal flowsheet topology together with its overall cost can be quantified through solving the MINLP problem under different scenarios (biorenewables type/property, plant capacity, product distribution, etc).[139] Recently, Richard expanded the aforementioned superstructure for optimal synthesis to include thermochemical and catalytic route such as ZSM-5 catalytic conversion.[140] The relationship between plant capacities and optimal topology configurations and technology selections can be demonstrated. Obviously, these outcomes will offer a reference for the decision-making of the technology and the relevant total flowsheet topology together with the operating mode to formulate a sustainable energy system with high carbon conversion efficiency.

Optimal Synthesis for Carbon Dioxide Capture Process

Energy utilization in modern societies is based on the combustion of carbonaceous substances such as coal, petroleum, and natural gas. Over two-thirds of anthropogenic carbon dioxide (CO2) emissions arise from these combustion process.[144] Concerns due to the global climate change have heightened the interest worldwide for developing initiatives to reduce GHG emission, especially CO2 emissions. In general, exist technologies belong to the following categories.

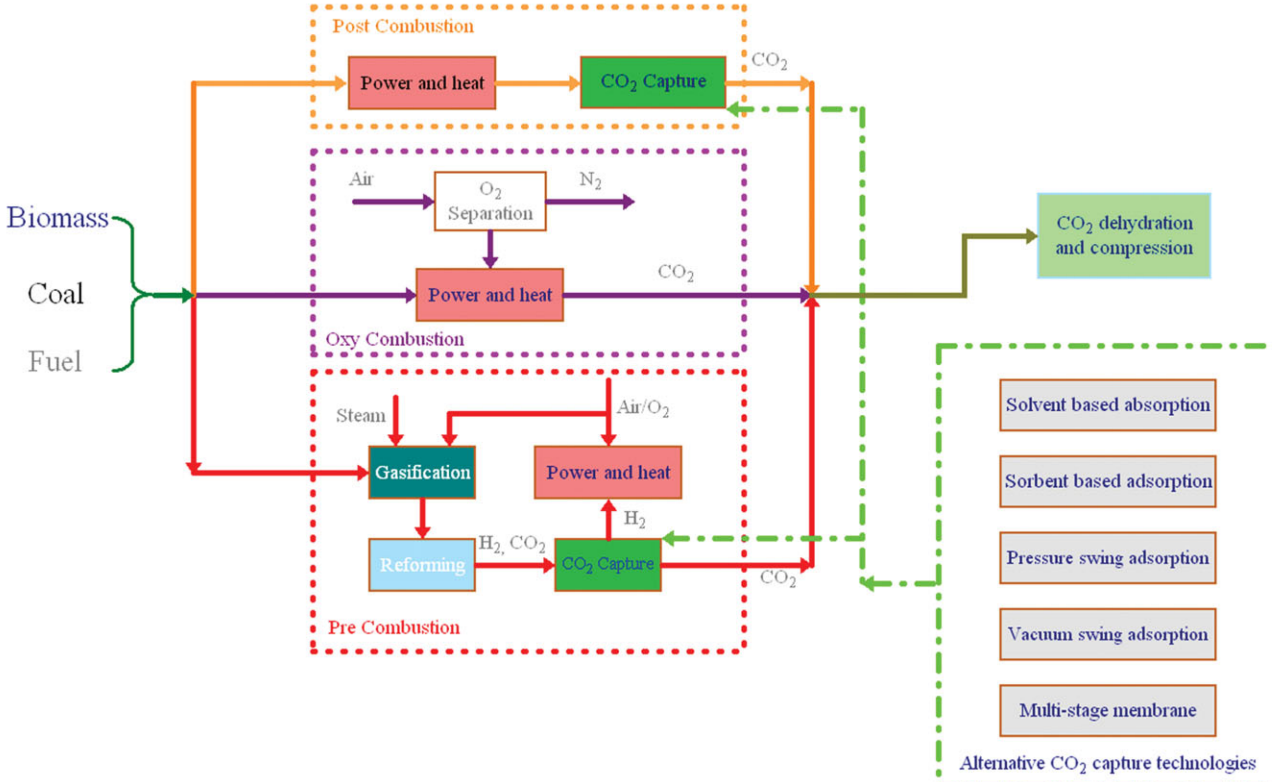

Figure 10. Technologies for carbon capture.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(1) Switch from carbon driven liquid fuels to renewable alternatives such as nuclear, wind, biomass, and solar energy.

(2) Use of advanced fossil-fuel technologies such as IGCC, supercritical, and ultra-supercritical pulverized coal power plants, and natural gas combined cycle to reduce the CO2 emissions.

(3) Capture CO2 emitted from coal based power plant.

Apparently, carbon capture technologies have the potential to allow continuously use of fossil fuel while mitigating CO2 emissions. A large number of technologies shown in Figure 10 have been explored to capture CO2 from various types of power plants.[145] How to formulate a high-efficiency, cost-effective carbon capture process has attracted more and more research works such as novel solvent/sorbent materials synthesis, optimal process flowsheet synthesis, advanced process control.[4]

In the context of carbon capture process synthesis, the main issues that should be focused are as follows:

- Minimize the cost of electricity that will drive the compressor and motor while achieve the carbon capture target.
- Reveal the influence of carbon capture targets on the technology selection, the optimal flowsheet configuration, operating condition, and overall cost.
- Investigate the influence solvent/sorbent material alternatives on the optimal flowsheet decision and environmental impacts.

Previous research has demonstrated that the saving of cost not only comes from the selection of solvent and pieces of equipment but also mainly comes from the optimal interactions between different operation units.[146] Agarwal et al. proposed a superstructure based method for the optimal synthesis of PSA cycles which would be used for precombustion and post-combustion CO2 capture.[147,148] They applied an optimization-based framework to generate optimal PSA cycles from a 2-bed PSA superstructure which has a co-current bed and counter-current bed. The bed connections in the superstructure are governed by time-different control variables, while the PSA system is represented by partial differential and algebraic equations. Through solving the formulated optimal control problem, relationships between the CO2 recovery targets and optimal process configurations as well as design/operation parameters are established. Also, the authors investigated the effect of power consumption on the optimal configuration. Of course, this optimal synthesis can be used to evaluate the influence of different kinds of adsorbents and flow patterns on the optimal configurations and overall cost.[148] Recently, Ahmad et al.[149] synthesized a membrane separation system for CO2 capture from natural gas. Based on the commercial simulators, six candidates of the flowsheet were compared, for each candidate, parameter sensitivities, along with economic performance were also taken into account.

Although various carbon capture technologies have been proposed, the large-scale implementations of carbon capture technology into commercial power plants have not reached as there are many challenges linked to this integration. For example, the performance of the CO2 capture process will be directly affected by time-varying operating conditions of power plants such as start-up, shut-down and changes in the flue gas load due to fluctuations in electricity demands. Retrofitting of exist power plants with the adding of carbon capture technology will obviously reduce the efficiency of the original power plant and consequently increase the cost of electricity. Hence, regardless in the context of the retrofitting of exist power plants or in the design of new power plant with carbon capture system, optimal synthesis should focuses

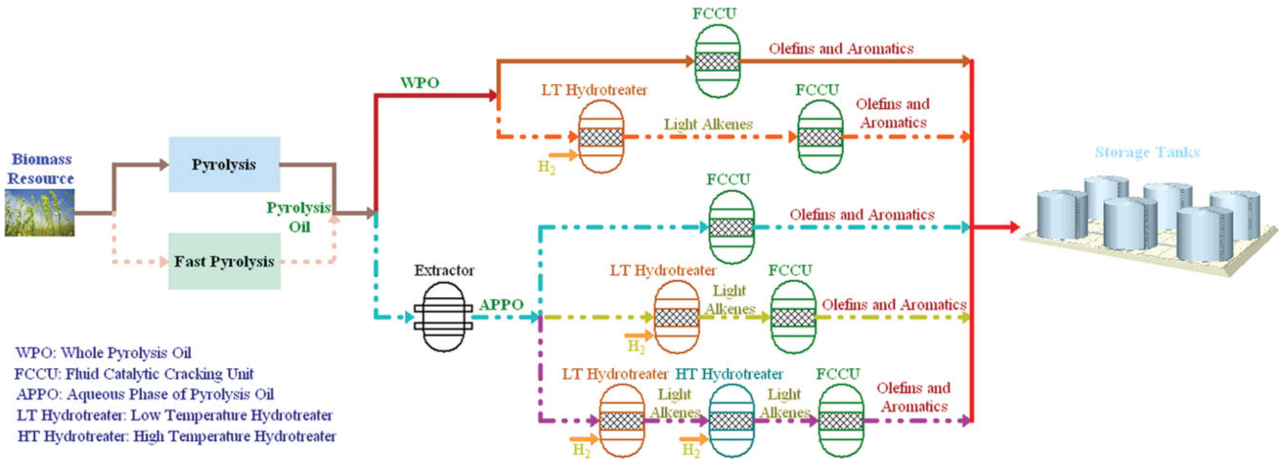

Figure 11. Superstructures for catalytic biorenewable conversion process flowsheet.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

on the following challenges while achieve the requirement of carbon capture:

- Trade-off the capital costs of new infrastructure linked to capture system and carbon capture targets.
- Trade-off the operability of the power plant with carbon capture system and its optimal flowsheet topology together with operating condition.
- Extract the robust flowsheet under uncertainties such as electricity demand and price and environmental impacts.
- Simultaneous optimal synthesis of power plant with carbon capture system and heat/power integration, as an example, incorporating the heat generating from the compression of the CO2 will significantly improve the energy balance.[145]

Further Potential Applications of Optimal Synthesis

Substantial applications of optimal synthesis have been highlighted in previous sections. Apart from these applications, due to improved requirements on environmental aspects and issues on the mechanism of biofuels,[150] several novel sustainable energy systems are proposing. In this section, we will prospect the relevant potential applications of optimal synthesis.

Optimal synthesis of catalytic routes-based biorenewable conversion process

The majority part of the existed biorenewable conversion processes mentioned before are based on thermochemical or biochemical conversion routes. As various disadvantages of thermochemical/biochemical conversion routes,[16,48] plenty of catalytic routes have been explored for the production of high quality transportation fuels.[22] Literatures have showed that catalytic routes can be incorporated into conventional petrochemical process flowsheet to save capital cost.[49,151,152] For instance, Figure 11 depicts a superstructure of a catalytic conversion process for the production of olefins and aromatics from biorenewables, in this formulation, pyrolsis unit, hydrotreater, and FCC unit are included.[153] According to requirements on the quality of transportation fuels, optimal synthesis will systematically generate the optimal flowsheet with low production cost and minimum negative environmental impacts. However, Biomass derived feedstocks are chemically different from petroleum derived feedstocks,[51] optimal synthesis is predicted to be able to fix the new optimal operating policies and give retrofits comments for the conventional refinery-based biomass catalytic conversion process. Conversely, optimal synthesis can also be utilized to extract the optimal catalytic conversion process comprised of novel operating units such as solvent extraction and membrane separation which have never been considered in the petrochemical process.

Optimal synthesis of hybrid solar/wind driven sustainable energy system

As reported, the upper limit of the photosynthetic efficiency of C3 plants is 4.5%.[150] However, depending on the temperature of absorption and concentration of sunlight through the use of concentrators, sun-to-heat collection efficiencies can reach as high as 50–70%.[154,155] Hence, solar energy holds out the promising of the production of heat and electricity for the sustainable energy system. Hertwich and Zhang[156] proposed a concentrating-solar biorenewable gasification process, in their designed process, high temperature heat from the solar concentrating tower is used to drive the endothermic operating units such as gasifier and rewater gas shift to significantly reduce the need of heat from combustion of fossil fuels, the hydrogen for rewater gas shift is from the water split where the electricity is also generated from solar concentrating tower. Of course, this novel diagram has built an exciting start point for the development of the solar energy driven biorenewable conversion process; without any doubts, optimal synthesis will play a significant role in the formulation of these novel biorenewable conversion processes with low production costs and high carbon conversion efficiency.

Actually, CO2 is not just a greenhouse gas, but also an important source of carbon for making organic chemicals, materials, and carbohydrates.[157,158] Hence, the captured CO2 from power plants and even from atmosphere should be recycled to produce high-value added chemicals.[159,160] For example, researchers from Los Alamos National Laboratory and University of Wisconsin have conducted a solar energy driven conversion process for the production of methanol from CO2 and H2O.[161,162] Figure 12 shows the superstructure flowsheet of a promising solar/wind driven CO2 conversion process, where the electricity and power are provided by solar energy or wind energy. To select optimal technologies (water splitting, separation operation, and reaction unit)

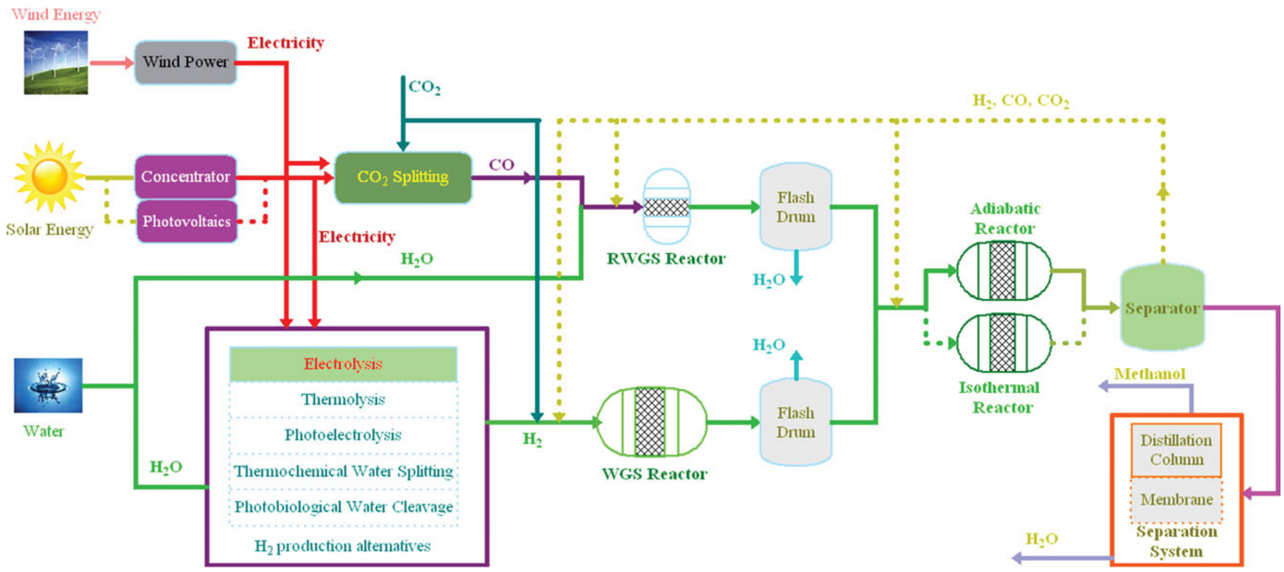

Figure 12. Solar/wind energy driven CO2 conversion process.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and to decide the total optimal flowsheet belong to the field of optimal synthesis.

Optimal synthesis of algal conversion process

Algae are recognized as one of the most promising biorenewable feedstocks for transportation fuels production.[163] The productivity of the algae which convert CO2 and solar energy into carbon-rich lipids exceeds that of agricultural oleaginous crops. Hence, algae do not compete with food crops and arable land while can supply abundant, cost-efficient and sustainable domestic biorenewables.[164] However, compared with conventional crops such as switchgrass and canola, algae have higher environmental impacts in energy use, GHG emissions and water.[165] Multiple approaches (direct fuel production, thermochemical/catalytic conversion, biochemical conversion, and anaerobic digestion) can be used to convert carbon-rich lipids into transportation liquid fuels. Following the above statement, simultaneous optimal synthesis and overall system compatibility and sustainability considerations[166] are crucial in guiding research efforts along the selected suitable pathway and optimal conversion process flowsheet that offer the most opportunity to practically enable a viable and sustainable algae-based liquid fuels and co-products industry.

Optimal synthesis of new material-based carbon capture process

The growing level of atmospheric CO2 is one of the widest environmental concerns currently. CO2 capture and storage is one promising option for reducing anthropogenic CO2 emissions. Besides the previously listed methods to capture CO2 from power plant, there are many other innovative technical possibilities to achieve the capture target, for example, several researches concentrate on the development of dense, porous, or ion-/electron-conducting membranes for carbon capture.[145] Conversely, as known, innovative new materials can reduce the time to commercialization of advanced capture technologies, more and more efforts are focusing on the novel materials synthesis such as grafted silicas, zeolites, and metal-organic framework for maximizing the separation efficiency.[167] Hence, in the further study, optimal synthesis should focus on the effects of novel materials and capture targets on the optimal flowsheet topology and operating conditions to reduce the overall cost of capture systems under different scenarios. Here, the key issue is the formulation of the models representing the behavior of the absorber/adsorber and regeneration units since detailed first principle models are computationally intractable for large scale superstructure optimization. The surrogate model for the description of absorber/adsorber and regeneration is a potential strategy.[168,169] When adding the novel carbon capture system into power plant, optimal synthesis of the total process should be coupled with CO2 compression and transportation.

Optimal synthesis of biorenewable conversion process for chemicals production

Existed biorenewable conversion processes have almost exclusively concentrated on the production of high-volume, low-value transportation fuels to meet national energy needs. Currently, the imbalance between the chemicals production and the transportation fuels production is the key stimulus for the integrated biorenewable conversion process.[170] It is well established that the production of low-volume, high-value chemicals will enhance the economic feasibility of the biorenewable conversion process.[171] As estimated, the majority part of chemicals used by the petrochemical industry can also be derived from biorenewables. However, bio-based chemicals production is challenged by an over abundance of targets,[172] which are different from transportation fuels production. Figure 13 shows the research approaches for transportation fuels and chemicals production. It can be easily found that transportation fuels research is convergent, while chemicals research is divergent with multiple outputs, process analysis, especially the conversion pathway identification, becomes complicated.

Apparently, the paradigm shift from petroleum hydrocarbons to highly oxygen functionalized, biorenewable-driving feedstocks will create remarkable opportunities for optimal synthesis and design. For example, separation, which

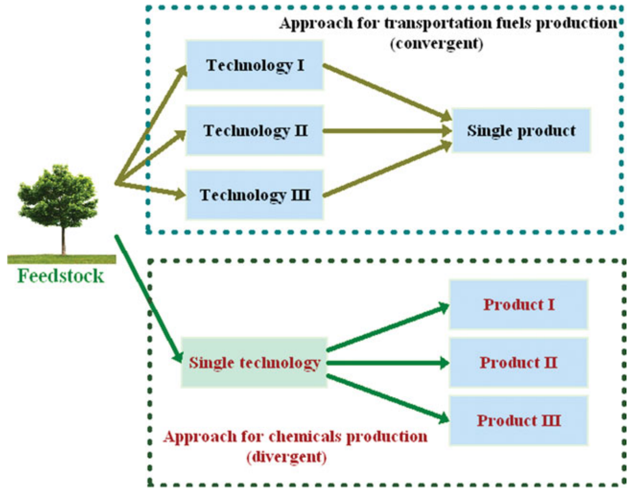

Figure 13. Differences between research approaches for liquid fuels and chemicals production (revised from Ref. 171).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

currently accounts for 60–80% of the overall cost of petrochemical processes, will continue to be the challenge associated with chemicals production from biorenewables. Hence, synthesizing a cost-competitive and environmental-benign separation system is needed.

Challenges and Needs

As aforementioned, the construction of a cost-competitive, energy-efficient, environmental-friendly, and renewable energy system has opened up several exciting new vistas in optimal synthesis. However, challenges emerge, and they span a wide spectrum involving multiscale process synthesis, novel mathematical formulation for optimal synthesis under uncertainties and the corresponding solution algorithms.

Multiscale optimal synthesis for biorenewable conversion process

Biorenewable conversion process synthesis shown in Figure 14 involves the following (Yuan et al., submitted for publication)[173]: reaction pathway synthesis, reactor network synthesis, utility system synthesis, and total flowsheet synthesis. The above activities are currently investigated in a sequential manner. As known, multiple conversion routes exist between biorenewables and intermediates and final products, clearly, each route corresponds to the special solvent, reactor and separation unit as well as the relevant operation mode. For example, the reactor synthesis level should provide the optimal reactor network that satisfies the requirements of the thermo chemistry and kinetics. At the same time, the regional and seasonal availability of biorenewable feedstocks together with transportation fuels demand, in other word, the enterprise supply chain optimization should be incorporated into the optimal synthesis framework.[174,175] To meet the above requirements and to achieve the high carbon conversion with lowest production cost, multiscale optimal synthesis should be given adequate concentrates. To develop an effective multiscale model for the simultaneously selection of molecular structure, reaction route, reactor/separator network and flowsheet configuration is the main challenge.

Integration controllability and stability analysis with optimal synthesis

Controllability and stability, namely operability, indicate the attainable operation with suitable dynamic performance of a given process.[176,177] Usually, several operation units in biorenewables processing and CO2 conversion process such as gasification unit and Fischer–Tropsch synthesis unit exhibit highly nonlinear dynamics which probably negatively affect the product quality and distribution. Alvarado-Morales et al.[178] proposed an integrated framework for the optimal synthesis, design, and control of a bioethanol production process. The formulated process exhibits excellent dynamic performance on the external disturbance rejection and the

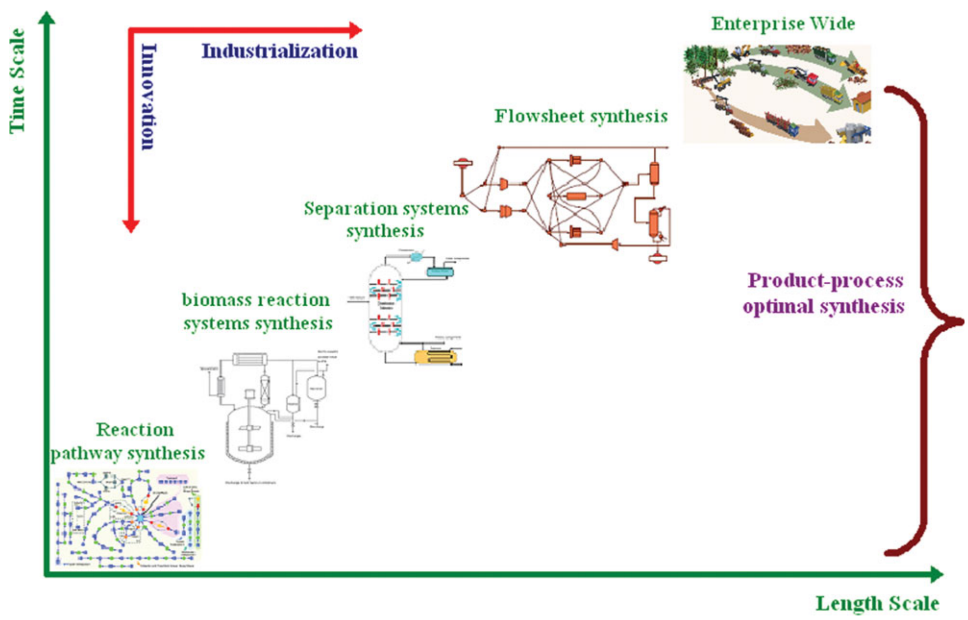

Figure 14. Multiscale optimal synthesis for the biorenewable conversion process.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

set-point tracking. So, the operability indicator establishment and its incorporation into optimal synthesis of the renewable energy system are another two challenges for further research.

Environmental management for sustainable energy systems

During the development of sustainable energy systems, the environmental implication assessment becomes more important than ever before.[179] Researchers have reached an agreement that the environmental performance assessment of a chemical process should be carried out over its entire life cycle.[180] The environmental impact assessment methods can be found elsewhere,[179,181] among these methods, LCA[182,183] is currently the main approach for environmental management in the field of chemical process, and the key idea is to formulate a multiobjective optimization framework which accounts for environmental concerns together with economic objectives.[184] Till now, the combined use of LCA and multiobjective optimization has been successfully applied to environmental management of supply chains,[100,102,185–187] solvent design[188,189] and flowsheet design.[190] However, it is not clear that which environmental metric should be minimized during the environmental management of sustainable energy systems. Therefore, to identify and quantify the environmental impact of sustainable energy systems, in other words, which indicators should be used and how to incorporate indicators into optimal synthesis framework will be the focus of further more research activities.

Mathematical formulation for optimal synthesis under uncertainties

It is clearly that various uncertainties[191] may put negative effects on sustainable energy systems. For the biorenewable conversion process, its success depends impart on the quality and quantity of biomass derived feedstocks available, the industry's ability to collect, store, and cost-efficiency transport these biorenewables, as well as the market demand. For the integrated power plant with carbon capture system, the fluctuation in electricity demand and carbon capture target requirements should be given attention; while for the solar energy driven renewable energy systems, disturbances due to cloud cover, wind or other weather events will make the CO2 conversion process highly variable. How to drive an efficient mathematical formulation for optimal synthesis under these uncertainties is waiting for plenty of careful studies.

Global and robust algorithms for solving optimal synthesis under uncertainties

Mathematical programming-based optimal synthesis for sustainable energy conversion systems will result a large scale mixed integer nonlinear optimization formulation, especially when considering the flowsheet synthesis, integrated water network, and energy/power integration simultaneously. The challenge is how to efficiently solve the formulated optimization problem. The need for the theoretical and algorithmic development of new efficient, rigorous, and robust optimization methods for advanced mathematical programming formulation becomes extremely important to prevent the generation of economically undesirable flowsheet under uncertainties.

Conclusions

In view of changing world energy needs and environment protection, methods of producing renewable transportation liquid fuels/chemicals and reducing CO2 emission are currently the concentrates of numerous large research efforts across the globe. Truly sustainable and economic solutions call for a more important role of PSE than presently one, optimal synthesis of the sustainable energy system is recognized as the core methodological paradigm. This article intends to assess the current activities on optimal synthesis of sustainable renewable energy systems and to illustrate the opportunities and challenges opened up by further roadmaps of sustainable energy systems. In collaboration with experts in other fields such as physicist, materials scientist, chemists, and biochemical engineers, optimal synthesis will take a leading role in constructing the economically viable, environmentally benign, and socially beneficial sustainable energy processes.

Acknowledgments

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