Modeling and Optimization of Novel Fuel Production Strategies

by

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Abstract

Environmental problems such as global warming and fossil fuel shortage are some of the biggest challenges that human beings are facing nowadays. Alternative fuels are the potential answer to many future energy needs and current environmental concerns. A polygeneration plant is a complex system that can produce multiple products through different processing routes. The study of novel alternative fuel production through optimal processing strategies is the key to solving worldwide energy and environmental problems in a more efficient and cost-saving way.

The objective of this research is primarily focused on the development of methodologies that integrate simulation, modeling and optimization tools for evaluation of the economic/environmental potentials of polygeneration facilities. The production of hydrogen and Fischer-Tropsch fuels are presented as case studies. Hydrogen is a “clean” energy source. The only product from the combustion of hydrogen is water, leaving zero carbon footprints. Fischer-Tropsch fuels, on the other side, can be matched directly to the fuel market. Therefore, case studies of different hydrogen production schemes and a comparison between traditional and novel FT fuel production processes have been developed to illustrate the methodology. This work successfully compared reformation strategies based on the impact of utility requirements, energy integration potential, equipment costs, and raw material costs on the total production cost. Meanwhile, different production scenarios of alternative fuels such as Fischer-Tropsch fuels were investigated. A comparison between the traditional gas phase Fischer-Tropsch process and the novel supercritical phase Fischer-Tropsch process was made. The results could lead us to a more efficient and environmental friendly alternative answer to satisfy many of the future energy needs.

In addition, a novel method has been developed to optimize complex process networks. Disjunctive-Genetic Programming (D-GP), which is based on the integration of Genetic Algorithm (GA) with the disjunctive formulations of the Generalised Disjunctive Programming (GDP) for optimization of process networks, has been developed. This proposed approach eliminates the need for reformulation of the discrete/discontinuous optimization problems into direct MINLP problems, thus allowing for the solution of the original problem as a continuous optimization problem but only at each individual discrete and reduced search space. This method was used to optimize the selection process for complex products and production routes.

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Chapter 1 Introduction

Polygeneration is the integrated production of three or more outputs in the form of tangibles, i.e. chemicals and fuels, or intangibles, i.e. heat and electricity from one or more natural resources. It has multiple products and production routes and has tremendous integration potential, not only limited to recycling unused materials, but also in the form of energy recovery. It is an advanced chemical energy conversion technology, which provides opportunities for higher energy utilization efficiency and lower/zero emissions compared to conventional stand-alone power plants and chemical facilities [Serra, 2009; Gamou, 2002]. Many researchers have studied the processes, feasibility and environmental impact of different polygeneration systems. Gao *et al.* (2004) investigated a coal-based polygeneration system for power and methanol production. By comparing with the original individual processes, the results indicated that the main contribution to the performance benefit of the polygeneration system is the synthesis on the basis of thermal energy utilization. Joelsson *et al.* (2010) compared different options for the use of lignocellulosic biomass to reduce CO_2 emission and oil use with traditional individual plants, focusing on polygeneration of biomass-based motor fuels and electricity. The results indicated that the most efficient route to produce motor fuel from biomass was dimethyl ether (DME) via black liquor gasification through polygeneration facilities. Polygeneration process designs are not only used to produce electricity and chemical fuels, but also for specific purposes, such as combining a lignocellulosic wood-to-ethanol process with an existing heat and power plant for higher energy utilization rates [Starfelt, 2010]. During the evaluation process, a model was built to compare the performance of the polygeneration system. The results showed that the combined facility produced 2.7% more electricity per year.

While the reported works provide a good fundamental understanding of different polygeneration facilities and their benefits, most of them focus on specific requirements or conditions. The evaluation of different complex polygeneration concepts is associated with the difficulties of comparing systems with different inputs, i.e. biomass feedstock and different outputs (i.e. heat, electricity and fuels) with respect to multiple criteria such as economic feasibility and energy security. Thus, a general systematic methodology is needed to determine this complex, large-scale and highly nonlinear process system.

The scope of this dissertation will mostly focus on developing a methodology that leads to optimal novel fuel product portfolios through polygeneration facilities. A systematic approach is utilized to reduce the complexity of the polygeneration plants and conceptual processes are developed for the production of clean and renewable energy sources such as H_2 and Fischer-Tropsch fuels. The methodology developed to achieve this stated research objective consists of several steps. The first step involves gathering the initial data for the proposed process including the possible feedstocks and processing routes. The primary purpose of this step is to determine the general technical feasibility of the process chemistry and to determine the general process operating conditions of the proposed processes. Then data gathered from literature sources or collected from laboratory experimentation are extracted to develop the base case simulation models using computer-aided tools like Aspen Plus and Pro/II. If the process is solvent-based, molecular design tools are utilized to design the alternative solvents that perform the same function but are safer and less hazardous to the environment. Heat and mass integration techniques are applied to optimize the simulation models. This key step ensures the minimum usage of heating and cooling duties and raw materials that flow into the system. Optimized models are utilized to generate economic and environmental performance metrics. Mathematical optimization is used at this stage of development to identify candidate solutions that achieve the highest profitability. Environmental impact is also measured and incorporated into the profit oriented optimization step. Once the models are created, an evaluation based on economic performance and potential environmental impact can be completed.

Chapter 2 gives a brief introduction on product and process design, process integration, economic and environmental analysis as related to the optimization and evaluation steps of the methodology. This chapter also outlines concepts of polygeneration facilities and the alternative fuels that were studied using polygeneration technologies. Chapter 3 describes the methodology to design polygeneration facilities, which decreases the complexity of the process design problem, through optimization and evaluation of desirable processes. Chapter 4 includes several case studies on alternative fuel production; different hydrogen and Fischer-Tropsch fuel production schemes through polygeneration facilities are investigated to give a more complete view of the methodology illustrated in Chapter 3. A Disjunctive-Genetic Programming (D-GP) approach is presented in Chapter 5 based on the integration of Genetic Algorithm (GA) with the disjunctive formulations of the Generalised Disjunctive Programming (GDP) for the optimization of process networks. This algorithm provides a broader application of the methodology to solve complex chemical synthesis networks. Several examples are presented based on the algorithm to illustrate its benefits over existing methods. Chapter 6 summarizes the achievements in this dissertation discusses future directions.

The work related to alternative fuel production and optimization methodology development has been published in several papers [Odjo *et al.* 2008, 2011; Yuan *et al.*, 2008, 2009a, 2009b, 2011]. The work on the comparison of different hydrogen production strategies has been published in Computer Aided Chemical Engineering [Yuan, 2008]. The work related to Fischer-Tropsch fuel synthesis has been published in Computer Aided Chemical Engineering [Yuan, 2011]. Meanwhile, the work on the D-GP framework has been published in Industrial and Engineering Chemistry Research [Odjo, 2011], Computer Aided Chemical Engineering [Yuan, 2009a] and Design for Energy and the Environment [Yuan, 2009b].

Chapter 2 Theoretical Background

2.1 Polygeneration Facilities

Polygeneration is considered as a potentially attractive technology as it could provide feasible solutions to the worldwide problems of excessive greenhouse gas (GHG) emissions and ever-increasing depletion of fossil fuels. Figure 2.1 shows an example of a polygeneration plant. Polygeneration systems offer the possibility to produce chemical products, synthetic fuels, hydrogen and electricity simultaneously. They have multiple products and production routes. The carbonaceous feedstock possibilities include forest-based biomass, agricultural biomass, and coal. The yellow diamonds represent the classes of chemicals that can be sold externally on the market or used internally by the biorefineries and/or their partners. The blue rectangles represent the chemical processes that may include more than one subprocess and multiple production routes, which can achieve the goal of producing the desired products. A typical polygeneration plant produces electricity and chemical synthesis products, in particular alternative fuels, such as methanol, dimethyl ether (DME), Fischer-Tropsch fuels and hydrogen. It integrates existing or new techniques to produce multiple energy products including electricity, heat, ethanol and biogas. Such a system could preferably use local arable land and forest by-products to supply the feedstock. Thus, it requires a higher degree of integration than conventional power plants, because it must adapt to disparate infrastructures. There will also be different markets and players and regulatory regimes to relate to it.

Many researchers have studied the processes, feasibility and environmental impact of the polygeneration systems [Li, 2003; Ni, 2004; Yamashita, 2005].

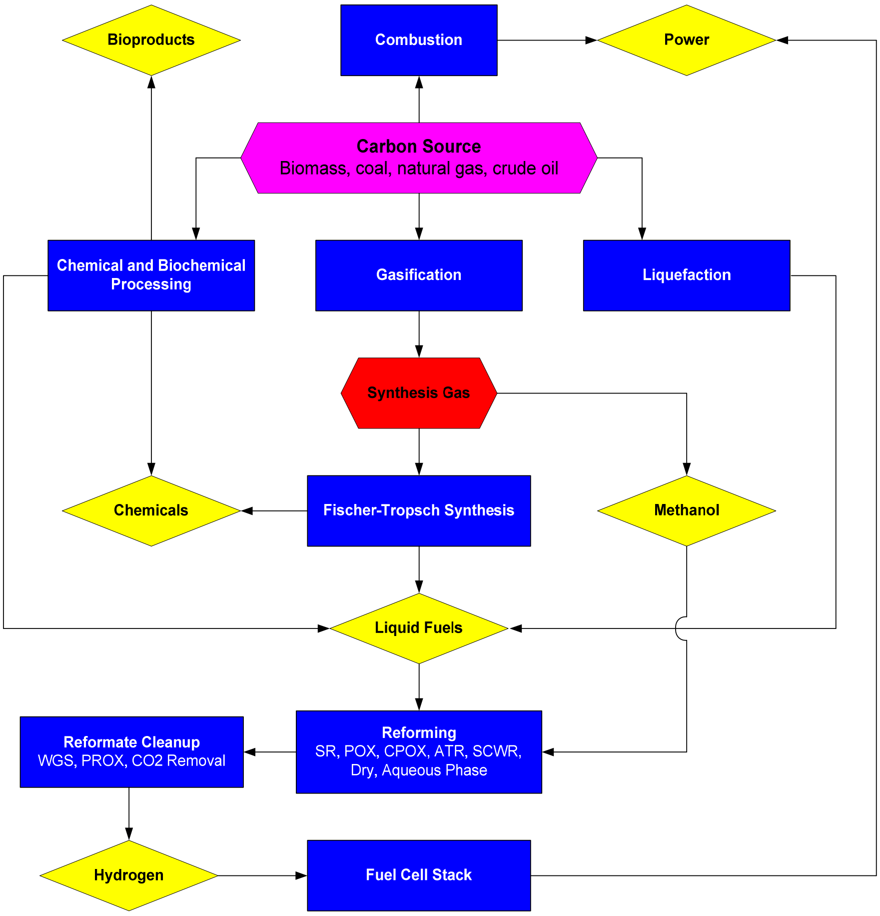


Figure 2.1: Visualization of a polygeneration plant [Yuan, 2008]

A successful integration requires that a number of conditions be satisfied, including the appropriate pricing mechanisms and that any significant barriers for market entry be identified and removed. Polygeneration energy systems are considered to be superior to conventional stand-alone plants. Their advantages rely on three main aspects. First, integration techniques are applied to both chemical synthesis sections and the power generation, making the system more efficient. Second, chemical products produced by a polygeneration plant can be used as substitutions for traditional liquid fuels; such as Fischer-Tropsch fuel for fossil fuels, hydrogen can also be a product. Finally, the large scale energy systems are expected to result in cost effective solutions for the implementation of CO_2 capture and sequestration units.

2.2 Alternative Fuel Production

2.2.1 Introduction

The possibility of climate change and the likely exhaustion of fossil fuel resources are two of the main energy concerns in the world today. Human activities are most likely the reasons for the warming. The world's economy literally runs on energy. More energy will be needed with the continuously fast-growing world population, even with significant improvements in energy efficiency. The search for an environmentally friendly and energy efficient replacement for fossil fuel is very important.

Alternative fuels can be defined as materials or substances, which can be used as a fuel, other than conventional fuels. Biofuels, hydrogen, ethanol, and Fischer-Tropsch fuels are all within the scope of alternative fuels.

In summary, the world energy development program has taken a few turns to produce alternative fuels for various reasons, some of which are listed below [Lee, 1996]:

- The recessions in the early 1980s; the government cut spending, making long-term research and development a lower priority.
- The Clean Air Act Amendments of 1990: additional restrictions on the use of conversional fuels have been implemented.
- Energy integration concepts have been very popular, because of easy adaptation to existing facilities as well as enhanced efficiencies.

The field of alternative fuels is strategically important to the long-term future of human life as well as better utilization of global resources.

2.2.2 Hydrogen as Alternative Fuel

Hydrogen can become a potentially very promising fuel for transportation uses in the future. It is very “clean”. During combustion, it only produces water [Barretoa, 2002]. In addition, hydrogen has the highest gravimetric energy density of any known element (but the lowest volumetric energy density, which makes storage challenging). It has a higher heating value than other fuels [U.S Department of Energy, 2004].

Hydrogen can be produced from hydrogen-containing compounds, including fossil fuels, biomass or water through a variety of processes. Different sources of energy will be needed depending on the processes, such as thermal, photolytic and electrolytic energy.

2.2.2.1 Reformation Strategies

Reforming is the process of converting hydrocarbon compounds to produce hydrogen containing products. Hydrogen can be derived from hydrocarbons through various reformation techniques, such as thermal processes, electrolytic processes and photolytic processes, among which thermal processes are the most investigated reforming strategies, and believed to be key technologies for the potential development of a future hydrogen energy economy.

Several reformation strategies were investigated, including steam reforming (SR), partial oxidation (POX), auto thermal reforming (ATR), supercritical water reforming (SCWR), dry reforming (DR), and catalytic dehydrogenation (CDH) [Godat, 2003; Seo, 2002; Gadhe, 2005; Shao, 2005; Shah, 2001]. Each of these has advantages and disadvantages [Corma, 2007]

Among all of the processes, steam reforming is the most common and technically well-proven industrial reformation strategy. Highest hydrogen yield could be expected through steam reformation. In the chemical manufacturing industry, most hydrogen is prepared using steam reforming process [Bellona, 2004]. Steam reforming is an endothermic process that requires heating. The hydrogen produced from steam reforming of methane makes up about 95% of the hydrogen produced in the United States today. In this process, high-temperature steam (700 °C-1000 °C, 3-25 bar) reacts with methane over a heterogeneous catalyst. The primary products are CO and H_2, which are then further reacted using a catalyst to produce carbon dioxide and more hydrogen. This is called the "water-gas shift reaction". In the last step, impurities, such as carbon dioxide, are removed from the gas stream [Wu, 2009; Martavaltzi, 2010].

Partial Oxidation, on the other hand, is an exothermic process. It is typically faster than steam reforming and requires smaller reactor vessels. In this process, a limited amount of oxygen is provided, which is not enough to completely oxidize the hydrocarbons to produce carbon dioxide and water. Instead, hydrogen and carbon monoxide are produced, which is often referred to as synthesis gas. In order to maximize the amount of hydrogen produced, partial oxidation usually includes a water-gas shift (WGS) reaction to generate additional hydrogen from the oxidation of carbon monoxide to carbon dioxide by reaction with water [Heil, 2001; Kim, 2004].

Auto-thermal reforming (ATR) consists of endothermic steam reforming and exothermic partial oxidation to give a close to energy neutral process. It has been recognized as a feasible process for hydrogen production with regard to both hydrogen yield and heat management. Catalysts are critical factors that affect the conversion of the auto thermal reforming process [Youn, 2009].

Supercritical water reforming (SCWR) utilizes water above its critical point as a reaction medium. The supercritical phase combines the desired properties of gas-like diffusivity along with liquid-like heat transfer. Gases are soluble in all proportions in SCW, as are non-polar molecules [Gadhe, 2005]. The reaction happens at high temperature and pressure, which may be attractive to some applications where high pressure hydrogen is needed.

Reactions pertinent to hydrocarbon reforming (Eqn. 2.1-2.2) and the water-gas shift reaction (Eqn. 2.3) may be summarized as follows:

Steam reforming

$C_nH_m + nH_2O \longrightarrow nCO + (n+0.5m)H_2$ endothermic process (Eqn. 2.1)

Partial oxidation

$C_nH_m + 0.5O_2 \longrightarrow nCO + 0.5mH_2$ exothermic process (Eqn. 2.2)

Autothermal reforming

$C_nH_m + nH_2O \longrightarrow nCO + (n+0.5m)H_2$ (Eqn. 2.1)

$C_nH_m + 0.5O_2 \longrightarrow nCO + 0.5mH_2$ (Eqn. 2.2)

All processes include the water-gas shift reaction

$CO + H_2O \leftrightarrow CO_2 + H_2$ (Eqn. 2.3)

Electrolytic processes use electricity to produce hydrogen and oxygen using water in a unit called an electrolyzer. Alkaline electrolyzers, polymer electrolyte membrane (PEM) electrolyzers and solid oxide electrolyzers are the most widely used. Electrolysis using renewable sources of electricity as well as nuclear high-temperature electrolysis produces nearly zero greenhouse gas, which could be potentially very attractive. However, this process is one of the most energy intensive processing methods [Mueller-Langer, 2007; Bellona, 2002]

In photolytic processes, light energy is usually used to produce hydrogen and oxygen from water. This method also provides a promising way for hydrogen production with low environmental impact. Photobiological and photoelectrochemical are two subcategories. Photoelectrochemical processes were first conducted by Fujishima (1972). A cell, which contained an n-TiO2 photo-electrode, a Pt counter electrode, and an electrolytic iron solution, was used. The photobiological process requires specialized photosynthetic, which is an electron-donating substrate, and light as the energy to split water into hydrogen. Ghirardi and co-workers (2009) summarized several processes in this area.

2.2.3 Fischer-Tropsch Fuel Production

More focus has been put into Fischer-Tropsch (FT) fuel production due to the stringency of environmental regulations as well as decreasing fossil fuel reserves. With the development of new technology, the FT process is becoming a potential answer to meet many future energy needs and may significantly reduce the carbon emissions. FT-liquids can be directly sold to the market. Conventional fuels, such as diesel, kerosene and gasoline can be replaced directly [Leckel, 2009]. Historically, Franz Fisher and Hans Tropsch developed the Fischer-Tropsch process in Germany during the 1920s and later the process was commercialized during World War II. Recently many studies of different processes, feedstocks, and catalysts have been undertaken in this area [Casci, 2009].

The Fischer-Tropsch process is an exothermic catalytic chemical reaction. Hydrogen and carbon monoxide are the primary feedstock. Liquid hydrocarbons are formed with various chain lengths. The main reaction and the mechanism are shown in Eqn. 2.4 and Eqn. 2.5 respectively [Schulz, 1999]:

$$nCO + (n + m/2)H_2 \xrightarrow{Catalyst} C_nH_m + nH_2O \qquad \text{(Eqn. 2.4)}$$

$$CO + 2H_2 \rightarrow -CH_2 - + H_2O \qquad \Delta H = -165 kJ/mol \qquad \text{(Eqn. 2.5)}$$

The FT process is normally operated with two temperature ranges: a lower temperature range (180-250 ˚C) and a higher temperature range (300-350 ˚C) and at pressures from 20 to 40 bar. In the low temperature range synthesis process, Co-based catalysts are usually utilized with the production of n-paraffins and n-olefins (wax) [Bouchy, 2009]. In the higher temperature range, Fe-based catalysts are used and produce more gasoline [Kamara, 2009].

No matter what reaction conditions and catalyst are used, the Fischer-Tropsch reaction produces a wide range of aliphatic hydrocarbon chains. The carbon number distribution of the products is commonly described by the Anderson-Schultz-Flory (ASF) model which was developed based on Flory's pioneering studies [Flory, 1936], and later extended by Herington (1946), Friedel (1950) and Henrici-Olive (1976). The basic formula is shown in Eqn. 2.6 and Eqn. 2.7, where W_n stands for the weight percentage of all hydrocarbon products with carbon number n and α is the chain growth probability. α mostly depends on the operating conditions and catalyst. Usually a heavier hydrocarbon weight percentage should be observed with a higher α value. In order to get a high selectivity toward heavy products, the growth probability α should be close to 1 [Schulz 1999].

$$W_n = n\alpha^{n-1}(1-\alpha)^2 \qquad \text{(Eqn. 2.6)}$$

$$\ln(\frac{W_n}{n}) = n\ln\alpha + \ln(\frac{(1-\alpha)^2}{\alpha}) \qquad \text{(Eqn. 2.7)}$$

The FT synthesis processes can use a variety of feedstocks, such as coal, biomass and natural gas and different reaction media, such as gas-phase and liquid-phase. Traditional FT processes have been performed in both reaction media. For the gas-phase FT processes, the syngas feed reacts on the surface of the catalyst. Due to the production of waxes, these processes are used widely. However, it has some drawbacks such as the accumulation of heavy wax in the catalyst pores and overheating on the catalyst surface, which may lead to short catalyst lifetimes and low conversion [Dry, 2002]. FT performed in liquid-phase reaction media has benefits such as greater temperature uniformity. However, liquid phase FT is limited by the mass transfer which leads to relatively large reactor volumes [Anderson, 1984]. Recently, a lot of efforts have been put into the studies of supercritical phase FT processes. Supercritical phase has the characteristics of gas-like transport properties and liquid-like heat capacity and solubility. Elbashir and co-workers (2005) used supercritical hexane as the reaction media, and the IR results indicated that it could provide a well-controlled FT reaction in the supercritical phase.

2.3 Product and Process Design

The concept of process design is the process of assembling knowledge from known routes, such as experimental or literature data, combined with approximation and assumptions to design simulation models for certain processes. It provides ways to search among the feasible options. The designs are expected to be reliable, economically attractive and generated within a limited time frame [Seider, 2004]. Historically, experimental based analysis and approximate approaches were used to develop and design the desired chemical products. A more modern approach to the design and development of chemical products involves computer-aided modeling to simplify the design process by reducing time-consuming experiments.

Conceptual process synthesis and design is becoming an increasingly important field in both industry and in academia. The total cost savings by industrial application of process synthesis range from 20% to 60% during the last several decades [Harmsen, 1999]. There are several reasons for its importance. First is because of the reduced profitability due to increase in global industrial capacity and in the number of total producers. The rising prices of raw material and energy have sustained interest in the development of process synthesis tools as well. Government funding shifted to research that encourages process design [Gadewar, 2004].

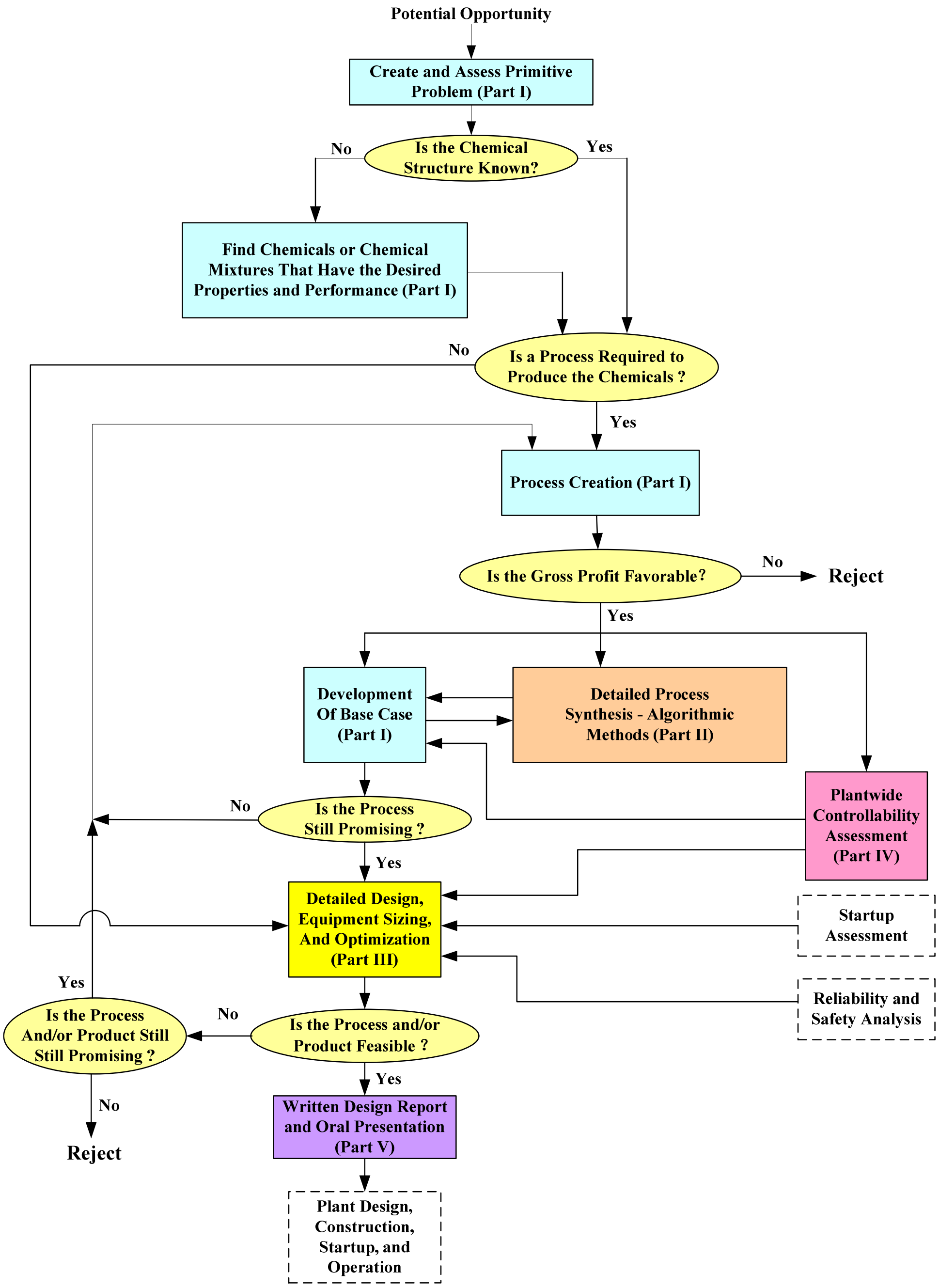


Figure 2.2: Steps in product and process design [Seider, 1999]

Chemical engineers who participate in product and process design usually face different challenges. These challenges include analyzing and selecting the composition of chemical mixtures which can provide the desired properties with low utility costs and easier operations, development of desired products, and the selection of proper operating conditions [Seider, 1999]. Figure 2.2 shows the basic steps in designing chemical products and processes. Beginning with a potential opportunity, the design team creates and assesses an initial model. If necessary, the design team seeks to find chemicals or chemical mixtures that have the desired properties and performance. If the gross profit is favorable, a base case is designed. The steps illustrated above belong to part one in figure 2.2. At the same time, detailed process synthesis based on algorithmic methods is commenced in order to find a better flowsheet. Meanwhile, plant wide controllability assessment is undertaken to eliminate processes that are difficult to control. Then the promising designs are passed down and used as a basic model for detailed design, including equipment sizing and further optimization.

The objective in the product design is to identify the most appropriate chemicals that satisfy the final goal, such as general behavior or characteristics. Moggridge and Cussler (2000) suggested four steps for the design procedure which is shown in figure 2.3:

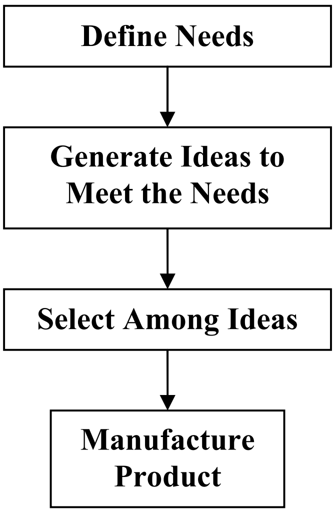


Figure 2.3: Design procedure [Moggridge and Cussler, 2000]

First, we define the needs as a marketing function, which includes customer desires and their requirements. The next step is the generation, production and screening of ideas from human, chemical sources, etc. The ideas are then ranked. The best one or two are selected. The most promising candidates are introduced for the manufacturing step. The products which have the required quality are then tested as prototypes before final production.

Process synthesis reviews are readily available in the open literature. Early work on construction design processes reflects decisions that led to state-of-the-art continuous processes. The rule-based hierarchies, developed by Siirola (1996) and Douglas (1988), can be divided into five main decision levels:

- Batch vs. continuous
- Input-output structure of the flowsheet
- Reactor and recycle structure of the flowsheet
- Separation system synthesis
- Heat recovery network

In the hierarchical decomposition method developed by Douglas (1988) one only looks at the input-output structure of the process at the first level. In subsequent levels more detail is added, finally ending with the entire flowsheet. Later, Biegler (1997), Harmsen (1999) and Seider (2004) further developed the method based on the fundamental work by Douglas et al (1988). Biegler et al. (1997) lists the basic steps in flowsheet/process synthesis as: (1) gathering information, (2) representation of alternatives, (3) assessment of preliminary design, and (4) the generation and search among alternatives.

2.3.1 Conceptual Process Design Approaches

Based on the structure, the various approaches can be organized as: 1) structure-independent methods, which solve the synthesis problem by breaking it down into multiple stages to reduce the dimensionality of the problem. Within each stage, the design targets are identified and used in the following stage; 2) structure based methods, which include the structure of the process as well as all the design and operating parameters for each piece of equipment as part of its formulation; therefore, the superstructure encompasses many redundant paths and equipment alternatives for achieving the design objectives. Both methods follow the basic steps of process synthesis and design which are summarized by Biegler and co-workers (1997).

The methods which try to address the problems outlined and design the desired products can also be further divided into three groups: conceptual process design by function-integration design; conceptual process design by heuristic selection of unit operations and recycle structure; and conceptual design by superstructure optimization. The principal difference among these is that the optimization-based and heuristic methods solve problems by generating and searching flowsheet structures, while the others focus on the representation of physical knowledge of the system [Grossmann, 1996].

2.3.1.1 Conceptual Process Design by Heuristic Selection of Unit Operations and Recycle Structure

The sequence and structure of heuristic methods for the selection of the best designs are based on the long-term experience of engineers and researchers [Douglas, 1988]. These methods are usually used for industrial process synthesis problems, which only solve the constraint equations of the optimization problem and develop feasible but not necessarily optimal solutions. The search space is reduced by analyzing the problem and fixing many of the discrete variables. Heuristics are developed as a tool to aid in deciding which decisions should be made and how. There are advantages and disadvantages of these methods. Without heuristics, design problems are usually too difficult and too large to converge. However, it is not guaranteed that the optimal solution is generated [Westerberg, 2004]. When and only when the problem that needs to be solved is related closely to the types of problems that have been solved, the approaches become useful [El-Halwagi, 1997]. Shortcut calculations are carried out at every stage of process design based on economic criteria. A representative example of the heuristic search approach is the hierarchical decomposition method by Douglas [Douglas, 1985; 1988; 1990]. The major advantage of this method is that it allows for the quick identification of flowsheet structures that are often close to optimal solutions so that a large problem can be solved more efficiently. However, heuristic methods cannot communicate well between different design levels [Westerberg, 2004].

2.3.1.2 Conceptual Process Design by Superstructure Optimization

Superstructure optimization, which is also referred to as the optimization-based approach, is the combination of stochastic algorithmic methods, e.g. genetic algorithms (GA) with traditional methods, e.g. mixed-integer non-linear programming (MINLP) [Grossmann, 1985]. This method was described by Seider (2004), Biegler (1997) and Floudas (1995). It solves the entire optimization problem including the objective function. Depending on the complexity of problems, a globally optimum solution cannot be guaranteed using current solvers. Using these methods, a process structure is first developed, which combines all potentially useful unit operations and relevant interconnections. Then, a mathematical model including unit models and a group of equations, such as interconnection equations, is derived into an optimization problem. There are two common characteristics, including the subsequent use of optimization as well as mathematical representations. The advantage of the optimization-based approach lies in modeling and simultaneous optimization. It shows a systematic framework, and for synthesis problems, it provides automated capabilities. That is to say, it generates a superstructure that contains all potentially profitable alternatives. The weaknesses of this approach lie in the fact that it cannot automatically form the superstructures of a flowsheet and there are difficulties in solving large-scale problems. Sometimes it also has the possibility of getting trapped into poor suboptimal solutions [Subramanian, 2001; Bagirov, 2003].

2.3.1.3 Conceptual Process Design by Function Integration Design

The function integration design method could be illustrated as follows: Define objective functions and then integrate these functions into a process design containing novel process units [Harmsen, 2004]. The process is illustrated by functions and combinations of functions. Many case studies can be found in the open literature. Siirola (1996) described a design example of a methyl acetate process using this method and Stankiewicz (2000) also introduced several industrial examples. It utilizes heuristics, thermodynamic insights and/or other qualitative process knowledge to impose bounds on the optimization variables.

The process is designed by functions and also defined by combinations of functions. That enhances creativity and the number of attractive alternative processes are increased. Functions that are operated under the same conditions can be combined into one. The capital expenditure and energy losses are often reduced [Harmsen, 2004].

2.3.2 The Combination of Experimentation and Mathematical Models in Product and Process Design

Mathematical modeling, simulation, and optimization are important in understanding, explaining, and exploiting the behavior of large and complex dynamic systems. Usually it is desirable in the modeling area to replace as much as possible the experiment-based tasks, which normally are expensive and time-consuming. However, accurate experimental data are crucial for the evaluation/accuracy of mathematical models. A smart combination of experiment-based and model-based approaches may be a better alternative in chemical product-process design. The use of mathematical models can easily overcome the limitations of time and resources which prevent the experimental exploration of all of the potentially feasible solutions for a certain process, and the necessary experimental data could further improve the mathematical model. The integration of laboratory experimentation with mathematical modeling can be mutually beneficial.

2.4 Process Integration

Process integration is a holistic approach to process design. It is one of the most important means for improving process efficiency, reducing environmental impact and increasing economic feasibility. Before defining the details of the process, the entire chemical process is addressed with the consideration of the interactions between unit operations from the outset, instead of simulating and optimizing separately [Smith, 2005; El-Halwagi, 1997]. Integration requires the ability to translate the objectives in terms of engineering parameters. For example, the objective of maximizing profit can be defined as minimizing raw material usage. The global performance targets need to be identified before any development activity. The optimal strategy to reach the targets also needs to be defined [Srinivas, 1997]. It is necessary to find and evaluate the maximum performance targets before creating the design to obtain understanding about potential opportunities. Process integration techniques could improve process design, increase process productivity, reduce mass and energy resources usage, and save expenses in the operating and capital costs.

There are two main fields of process integration: energy integration and mass integration. Energy integration aims at heat recovery within a process through system-level optimization of heat, power, fuel and utilities. It can also identify the optimal system configuration for the minimal energy consumption [Linnhoff, 1982; 1983]. Mass integration techniques provide means of identifying optimum performance targets by generating and selecting among alternatives for allocating the flow of material (species) in the process [El-Halwagi, 1989;1997].

2.4.1 Energy Integration

Energy integration has become more and more attractive due to significant increases in cost of energy. Integration between processes can reduce energy usage and emissions, saving expenses. One of the most important pieces of equipment used in energy integration is the heat exchanger. A heat exchanger exchanges heat from a hot process stream to a cold process stream. Using the system energy, the hot streams could be cooled down to desired temperature utilizing the energy capacity of the cold streams. Meanwhile, the cold streams could be heated to the desired level. The target of energy integration is to recover maximum system energy while minimizing the external utility usage. An heat exchanger network (HEN) is usually designed in a process plant to achieve the integration target. To design the best heat exchanger network, the total cost is minimized. It is then translated into an optimization problem that needs a cost-effective approach. The total cost mainly consists of two parts: the exchanger units and the utilities.

Identifying the heat exchange area, the unit cost and annual consumption are the key factors to solving the cost objective functions. The studies of process integration using HEN began with Masso and Rudd (1969). They first defined the heat exchanger network design problem in a rigorous manner. The minimization of the total cost for designing an optimum heat exchanger network was proposed.

The basic heat exchanger network synthesis (HENS) problem can be formulated as follows, given:

- A set of hot process streams which need to be cooled
- A set of cold process streams which need to be heated
- The heat capacities for each of the streams with the temperature changes as they pass through the heat exchange process
- The available utilities, their temperatures, and their costs per unit of heat provided or removed

Determine the heat exchanger network for energy recovery that will minimize the annualized cost of the equipment plus the annual cost of utilities [Biegler, 1997].

To solve HEN optimization problems, El-Halwagi (1997) presented the solution of synthesizing an optimal HEN as identification of the answers to the following questions:

- Which heating/cooling utilities should be used, if any?
- What is the optimal heat load removed or added by these utilities?
- How should the hot and cold process streams be matched?
- What is the optimal system configuration in terms of arrangement, stream splitting, and stream mixing?

By answering these questions, the cost objective functions could be solved.

There are two main areas to solve the energy integration problems: sequential synthesis methods and simultaneous synthesis methods.

2.4.1.1 Sequential synthesis methods

For the sequential synthesis method, the HEN problem is divided into subproblems. In this way, the entire problems could be simplified by reducing the computational requirements. The laws of thermodynamics should be used as rules throughout the simplification process. The optimal or near optimal process network has the following characteristics:

- Minimum utility cost
- Minimum number of units
- Minimum investment cost

It is possible to have conflicts among these characteristics. Therefore, assumptions should be made: the problems should be solved base on the heuristic of identifying the minimum number of units, subject to the minimum utilities cost [Biegler, 1997].

Sequential synthesis methods can be further divided into two subcategories:

(1) evolutionary design methods: such as pseudo-pinch methods and pinch design methods [Linnhoff, 1983; 1990; 1993; Trivedi, 1989]

(2) mathematical programming techniques [Floudas, 1986; 1990]

The pinch method is an innovative development in process design [Linnhoff, 1983]. The first and second laws of thermodynamics are used as the fundamentals to solve the HEN problems. The main objective is to save expenses by maximizing process to process heat recovery and reducing the external utility usage. A minimum temperature difference should be given first. Then, the design targets are set in terms of minimum utility consumption, minimum number of units and minimum area and cost. Three steady state parameters should be defined, including hot and cold source temperature T_s, target temperature T_t and heat capacity flowrate HCp.

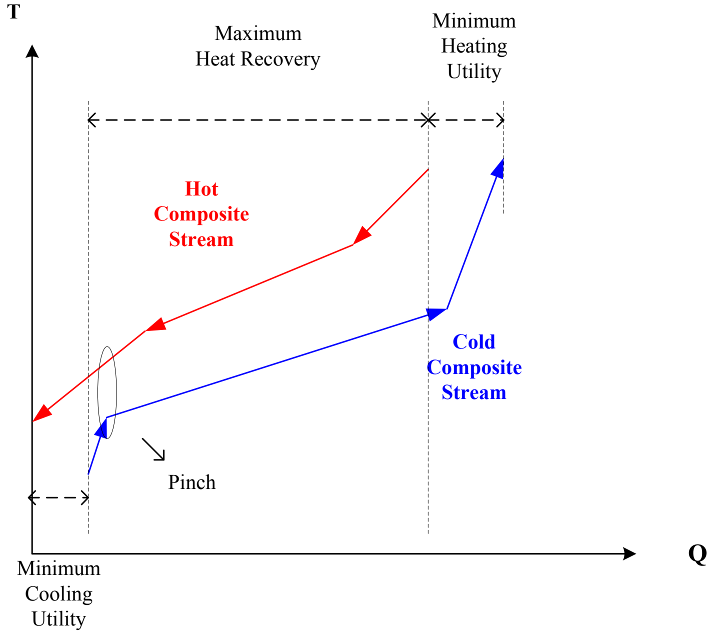


Figure 2.4: Thermal pinch diagram - maximum heat integration [El-Halwagi, 1997]

Usually a grid diagram is used to present the HEN as shown in figure 2.4. First, the process streams are sorted into hot and cold streams. Then, all the hot and cold streams are combined individually to construct the composite curves, which are used to determine the minimum energy consumption target for a given process. As shown in figure 2.4, all of the hot streams are combined to generate the Hot Composite Curve and all the cold streams are combined to give the Cold Composite Curve, which are generated by summing up the parameters of heat capacity of all streams of the same kind (hot or cold) within each temperature interval. The temperature interval is defined as the temperature difference of the inlet and outlet streams. Each temperature interval transfers heat from the hot streams to the cold streams, provides heat to the cold streams and passes on a heat residual to the next temperature interval.

After the hot and cold composite curves are generated, the lowest heat supply and heat demand for the process could be calculated. The hot composite streams and cold composite streams are represented as straight lines as shown in figure 2.4. Then, the curves are moved from left to right and from right to left, respectively. The relative position of the hot and cold composite curves could be identified by the minimum temperature differences, which should be defined ahead of time. When the two curves are drawn together to achieve the minimum temperature difference, the pinch point is obtained and the minimum energy usage could be measured. The HEN can be designed above the pinch and below the pinch separately. The pinch point divides the diagram into two regions, which are thermodynamically separated. Different sources of energy are needed below and above the pinch point: cooling utility and heating utility, respectively. If heating is provided below the pinch point, the amount of cooling requirement will be increased, while the objective of minimum utility cost and minimum external utility usage could not be achieved. Similarly, no cooling utility is needed above the pinch point in order to achieve the objective function [Seider, 2004].

When solving a HEN problem, three rules need to be followed [Linnhoff, 1983]:

- Do not transfer heat across the pinch.

- Do not use external cooling utilities above the pinch.
- Do not use external heating utilities below the pinch.

The second parts of sequential synthesis approaches are mathematical programming techniques. The sequential solution of continuous, integer linear programs and nonlinear optimization problems are the fundamentals of these methods [Papoulias, 1983; Cerda, 1983; Floudas, 1986]. The HEN synthesis problem is sequentially decomposed. The solutions of previous objective functions are usually used as parameters in the next step. Similar to the other methods, the basic subproblems also include minimum utility cost, minimum number of units and minimum investment cost. There are several disadvantages of the mathematical programming problems. Suboptimal solutions may exist and it is not as easy to implement as the pinch analysis method. An important character of pinch analysis is that prior to detailed design, the performance targets for utility consumption could be set for any processes. However, the heat transfer coefficients and heat exchanger area are not considered properly. In addition, the composite curves are assumed to be straight lines; thus the heat capacity flow rate needs to be constant over the entire temperature range.

In summary, the sequential targeting and optimization approach has the advantage of decomposing the synthesis problem. The problem is made more manageable by solving a sequence of smaller problems. However, it has the disadvantage that the trade-offs between energy, number of units and area are not rigorously taken into account. Meanwhile, it does not guarantee the design of a network with the minimum annual cost [Biegler, 1997].

2.4.1.2 Simultaneous synthesis methods

The goal of simultaneous HEN synthesis is to find the optimal network without decomposition of the problem. Simultaneous synthesis methods are primarily MINLP formulations of the HEN synthesis problem subject to various simplifying assumptions used to facilitate the solution of these complex models. One of the earliest simultaneous HEN synthesis formulations was proposed by Yuan (1989). Later, Yee (1990) and Ciric (1991) proposed more detailed HEN synthesis formulations.

Floudas (1990) developed a simultaneous match network hyperstructure model to optimize all of the capital costs of a HEN. The proposed approach for solving HEN synthesis problems includes four basic steps as shown in figure 2.5. First, one decides to construct the problem as a pinch point synthesis problem or as a pseudo-pinch synthesis problem. If it is selected as a pinch point synthesis problem, the problem should be divided into two independent sub networks strictly. The pseudo-pinch problem means the heat is allowed to flow across the pinch point. Therefore, if it is chosen as a pseudo-pinch synthesis problem, the problem must be solved as a single network. Then, the utility consumption levels are designed. For pseudo-pinch design, the utility consumption levels are measured as independent variables. For strict-pinch design problems, the utility consumption levels are treated as functions. Next, the information on the utility consumption levels is combined to formulate MINLP problems, which contain all potential network configurations. Finally, the resulting MINLP problem is solved utilizing the Generalized Benders Decomposition proposed by Geoffrion (1972), to provide an optimal HEN in the fourth and final step.

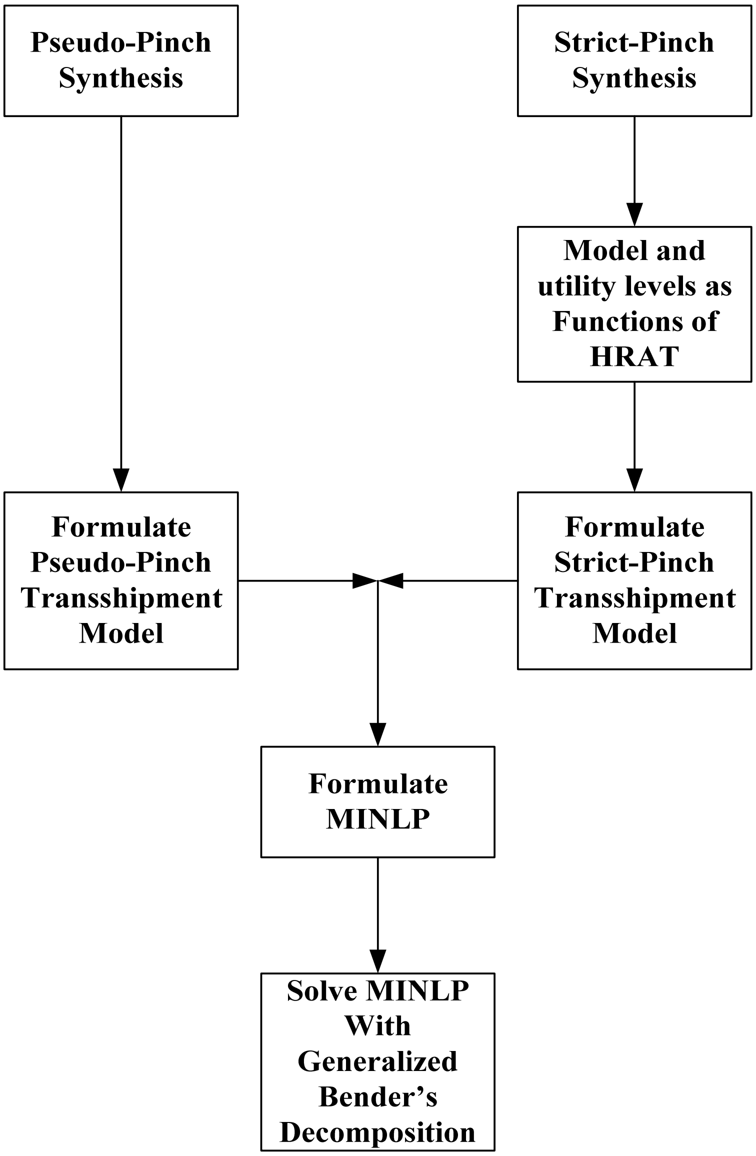


Figure 2.5: Outline of simultaneous match network procedure [Ciric, 1991]

One important aspect of simultaneous optimization methods is that they do not rely on heuristics. The advantage of the simultaneous approach is that the trade-offs are all taken simultaneously into account, so the possibility of finding improved solutions are increased. However, the computational requirements and time are greatly increased.

2.4.2 Mass Integration

Mass integration is a holistic, systematic approach which could provide a fundamental understanding of global flow of mass throughout the process. It illustrates a comprehensive methodology for targeting yields, emissions, and capacities, as well as designing reaction, separation, and waste-processing systems [El-Halwagi, 1998]. The concept of Mass Exchanger Networks (MENs) was first introduced by El-Halwagi and Manousiouthakis (1989, 1988) on a continuous model, where they pointed out that mass exchangers use mass-separating agents (MSAs) to transfer material from solute-rich streams to solute-lean streams. In order to synthesize a cost-effective MEN, a mixed-integer linear programming method is used. The objective is to recover waste chemical species to the maximum extent possible with the lowest possible cost. Figure 2.6 is a general representation of the MEN synthesis problem. A MEN consists of a number of mass exchangers. The mass exchangers transfer mass of certain species among process streams. In general, it is assumed that the equipment used in the MEN employs countercurrent flow of the rich and lean streams. This is similar to the assumption of the use of countercurrent flow heat exchangers in HENs.

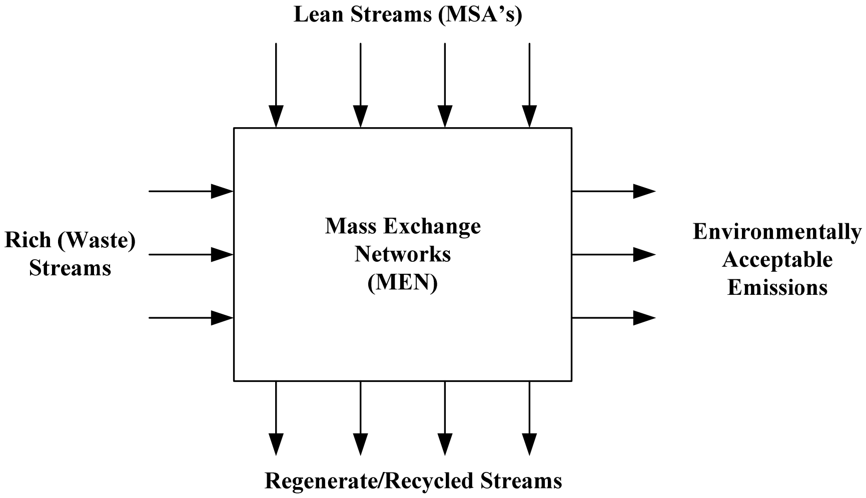


Figure 2.6: Mass exchange network (MEN) synthesis [El-Halwagi, 1989]

The general MEN synthesis problem is stated as follows, given:

- A set of rich process streams;
- A set of lean process streams;
- A set of external lean external streams

Synthesize a network of mass exchanger units that can transfer a set of certain species from the rich streams to the lean streams at minimum cost.

Major goals in the development of a MEN are to find and minimize the need for MSAs [Seider, 2004]. The solutions are usually based on design targets like minimum cost of MSAs and minimum number of mass exchanger units. El-Halwagi and coworkers (1989, 1988) proposed a systematic, two-stage procedure for the synthesis of cost-effective MENs:

- Generation of preliminary networks: the pinch points are identified using a thermodynamically-oriented procedure based on maximizing mass exchange.
- Development of the final configuration: the preliminary networks are defined. The MEN meets the assigned exchange duty based on the minimum cost.

El-Halwagi and Maniousionthakis (1989) developed a mass pinch method for the design of MENs. Similar to thermal pinch analysis in the above section, the rich and lean process streams can be combined into composite curves. Then, mass pinch analysis could be performed similar to the heat pinch analysis, which is introduced and extended by Linnhoff (1983) and others. Figure 2.7 shows a mass pinch diagram. The red line represents the lean composite stream that combines all the lean streams. The blue line represents the rich composite stream that contains all the rich steam information. The two composite curves are moved towards each other when mass is transferred from a rich stream to a lean stream until reaching the pinch point. The pinch point is defined as the minimum composition deference. It can be identified by moving the lean composite curve down vertically until it meets the rich composite line. If the lean process stream is to the left of the rich that means that mass can be exchanged between the two streams.

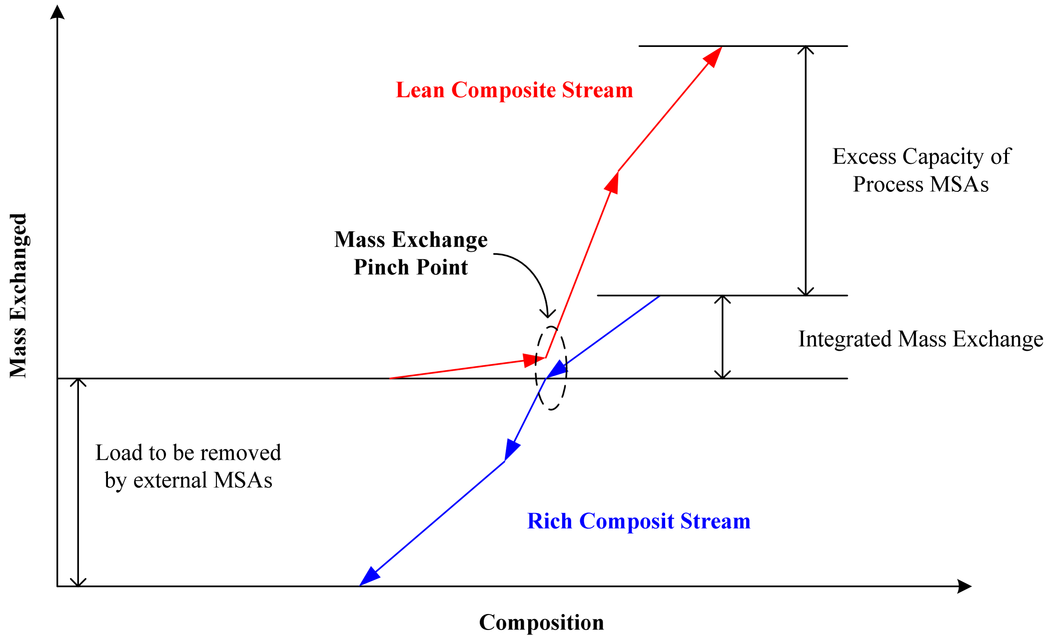


Figure 2.7: Mass pinch diagram [El-Halwagi, 1998]

From the diagram, the excess capacity of the internal process streams can be calculated. No external MSAs should be used above the pinch. The load should be removed by external MSAs and could also be measured. The integrated mass exchange gap in between represents the maximum amount of mass that can be exchanged internally.

The target compositions of streams may need to be controlled with different degrees of precision. Consequently, the MEN synthesis should strive to attain not only the minimum total cost, but also the superior control performance.

2.5 Environmental Impact Assessment

2.5.1 Environmental Protection

Global scale environmental problems have attracted more and more attention and efforts since the late 1970s. The Environmental Protection Agency (EPA) and the U.S. Congress cooperated to focus on the environmental protection. It is becoming a primary issue throughout the manufacturing and transportation sectors all over the world. Due to the stringent regulations, the manufacturing costs of the end products have increased to satisfy requirements of environmental protection.

A pollution minimization methodology, which is called the Waste Reduction (WAR) algorithm, was developed to evaluate the environmental impact for chemical processes [Young, 1999]. It is based on measuring the mass flows that are entering and leaving both the chemical process and the corresponding processes that provide energy with normalized scores.

2.5.2 Waste Reduction Algorithm

The advantages of pollution prevention to minimize waste production lie on better utilization of raw materials, energy, and reduced waste treatment and disposal costs [Mallick, 1996]. El-Halwagi and Manousiouthakis (1989) were the first to introduce pollution prevention techniques into process design. They implemented the idea of mass exchange networks (MENs). The principle is to concentrate pollutants in desired waste streams by removing them from other streams. However, there are some limitations, such as it failed to calculate the impact of the pollution generated within a process [Young, 1999]. To fill this gap, a potential environmental impact (PEI) balance as an amendment to the Waste Reduction (WAR) algorithm was developed by Hilaly (1994) and later refined by Mallick (1996). Cano-Ruiz and McRae (1998) provided a comprehensive review of the different techniques used to incorporate environmental considerations into process design. All of the procedures above simply included the chemical process. Based on Cabezas's work (1997), Young (1999) made an improvement of the WAR algorithm which includes the energy generation process into the balance.

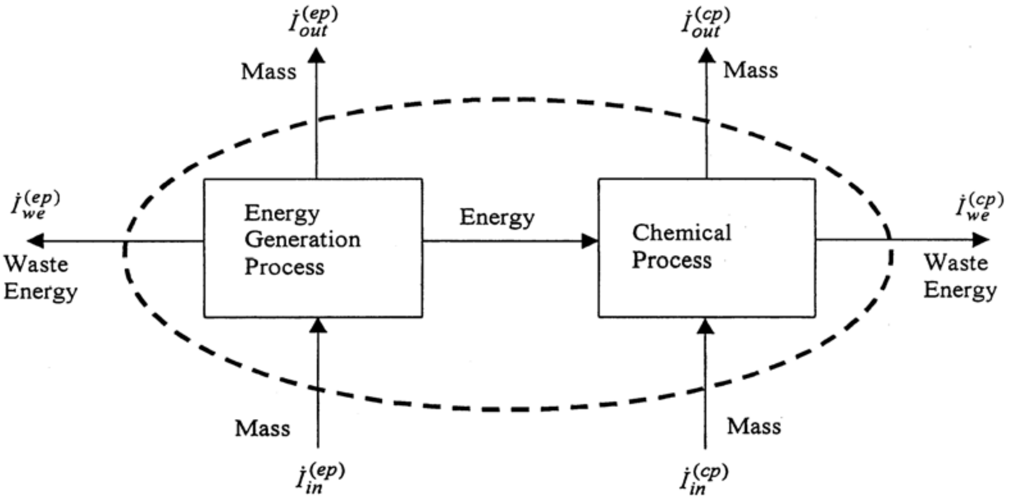


Figure 2.8: Potential environmental impact (PEI) for a given system [Young, 1999]

The WAR algorithm is a methodology used to evaluate the relative environmental impact of a chemical process. It only takes into account the manufacturing aspect of the product's life cycle. Figure 2.8 shows the overall mass and energy balance around a chemical process. The dashed line represents the system boundary. Both the chemical process and the energy generation process are taken into account to measure the potential environmental impact (PEI). It can either enter the system, exit the system, or even be generated and accumulate within the system. The PEI balance for a process and energy generation system can be formulated as [Young, 1999]:

$$\frac{\partial \dot{I}_{system}}{\partial t} = \dot{I}_{in}^{(cp)} + \dot{I}_{in}^{(ep)} - \dot{I}_{out}^{(cp)} - \dot{I}_{out}^{(ep)} - \dot{I}_{we}^{(cp)} - \dot{I}_{we}^{(ep)} + \dot{I}_{gen}^{(t)} \qquad \text{(Eqn. 2.8)}$$

where, $\dot{I}_{system}$ is the PEI for both the chemical process and the energy generation process, $\dot{I}_{in}^{(cp)}$ and $\dot{I}_{out}^{(cp)}$ are the PEI input and output rates for the chemical process, $\dot{I}_{in}^{(ep)}$ and $\dot{I}_{out}^{(ep)}$ are the PEI input and output rates for the energy generation process, $\dot{I}_{we}^{(cp)}$ and $\dot{I}_{we}^{(ep)}$ are the outputs of PEI related to waste energy lost from the chemical process and energy generation process. $\dot{I}_{gen}^{(t)}$ is the rate of generation of PEI inside the system [Young, 1999].

For steady state processes, equation 2.8 can be simplified as follows [Young, 1999]:

$$0 = \dot{I}_{in}^{(t)} - \dot{I}_{out}^{(t)} + \dot{I}_{gen}^{(t)} \qquad \text{(Eqn. 2.9)}$$

There are eight categories of environmental impacts for each process [Young, 2000].

- Human toxicity potential by ingestion (HTPI)
- Human toxicity potential by exposure both dermal and inhalation (HTPE)
- Terrestrial toxicity potential (TTP)
- Aquatic toxicity potential (ATP),
- Global warming potential (GWP)
- Ozone depletion potential (ODP)
- Photochemical oxidation potential (PCOP)
- Acidification potential (AP)

Based on these eight categories, each potential environmental impact index $I^{(t)}$ can be calculated individually as follows [Young, 1999]:

$$I^{(t)} = \sum_{i}^{EnvCat} \alpha_i I_i^{(t)} = \sum_{i}^{EnvCat} \alpha_i \sum_{j}^{Streams} M_j \sum_{k}^{Comps} x_{kj} \psi_{ki}^{s} \qquad \text{(Eqn. 2.10)}$$

Where $I_i^{(t)}$ is the PEI index for category i, α is the weighting factor associated with potential environmental impact category i, M_j is the mass flow rate of stream j, x_{kj} is the mass fraction of component k in stream j, and ψ_{ki}^{s} is the specific potential environmental impact of component k associated with environmental impact category i, which is calculated using a normalization scheme [Young, 2000]. The individual weighting for each of the categories can be changed, depending on the emphasis.

2.6 Economics Analysis

2.6.1 Capital Investment

When making a cost analysis to measure capital investment, different categories of costs should be included, such as fixed costs, raw material costs, utilities and other miscellaneous items. These costs constitute the two main contributions to capital investment: Fixed Capital Investment and Working Capital.

The fixed capital investment stands for the capital that is related to complete all process operation, such as equipment installation. It is sorted as the nonmanufacturing fixed capital investment, which include components that are not directly related to process operation. The land, transportation, utilities and other permanent parts all belong to the plant components. The working capital investment stands for the total amount of expenses related to raw materials, products, monthly operating payment and so on.

2.6.2 Approximation of Capital Investment

The estimation of the capital investment is performed by using “Lang” factors, which were proposed originally by Lang [Peters, 2003]. The idea of this method is that the cost of a process plant may be obtained by multiplying the basic equipment cost by some factor to approximate the capital investment. The factors are given in Table 2.1. It should be noted that these factors include costs for land and contractor's fees.

Table 2.1: Lang Multiplication Factors for Estimation of Investment.
(Factor ×delivered-equipment cost = fixed-capital investment or total capital investment for major additions to and existing plant). [Peters, 2003].

Type of plant	Factor for	
	Fixed-capital investment	Total capital investment
Solid-processing plant	3.9	4.6
Solid-fluid-processing plant	4.1	4.9
Fluid-processing plant	4.8	5.7

In order to have a more accurate estimation, an improved method can be used by using a number of factors instead of just one factor.

2.6.3 Total Production Cost

The total product cost consists of total plant operating cost, selling the products, recovering the capital investment, and contributing to corporate functions. Determination of the necessary capital investment is only one part of the complete cost estimation. Another equally important part is the estimation of costs for operating the plant and selling products. These costs can be divided into two parts: manufacturing costs and general expenses [Peters, 2003]. Figure 2.9 shows the costs involved in total product cost for a typical chemical process plant.

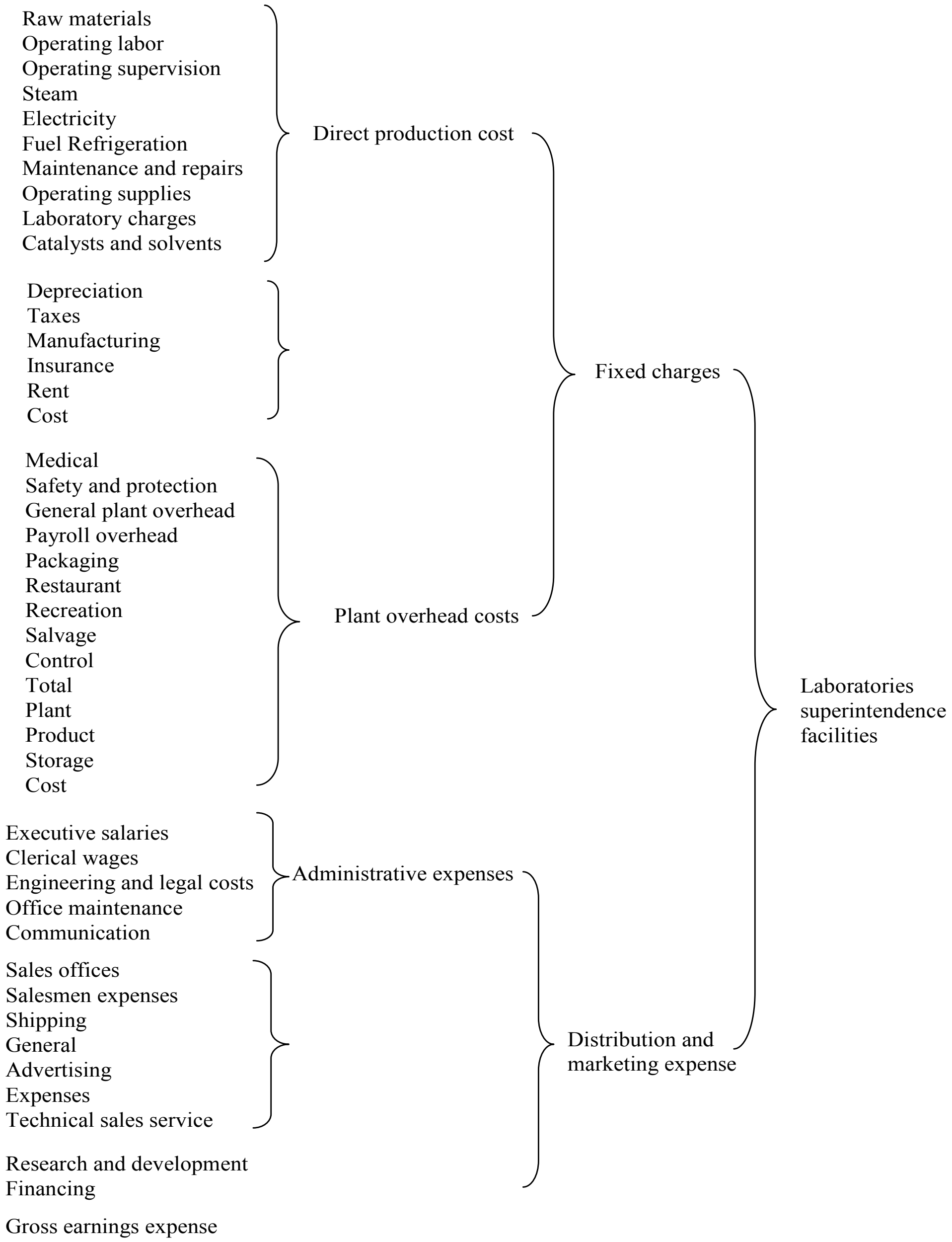


Figure 2.9: Costs involved in total product cost for a typical chemical process plant [Peters, 2003].

Chapter 3 Methodology

3.1 Introduction and Background

The objective of this study is to develop a methodology for integrating experimental and literature data with process simulation and optimization techniques, under the principles of process design to optimize the overall performance of novel fuel production through polygeneration facilities. In order to achieve pre-defined objectives which are subject to physical and/or practical constraints, process pathway design and mathematical optimization are necessary. Integration techniques such as heat and mass integration are introduced to maximize the usage of natural resources and minimize energy consumption. Economic evaluation must be taken into consideration in order to measure the profitability and added value that these possible polygeneration plants will impart to any given product portfolio. The evaluation of overall performance is not only limited to economic considerations, but also takes into account the potential environmental impact. While profitability is indeed critical for a chemical facility to sustain operation, the environmental impact must also be estimated for each possible fuel production design.

This methodology is illustrated by several case studies. A variety of hydrogen production schemes including traditional and novel processes are simulated and compared. Fischer-Tropsch fuel production through different processes such as gas-phase and supercritical phase are also investigated.

Polygeneration facilities have many advantages over conventional single production chemical plants and will result in lower capital costs and lower product/energy costs in comparison to construction and operation of separate facilities. It can provide alternatives for solving the increasing global problems of fossil fuel shortage and greenhouse gas emissions by utilizing conventional and renewable resources through multiple production processes to produce various alternative fuels that can replace gasoline and diesel. Meanwhile, it also enhances energy conversion and utilization [Gamou, 2002].

Figure 3.1 shows an example of a polygeneration plant. The goal of a polygeneration plant is to select the most profitable pathway among many possible alternatives. The feedstocks in this system include multiple carbon sources, such as biomass, coal, natural gas and so on. The detailed classification of these primary energy feedstocks is not under consideration. The various carbon sources are processed through different production routes as shown in the blue rectangles, which may include more than one subprocess, through chemical and biochemical processes, combustion, gasification, liquefaction and so on. The yellow diamonds represent the products which are in the form of tangibles, such as liquid fuels and chemicals, or intangibles, such as electricity and heat. The products can be sold externally to the market or used internally by the other production routes in the system as raw material to be processed further to other products.

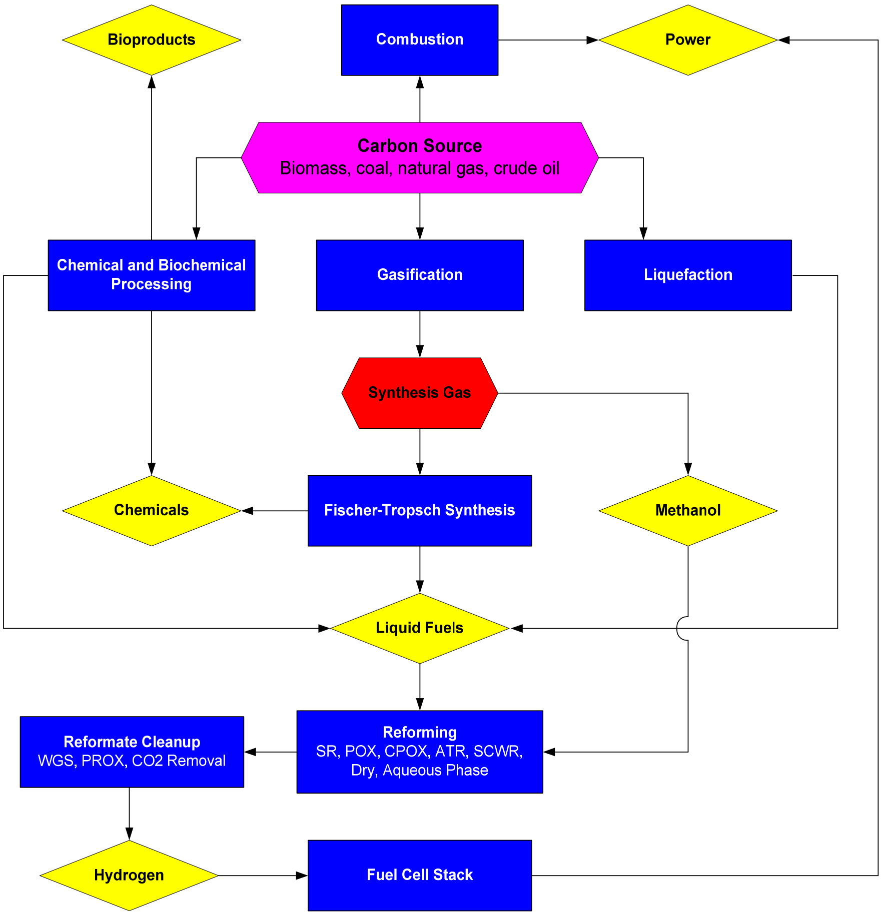


Figure 3.1: Visualization of a polygeneration plant [Yuan, 2008]

The main focus of a polygeneration plant is to produce the desired (primary) product, while increasing the profitability of the overall plant by manufacturing other valuable co-products. Although many of the fundamental processing steps involved in polygeneration are well-known, a methodology is still needed to evaluate the integrated processes to ensure optimal utilization of raw material and energy. Polygeneration plants possess tremendous integration potential, for recycling unused material as well as in terms of energy recovery.

The production of alternative fuels such as hydrogen and Fischer-Tropsch fuels is becoming more and more attractive due to stringent environmental regulations, technological developments and changes in fossil energy reserves. A methodology is needed to help determine the best fuel production scenario that provides maximum profitability in an environmentally friendly way.

3.2 Solution Methodology

A systematic optimization framework has been developed to determine the optimal production schemes for different plants based on the economic performance [Sammons, 2007]. The simulation models for each process are developed based on the information provided by the chemical processes, such as conversion, energy usage from both experimental and literature data. Process integration techniques are then used to optimize the simulation models. Finally, the economic and environmental performance metrics are generated using the optimized models. The Waste Reduction (WAR) algorithm is used for the environmental impact measurement step [Young, 2000].

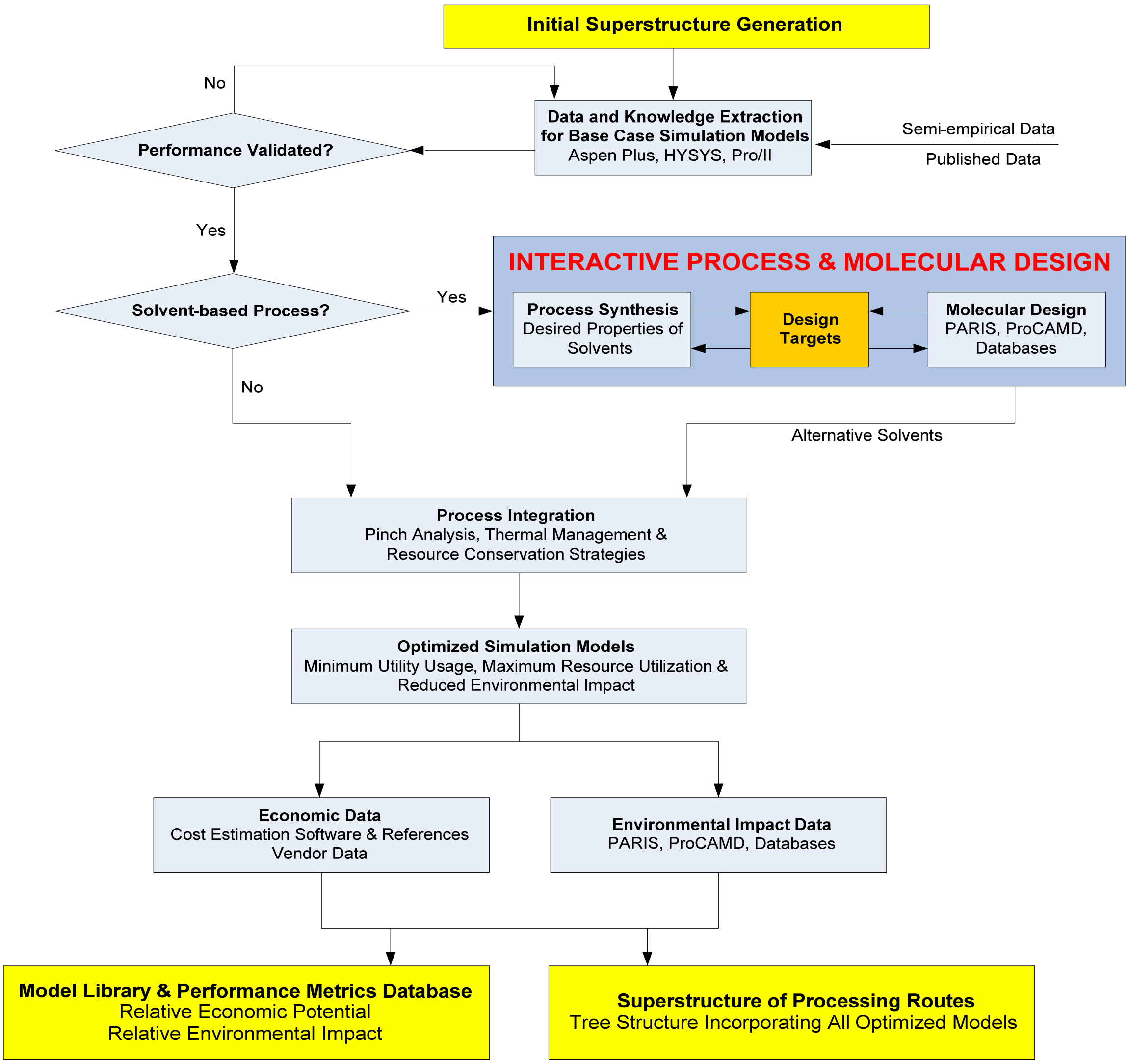


Figure 3.2: Strategy for identification of performance metrics [Sammons, 2007]

Figure 3.2 shows the methodology proposed by Sammons (2007) for process development and decision making. In the first step, the primary feedstocks are selected and a superstructure of all the feasible possibilities and production technologies for the chosen feedstocks is generated based on extracting knowledge on process conversion and energy usage from literature and experimental data. One can start from given feedstocks or types of feedstocks to determine what products could be made, or conversely, for certain desired products determine pathways that can be used to manufacture the products. At this point, it is necessary to do the capacity expansion planning, which includes the estimation of when to expand, which technologies to use, and exactly how much should be produced. At this stage it is also necessary to do the production planning, which includes the estimation of how much energy the selected technologies require.

If the given process is solvent-based, computer-aided molecular design techniques (CAMD) and property clustering techniques could be used to design alternative solvents, which perform the same function, but are safer and more environmentally friendly. At the end of this step, basic simulation models are constructed.

In the second step, process integration techniques are utilized to integrate the simulation model. Thermal pinch methods are usually applied to analyze the energy saving potential for each process. Mass exchange networks are generated at the same time, if necessary, to reduce the mass usage. During the process integration procedure, we look at mass and energy flows that are coming in and out of the system. This is the central part of the framework to ensure optimal utilization of materials and energy resources.

In the third step, integrated simulation models are then used to generate the performance metrics; here we refer to economic performance and environmental performance metrics. In the process optimization step, the financial and environmental objectives are evaluated. Both factors are critical in determining which polygeneration pathways should be pursued in order to add value while maintaining a minimal level of environmental impact. By integrating environmental impact analysis into the standard design, the design engineer can ensure that the resulting process is not only optimized in terms of overall performance but also based on minimizing the environmental impact of the process as well.

Only the economic and environmental performance metrics are incorporated in the solution framework; thus the complex models could be simplified from the decision making process. This approach has the advantage of continuously updating the results. The selection methodology is not needed to be reformulated to generate new data. Similarly, additional metrics can be introduced into the framework if new processes are added. The end result is a superstructure of all the possible processing routes, a library of simulation models for those routes, and a database of economic and environmental metrics for the simulation models.

3.3 Process Optimization Framework

An optimization framework is given in figure 3.3. This framework uses a numerical solver to optimize the solution networks. This is the central part of the solution framework to efficiently solve the problems. The objective of the optimization step is to identify candidate solutions that maximize economic performance, and then the candidates are ranked according to environmental performance. If a candidate satisfies the environmental objectives, the optimal production strategies have been identified. If there are no candidates who satisfy the environmental impact constraints, then the desired economic performance requirements are relaxed until a solution with acceptable environmental performance has been identified.

A novel solution methodology for process structure optimization is presented in Chapter 5. A Disjunctive-Genetic Programming (D-GP), based on the integration of Genetic Algorithm (GA) with the disjunctive formulations of the Generalised Disjunctive Programming (GDP) for the optimization of process networks, is proposed to solve the optimization framework. This approach provides a more efficient technique in solving the chemical process networks.

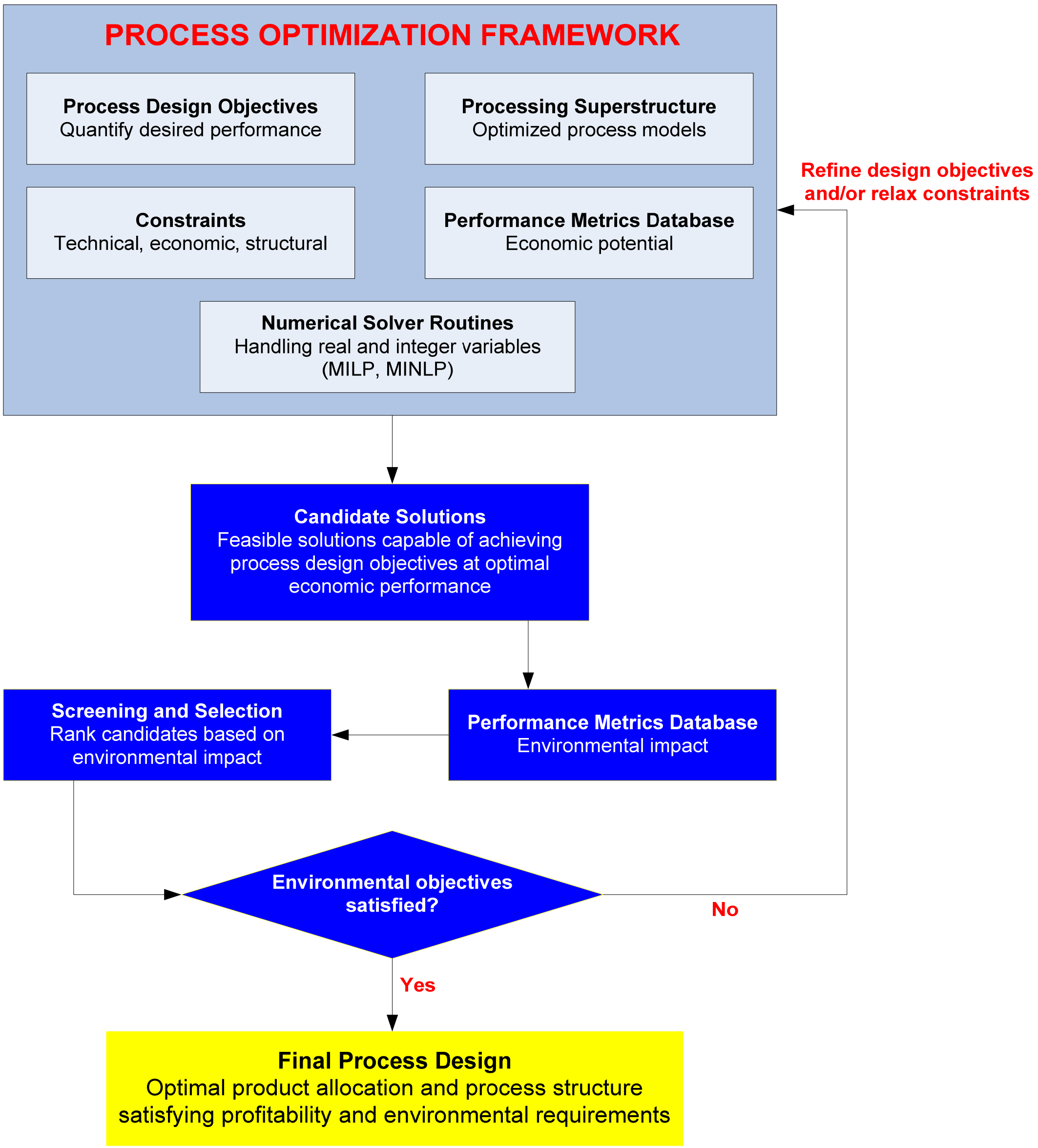


Figure 3.3: Optimization step for decision making process [Sammons, 2009]

Based on the process optimization framework, simulation models are developed and optimized, optimal solutions are selected. The simulation models for each process are developed based on data from experiments or literature. Then the data are introduced into computer simulation software, such as Aspen^{TM} Plus or Pro/II. If a solvent needs to be used and designed, property clustering techniques will be employed to identify alternative solvents that minimize environmental and safety concerns.

Once material recycles have been implemented and optimized, it is necessary to integrate the energy of heat sources to save energy. Thermal pinch analysis is utilized to identify the minimum energy requirements. Aspen Energy Analyzer generates candidate HEN designs based on minimizing the total annualized cost of the utility requirements and process equipment size, and is used to design the corresponding minimum cost heat exchanger networks that optimize the trade-off between capital and utility. The minimum hot and cold utility requirements are calculated based on the utilities anticipated to be available in an existing multiple user industrial facility. The minimum utility operating costs were based on the coldest cold utility and the hottest hot utility available. The integration of mass and energy of heating and cooling utility requirements and potential opportunities could reduce the overall process energy consumption.

Economic as well as environmental performance metrics are identified by using the simulation models. The initial equipment cost analysis is based on sizing data from the models, which are obtained from Aspen Icarus, which is software to estimate the individual equipment cost. The utilities cost is extracted from Aspen Energy Analyzer. Standardized process economics methods are employed to translate the equipment and utility cost into the total production cost, which accounts for everything from engineering to construction, monitoring, supervision and operation.

The environmental performance metric is developed by using the US-EPA Waste Reduction (WAR) algorithm. The WAR algorithm looks at mass flows that are entering and leaving the chemical process and the corresponding process that provides energy. Environmental impact is measured through eight categories that include atmospheric and toxicological concerns. As a simplification, steady state is assumed for all the processes and the following equations are used to calculate the impacts [Young, 2000]:

$$0 = \dot{I}_{in}^{(t)} - \dot{I}_{out}^{(t)} + \dot{I}_{gen}^{(t)} \qquad \text{(Eqn. 3.1)}$$

Each potential environmental impact index I can be approximated as follows [Young, 2000]:

$$I^{(t)} = \sum_{i}^{EnvCat} \alpha_i I_i^{(t)} = \sum_{i}^{EnvCat} \alpha_i \sum_{j}^{Streams} M_j \sum_{k}^{Comps} x_{kj} \psi_{ki}^{s} \qquad \text{(Eqn. 3.2)}$$

$$\psi_{ki}^{s} = \frac{(Score)_{ki}}{<(Score)_k>_i} \qquad \text{(Eqn. 3.3)}$$

Where $I^{(t)}$ is the PEI index for category i, α is the weighting factor for each potential environmental impact category i, M_j is the mass flow rate of stream j, x_{kj} is the mass fraction of component k in stream j, and ψ_{ki}^{s} is the specific potential environmental impact of component k associated with environmental impact category i, calculated by using a normalization scheme. $(Score)_{ki}$ represents the value of chemical k on some arbitrary scale for category i. $<(Score)_k>_i$ represents the average value of all chemicals in category i. Normalizing each category by the average value of non-zero entries in that category ensures that the average value in that category will be unity. The individual weighting for each of the above categories can be changed depending on the emphasis of the study. Each category will be given equal weight. It is assumed that each of the conceptual processes would be subject to the same regulatory environmental constraints, so the PEI after waste treatment would not provide a clear picture of the true impact of the production process itself. The contribution of the process and total energy to the total PEI is reported on a per kilogram of product basis.

In summary, the methodology illustrated above provides a guide for integrating experimental and literature data with process simulation to aid in discovering innovative designs. In the following chapters several case studies based on this approach are presented.

Chapter 4 Alternative Fuel Production Case Studies

4.1 Introduction

In this chapter, case studies of alternative fuel production are developed to illustrate the methodology outlined in the preceding chapters. Aspen Plus was used to simulate the processes. The heat integration was achieved through utilizing Aspen HX-Net, while the economic analysis was completed by introducing data into Aspen Icarus and an Excel spreadsheet.

4.2 Hydrogen Production Strategies

4.2.1 Background

Global scale environmental problems such as the increase in atmospheric CO_2 and the decrease in fossil fuel resources are some of the increasingly severe difficulties facing the world. The issue of global warming due to anthropogenic activities has been an international concern for the past two decades. Almost the entire world has united to address the concern, resulting in an international treaty called the Kyoto Protocol. The protocol requires developed countries to reduce the greenhouse gas (GHG) emissions below certain levels between period 2008 and 2012 [Energy Information Administration, 2008; United Nations Framework Convention on Climate Change, 2008].

Hydrogen-based energy systems are considered to be one of the most promising energy systems with a great potential of providing a future replacement for fossil fuel based energy systems. Hydrogen is a promising energy carrier for future transportation uses. A hydrogen fuel cell is one of the main schemes for utilizing hydrogen as a fuel [Derwent, 2006]. Utilizing hydrogen as an energy provider has the benefits, such as clean and efficient. No greenhouse gases and pollution chemicals are generated during combustion produces [Barretoa, 2002]. In addition, hydrogen has the highest gravimetric energy density of any known element although the volumetric energy density is the lowest [U.S. Department of Energy, 2004]. Thus, the study of hydrogen production is important.

A hydrogen polygeneration plant aims at increasing the economic and environmental sustainability potential of fossil fuel based production facilities. The polygeneration plant could provide a wider range of co-products, in addition to hydrogen.

4.2.2 Modeling of Hydrogen Production Strategies

4.2.2.1 Hydrogen Production Feedstocks

Several hydrogen production schemes with different feedstocks have been investigated, including natural gas, diesel, methanol, and biomass. Natural gas was approximated by methane. Diesel was approximated by dodecane, and biomass was approximated by glucose. Table 4.1 illustrates the different feedstocks and production routes.

Table 4.1: Hydrogen Production Schemes and Feedstocks (▲ stands for the corresponding feedstock and process).

	POX	**SR**	**ATR**	**DR**	**CDH**	**SCWR**
Natural Gas	▲	▲	▲	▲	▲	
Diesel	▲	▲	▲			
Methanol						▲
Biomass						▲

4.2.2.2 Hydrogen Production Schemes

Process models have been developed for a variety of hydrogen production schemes. Using process integration techniques and advanced computer-aided tools, the systems have been optimized and the economic potential of the technologies evaluated. Several reforming techniques including four developed within the Consortium for Fossil Fuel Science (CFFS) have been studied for small and large scale production of hydrogen. Literature data along with data obtained in another research project at Auburn University has been used to develop models for partial oxidation (POX), steam (SR) and autothermal reforming (ATR) of a variety of hydrocarbon resources [Wilder, 2007; Godat, 2003; Seo, 2002]. In addition, data provided by other researchers in CFFS has been used to build similar models for super critical water reforming (SCWR) of methanol [Gadhe, 2005] and biomass [Byrd, 2007], dry reforming (DR) of methane [Shao, 2005] and finally a catalytic dehydrogenation (CDH) of methane [Shah, 2001]. The last process is a single step process that in addition to high producing purity hydrogen also produces a valuable carbon nanotube byproduct.

- Steam Reforming (SR)

SR models were developed for both methane and dodecane to approximate natural gas and diesel fuel, respectively. First the reactants are heated and combined with steam with a C:H_2O ratio of 1:2 and fed to an isothermal SR reactor at 1 atm. The SR reactor is modeled as a conversion reactor and ran at 800ºC and 1 atm [Seo, 2002] as shown in figure 4.1. Equations 4.1 and 4.2 represent reforming of methane and dodecane, respectively. Hydrogen yields are further increased in a separate reactor at 200 ºC and 1 atm by the water-gas shift (WGS) reaction, given in equation 4.3. The conversion of WGS reaction is set as 0.991 of carbon monoxide [Seo, 2002].

$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad \text{(Eqn. 4.1)}$$

$$C_{12}H_{26} + 12H_2O \rightarrow 25H_2 + 12CO \qquad \text{(Eqn. 4.2)}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad \text{(Eqn. 4.3)}$$

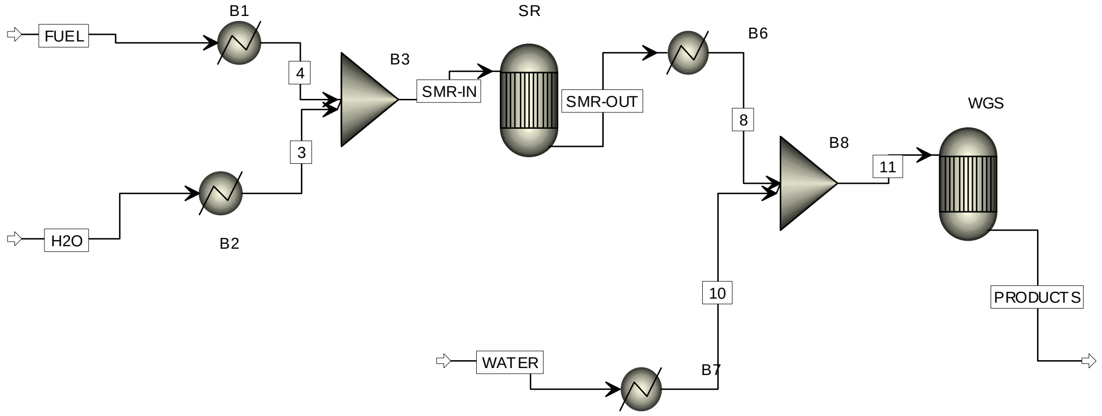


Figure 4.1: Steam reforming process in Aspen Plus

- Partial Oxidation (POX)

Methane and dodecane fuel are the feedstocks considered for this process. The process is illustrated in figure 4.2. The feedstocks are mixed with air in a C:O_2 ratio of 1.67:1. The reaction was modeled in a conversion reactor at 802 ºC and 1atm [Seo, 2002]. The product stream was fed into a water gas shift (WGS) reactor at 200ºC and 1 atm to produce carbon dioxide and more hydrogen with a feed of steam to carbon monoxide of 2.2:1 [Seo, 2002]. The extent of the reactions is assumed to be 0.9912. The reactions involved are shown in equation 4.4 and 4.5.

$$CH_4 + 0.6O_2 \rightarrow 1.87H_2 + 0.93CO + 0.07CO_2 + 0.13H_2O \qquad \text{(Eqn. 4.4)}$$

$$C_{12}H_{26} + 7.2O_2 \rightarrow 12H_2 + 10.36CO + 1.6CO_2 + 0.89H_2O \qquad \text{(Eqn. 4.5)}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad \text{(Eqn. 4.6)}$$

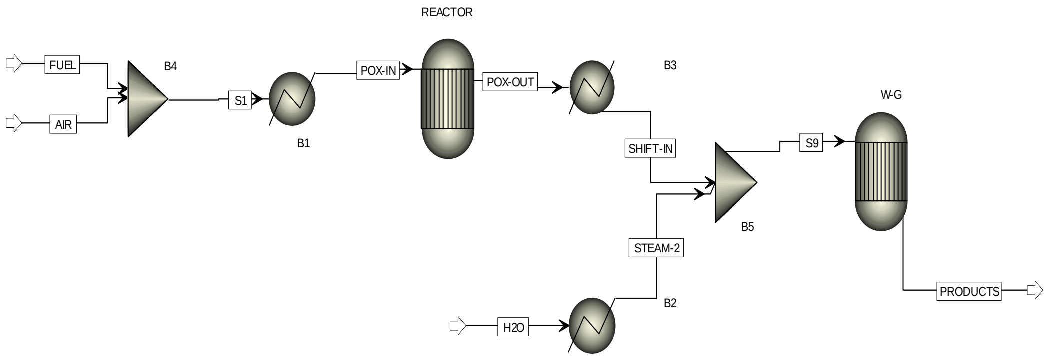


Figure 4.2: Partial oxidation process

- Autothermal reforming (ATR)

The autothermal reforming models were simulated for methane and dodecane mixed with air in a C:O_2 ratio of 1.75, and superheated steam fed at a C:H_2O ratio of 5. The ATR reactor is modeled as a conversion reactor and operates at 788ºC and 1 atm. The products were then introduced into an isothermal WGS reactor with a feed of steam to carbon monoxide of 2.2:1 [Seo, 2002]. The extent of the net fuel reformation reactions is 0.9912, while the extent of the water production is 1.0 [Seo, 2002] as all the oxygen is consumed in the reformer. The reactions involved are shown in equations 4.6 to 4.8. The stoichimetric coefficients are based on the model which was built by Seo (2002).

$$0.35CH_4 + 0.20O_2 \rightarrow 0.70H_2 + 0.31CO + 0.04CO_2 \qquad \text{(Eqn. 4.7)}$$

$$C_{12}H_{26} + 6.54O_2 \rightarrow 13H_2 + 10.92CO + 1.08CO_2 \qquad \text{(Eqn. 4.8)}$$

$$H_2 + 0.5O_2 \rightarrow H_2O \qquad \text{(Eqn. 4.9)}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad \text{(Eqn. 4.10)}$$

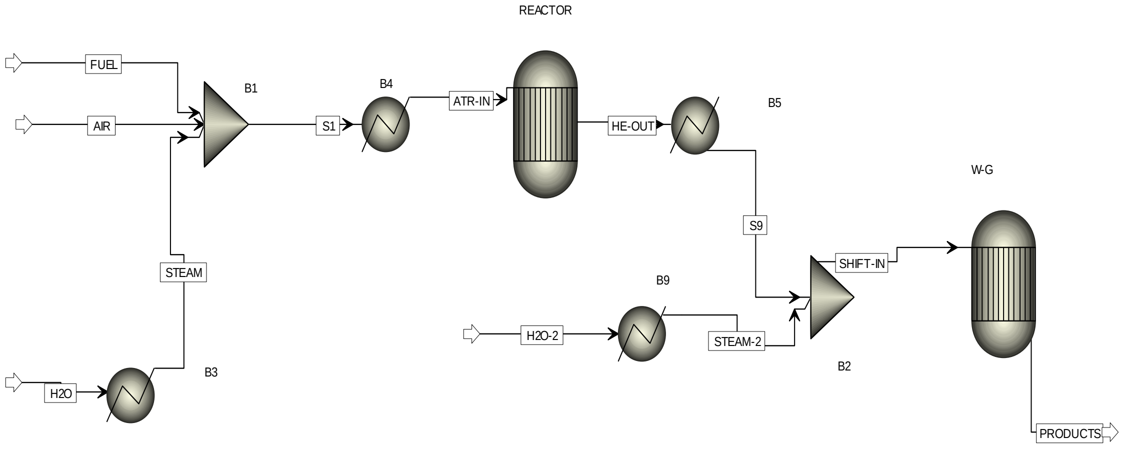


Figure 4.3: Auto thermal reforming process

- Supercritical Reforming (SCWR)

The supercritical methanol reforming simulation models were developed for methanol and biomass, which was approximated by glucose. For the methanol process, the methanol and water are compressed, then heated to 600ºC and 276 bar and sent to the SCWR reactor. The SCWR reactor is modeled as a yield reactor. The molar yields for methane, carbon dioxide, carbon monoxide, hydrogen, and water are as follows: 9.65×10^{-5}, 2.83×10^{-3}, 2.89×10^{-4}, 8.97×10^{-3}, and 4.73×10^{-2}, respectively which are defined as the product to feed molar ratio [Gadhe, 2005].

For the glucose process, the glucose and water are compressed to 276 bar and heated to 700ºC. Then the feed stream is sent to the SCWR reactor. Two weight percentages of glucose are investigated, 1 wt% and 5 wt%. The conversion is set as 1 [Byrd, 2007].

$$C_6H_{12}O_6 + 6H_2O \longrightarrow 6CO_2 + 12H_2 \qquad \text{(Eqn. 4.11)}$$

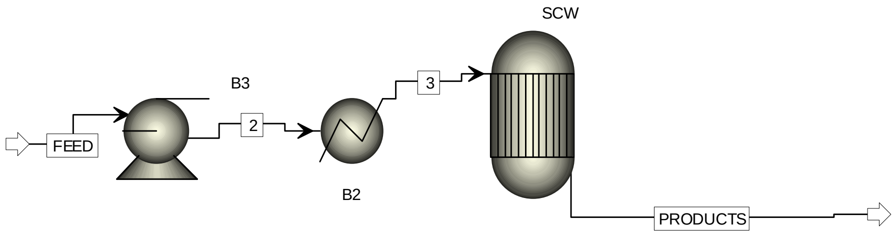


Figure 4.4: Supercritical water reforming

- Catalytic dehydrogenation process (CDH)

The catalytic dehydrogenation process uses methane as feedstock. The CDH reactor is modeled as a conversion reactor and operates at 750ºC and 5 atm, with a conversion of 0.8 [Shah, 2001]. This process produces a co-product of carbon nanotubes as illustrated in Figure 4.6.

$$CH_4 \xrightarrow[750°C]{M-Fe} C + 2H_2 \qquad \text{(Eqn. 4.12)}$$

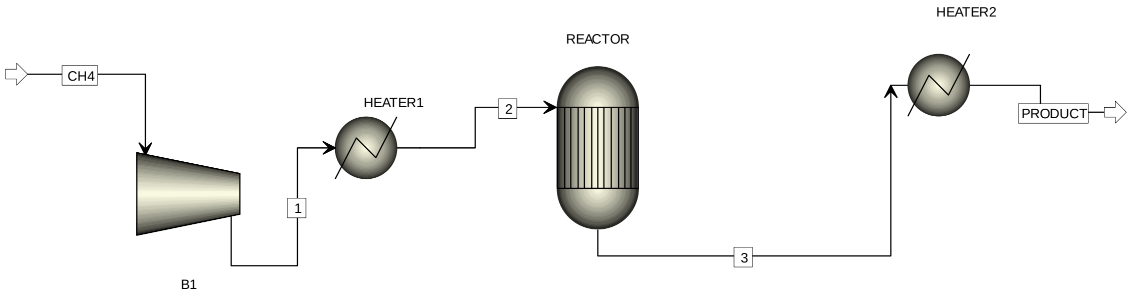


Figure 4.5: Catalytic dehydrogenation of methane

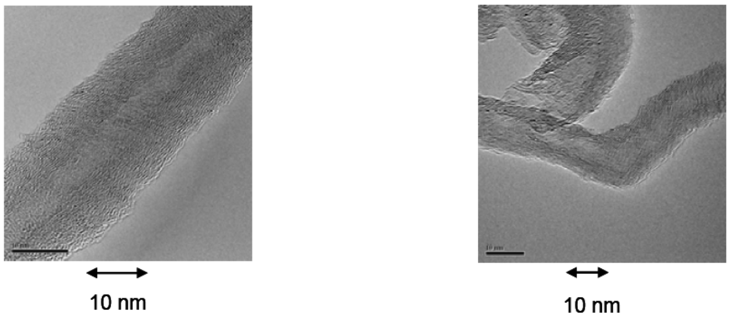


Figure 4.6: Multiwalled nanotubes (MWNT) (left) and stacked cone nanotubes (SCNT) (right) produced by dehydrogenation of methane over Fe-Ni/Mg(Al)O at 650ºC and 500ºC, respectively

- Dry methane reforming (DR)

For this process, methane and carbon dioxide were preheated and sent to a DR reactor operating at 850 ºC and 5 atm. Cobalt-tungsten carbide is used as catalyst. The conversion of the reformation process is 0.78 based on carbon dioxide and the methane decomposition reaction is defined by a methane fractional conversion of 0.18 [Shao, 2005]. The reactions are shown in equation 4.13 and 4.14. The water-gas shift reaction as shown in equation 4.3 is operated at 200 ºC and 1 atm [Seo, 2002].

$$CH_4 + CO_2 \rightarrow 2CO + H_2 \qquad \text{(Eqn. 4.13)}$$

$$CH_4 \rightarrow C + 2H_2$$ (Eqn. 4.14)

$$CO + H_2O \leftrightarrow CO_2 + H_2$$ (Eqn. 4.3)

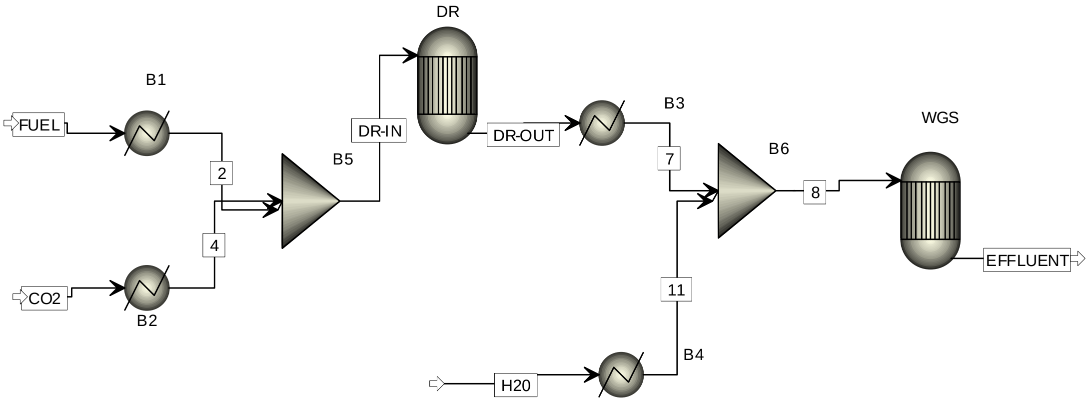


Figure 4.7: Dry reformation of methane

4.2.2.3 Hydrogen Production Scenario

Simulation models were developed for two scenarios, small scale (1,000 Nm^3/hr) and large scale (100,000 Nm^3/hr), based on different hydrogen production plants. Aspen Plus was used to generate these models. The models included all the feed pretreatment steps, reforming reactors, and effluent treatment including the water-gas-shift reactors. Once material recycles had been implemented and optimized, thermal pinch analysis was utilized to identify the minimum energy requirements. Aspen HX-Net was used to design the corresponding minimum cost heat exchanger networks that optimize the trade-off between capital and utility.

4.2.3 Results and Discussions

4.2.3.1 Economic Analysis

An economic analysis of all the generated case studies was performed to evaluate the hydrogen production cost. The initial equipment cost analysis was based on sizing data from the models themselves coupled with Lang factors provided by contacts in the chemical processing industry. Standardized process economics methods were employed to translate the equipment and utility cost into the total production cost, which accounts for everything from engineering to construction, monitoring, supervision and operation. The total production cost was then normalized using the results for steam reforming of natural gas, which is the prevailing means of producing hydrogen. The results are shown in figure 4.8 for both large and small scale hydrogen production. The x-coordinate represents all the hydrogen production schemes with different feedstocks and processes. The y-coordinate represents the relative hydrogen production cost compared with steam reforming of natural gas. The blue bar stands for the large scale hydrogen production. The purple bar stands for the small scale hydrogen production.

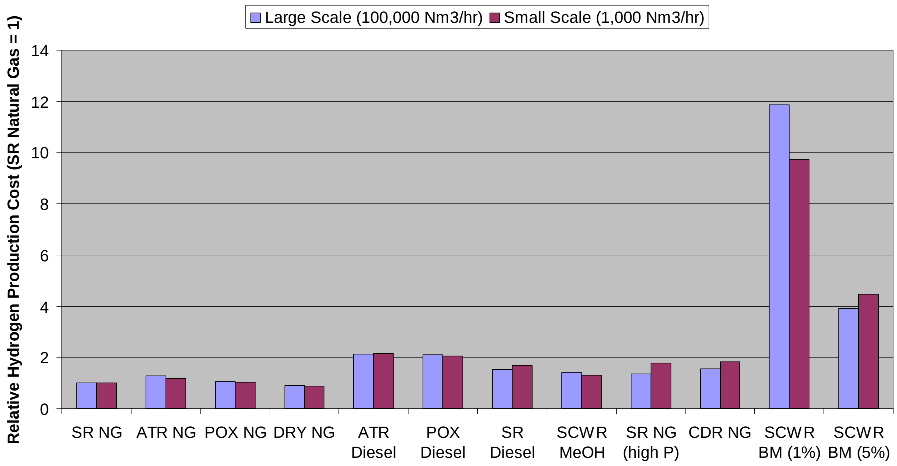


Figure 4.8: Relative hydrogen production cost for different hydrogen production schemes

The analysis of the various hydrogen production schemes clearly shows that for industrial scale production only the dry reforming (DR) of natural gas has the potential to compete with the traditional steam reforming (SR) process. The conversion of more complex liquid hydrocarbon fuels, e.g. diesel and methanol, are not competitive given the current market prices; however, such fuels have other benefits such as ease of storage and transportation etc. that can lead to different conclusions in specific cases. Also, with the recent development of biofuel production technologies, biodiesel and bio-alcohols could be another promising feedstock to investigate, especially with respect to sustainability. The supercritical water reforming (SCWR) of methanol does have one major benefit compared to the other technologies, i.e. the hydrogen is produced at very high pressures, which may be attractive for some applications. For comparison, if the hydrogen produced from conventional steam reforming was compressed to the SCWR pressure of 276 bar, that would result in the new SCWR process being only 30% more expensive than the traditional approach. If more efficient separation of the supercritical water phase from the hydrogen product can be developed, e.g. membranes or hydrogels, then the production costs could be significantly reduced by recycling the reaction phase without having to reheat and/or recompress the water to these extreme conditions.

The same considerations apply to SCWR of biomass, which is not profitable without the ability to recycle the water phase directly. Feed concentrations of 1 and 5 wt% biomass in water were investigated. Although a significant reduction in production cost was observed when increasing the glucose concentration, it was not enough to offset the high compression and recycle cost. Even if biomass wastes such as wood trimmings were used as feedstock, a significant tipping fee would still be needed to make the process profitable. Using the average tipping fee for unspecified biomass, in order to make the current SCWR process comparable in cost to conventional methods, the glucose feed concentration needs to be increased to around 18 wt%, which is still under development.

The catalytic dehydrogenation process (CDH) as described by Shah (2001) could potentially be a very attractive alternative to existing hydrogen production schemes. The process produces a valuable byproduct of carbon nanotubes. In addition, since the process has the benefit of integrated carbon capture, additional revenue can be secured through credits for reduced CO_2 emissions compared to conventional production schemes. Currently carbon credits are traded at approximately $35/ton [www.pointcarbon.com]. To break even with steam reforming of natural gas, the carbon nanotube byproduct would have to be sold at approximately $0.20/lb. Although this breakeven sale price of the carbon nanotubes is significantly lower than the open market value of carbon nanotubes, it is questionable whether a market exists for such huge amounts of nanotubes that would be available if/when the CDH process is introduced on an industrial scale.

4.2.3.2 Environmental Impact Analysis

The impact on the environment is considered for each process using the Waste Reduction (WAR) algorithm. There are eight categories to evaluate the environment [Young, 2000; 1999]. The individual weighting for each of the eight categories was set to be the same in this study. The contribution of the process and total energy to the total PEI is reported based on a per kilogram of product basis. Figure 4.9 gives the result of PEI for each process for both chemical and energy processes. Only the large scale scheme is shown, as the result of the small scale strategy is simply 100 times less than the large scale. The x-coordinate stands for all the processes and the y-coordinate stands for the relative score. The purple bar is the energy impact and the blue bar is the chemical process impact.

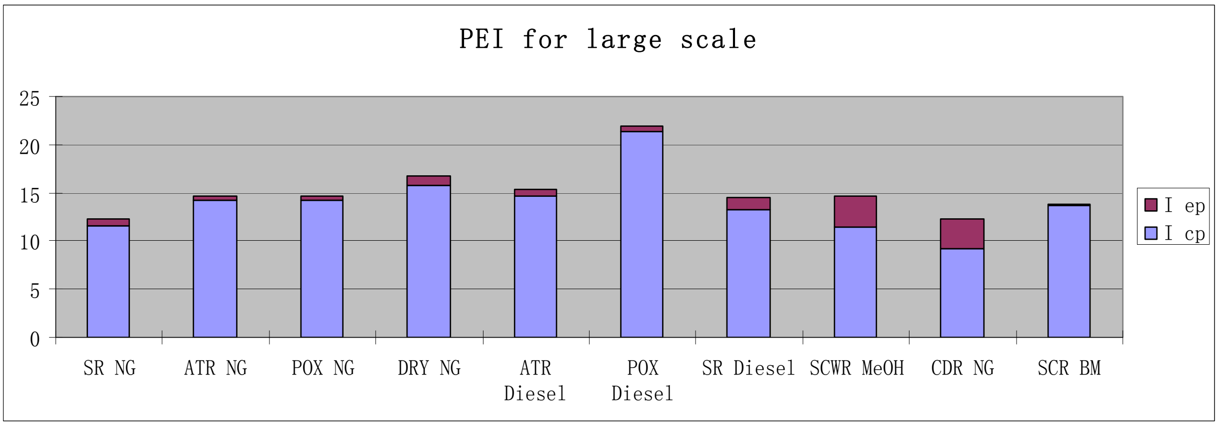


Figure 4.9: PEI analysis for large scale productions, where I ep stands for the impact of energy process while I cp stands for the impact of chemical processes

These results show that the environmental impacts of most of the hydrogen production strategies are similar. However, the impact of partial oxidation of diesel is much higher than SR NG. This is because the POX process produced more CO_2 than other processes, increasing the impact of the greenhouse gas factor of the evaluation process. The energy impacts from SCWR of MeOH and CDR NG are higher than any of the others. This is because the reaction phase is compressed and heated to a high pressure and temperature. More energy is needed to achieve the reaction conditions. If more efficient separation of the supercritical water phase from the hydrogen product can be developed, the energy consumption could be significantly reduced by recycling the reaction phase without having to reheat and/or recompress the water to these extreme conditions.

4.2.4 Conclusion

The main achievement of this case study is the holistic comparison of several reformation strategies based on the impact of their utility requirements, energy integration potential, equipment costs, and raw material costs on the total production cost. The results from the economic analysis allow the reformation strategies to be evaluated for a specific hydrogen application and determine which strategy is the most suitable for that specific application. Moreover, this study could provide a guide for the direction of novel hydrogen production methods in order to be competitive to the traditional one in terms of cost and environmental impact.

This work is an initial step in establishing a future alternative energy economy. The hydrogen energy infrastructure is still under development, which requires large investments in production and distribution systems. For specific fuel sources and reaction kinetics a simplified approach was used to study the feasibility of each process. The four different representative fuels investigated here were natural gas, diesel, methanol and biomass. In order to develop a basic understanding of the reformation relationships, minor simplification of the fuels were applied. For example, natural gas was simplified as methane, while dodecane provided a simple representation of diesel fuel and glucose is used to approximate biomass. More models, with specific detailed compositions of each fuel, should be further investigated to better understand the effects of fuel composition on the energy integration potential of the process system. Similarly, complex reaction kinetics were also simplified by stoichiometric equations. Yet again, more work is necessary to broaden the understanding and advance the development of the reaction equations, which is a critical component for the construction of efficient reformers. However, few kinetic works are available concerning the exact breakdown of complex hydrocarbon fuels during reformation.

The ability to produce hydrogen cheaply is only the first of many challenges that need to be addressed. It is apparent that the current technologies for producing hydrogen from liquid fuels are not attractive if evaluated only by the production cost along with the environmental impact. Benefits such as transportability etc. will need to be quantified for all types of fuels in order to better compare the technologies. However, the dry reforming technology being developed by CFFS researchers appears to be a potentially cheaper alternative to the current state of the art. Furthermore, supercritical water reforming shows significant promise for biomass waste processing but requires additional research focused on separation of the reactive water phase and the high pressure hydrogen. The catalytic dehydrogenation process developed by CFFS researchers also shows great potential to be competitive with current technologies due to the integrated carbon capture and marketable carbon nanotube byproduct.

4.3 Fischer-Tropsch Fuel Synthesis and Comparison

4.3.1 Introduction

Fischer-Tropsch (FT) processes are becoming more attractive due to the stringency of environmental regulations, decreasing fossil fuel reserves and development of new technologies. It is becoming a potential answer to meet many future energy needs and may provide a carbon neutral alternative. Paraffins and α-olefins are the main products. Table 4.2 summarizes the overall reactions. Table 4.3 summarizes the common names for the main products.

Table 4. 2: Major Overall Reactions in the Fischer-Tropsch Synthesis [Van Der Laan, 1999].

Main reactions	
1. Paraffins	$(2n+1)H_2 + nCO_2 \rightarrow C_nH_{2n+2} + nH_2O$
2. Olefins	$2nH_2 + nCO_2 \rightarrow C_nH_{2n} + nH_2O$
3. WGS reaction	$CO + H_2O \Leftrightarrow CO_2 + H_2$
Side reactions	
4. Alcohols	$2nH_2 + nCO_2 \rightarrow C_nH_{2n+2}O + (n-1)H_2O$
5. Catalyst Oxidation/Reduction	(a) $M_xO_y + yH_2 \Leftrightarrow yH_2O + xM$
	(b) $M_xO_y + yCO \Leftrightarrow yCO_2 + xM$
6. Bulk Carbide Formation	$yC + xM \Leftrightarrow M_xC_y$
7. Boudouard Reaction	$2CO \rightarrow C + CO_2$

Table 4.3: Common Name of Main Products[Van Der Laan, 1999].

Chain Length	**Common Name**
C_{1-2}	Fuel gas
C_{3-4}	LPG
C_{5-12}	Gasoline
C_{5-10}	Naphtha
C_{11-13}	Kerosene (Jet fuel)
C_{13-17}	Diesel (Fuel oil)
C_{10-20}	Middle distillates (Light gas oil)
C_{19-23}	Soft wax
C_{24-35}	Medium wax
C_{35+}	Hard wax

Traditional FT processes can be performed in both gas phase and liquid phase [Dry, 2002; Anderson, 1984]. Recently, many studies have been done to produce FT fuels in supercritical phase. Yokota and co-workers (1990) found that compared to gas phase, SCF medium has the benefit of efficiently transporting and extracting heavy products. Based on their work, Elbashir

(2005) used supercritical hexane as the reaction media and the results indicated that it could provide a better controlled FT reaction in supercritical phase. They noticed that because of the high compressibility, very small changes in pressure and/or temperature can lead to large changes in density-dependent properties with the presence of the supercritical solvent, which results in several improvements over the gas-phase FT process: the formation of undesirable products is reduced; less methane is produced; more long-chain olefins are generated; the desired reaction pathways are promoted and secondary reactions that reduce product selectivity are prevented.

In this work, several Fischer-Tropsch models for different process specifications were developed for a supercritical phase FT process (SCF-FTS) as well as a gas-phase FT process (Gas-FTS). In order to compare the two processes, models are built based on the same syngas feed flowrate. The objective is to construct and investigate the optimal flowsheet structures of the FT processes and compare different models based on their economic and environmental performance. The optimal flowsheet structure is selected for each process within the different simulated flowsheet structures. Gasoline and Jet-fuel were designed as our final products. The fuel produced from the FT process has a wide carbon distribution, but the percentage of heavy carbons (larger then C_{25}) is very small [Van Der Laan, 1999; Elbashir, 2005]. Accordingly, it is assumed that the FT fuel production range is from C_1 to C_{25}.

4.3.2 Supercritical-Fluid Fischer-Tropsch Process (SCF-FTS)

4.3.2.1 Process Illustration

Figure 4.10 is a simplified generic process block diagram representing the SCF-FTS process. The hexane and syngas streams are introduced into a FT reactor. The detailed data is based on the work presented by Elbashir (2005). Synthesis gas produced from steam reforming is introduced into the system with a H_2/CO ratio of 2.17. Hexane is initially fed with syngas to the system with a purity of 99%. 15% Co/Al_2O_3 catalyst is used in the FT reactor to convert syngas to hydrocarbons in the supercritical hexane solvent. After the FT reaction the liquid FTS products are refined to yield gasoline and jet fuel. This step includes an integrated cracking unit to hydrotreat/crack the heavy products. Extra hydrogen is added to crack heavy products (C_{16}–C_{25}) back to light and middle distillates (C_1–C_{12}) for further processing. The hexane and light carbons-rich stream coming out of the light fractionation unit and the two distillation columns are recycled back to the FT reactor.

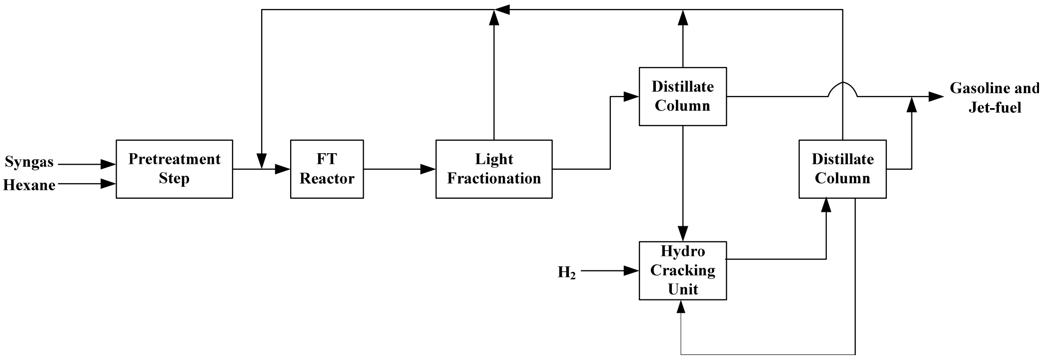


Figure 4.10: SCF-phase process block diagram

4.3.2.2 Simulation of SCF-FTS Reactor

Based on the experimental data from Elbashir and co-workers (2005), several SCF-FTS reactor models are built in order to understand the performance of the reaction. The experimental results from Elbashir (2005) are shown in figure 4.11 and figure 4.12. Sensitivity analysis was undertaken by varying the reaction conditions, such as temperature and pressure.

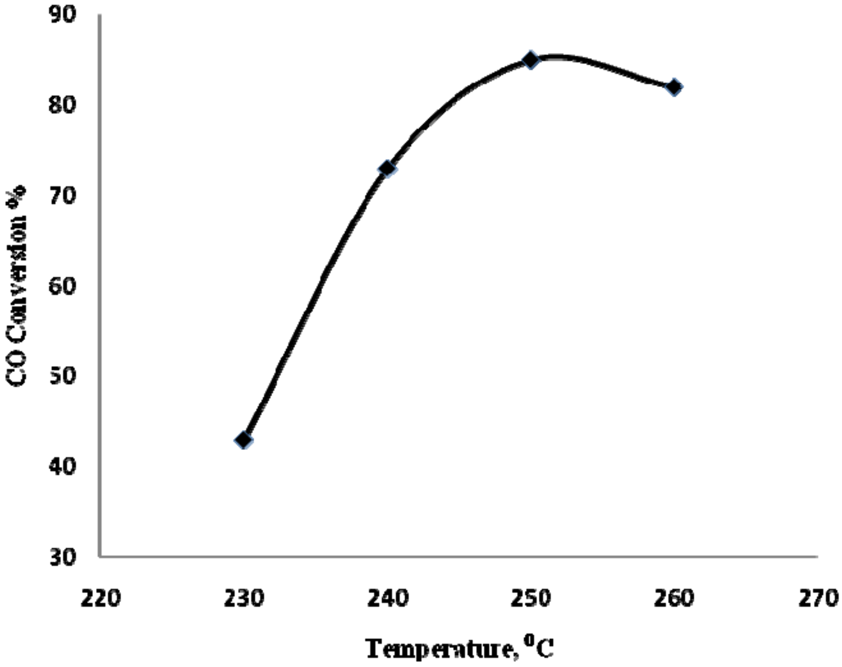


Figure 4.11: Effect of reaction temperature on CO conversion at a total pressure of 65 bar and syngas/hexane molar ratio of 1/3 [Elbashir, 2005]

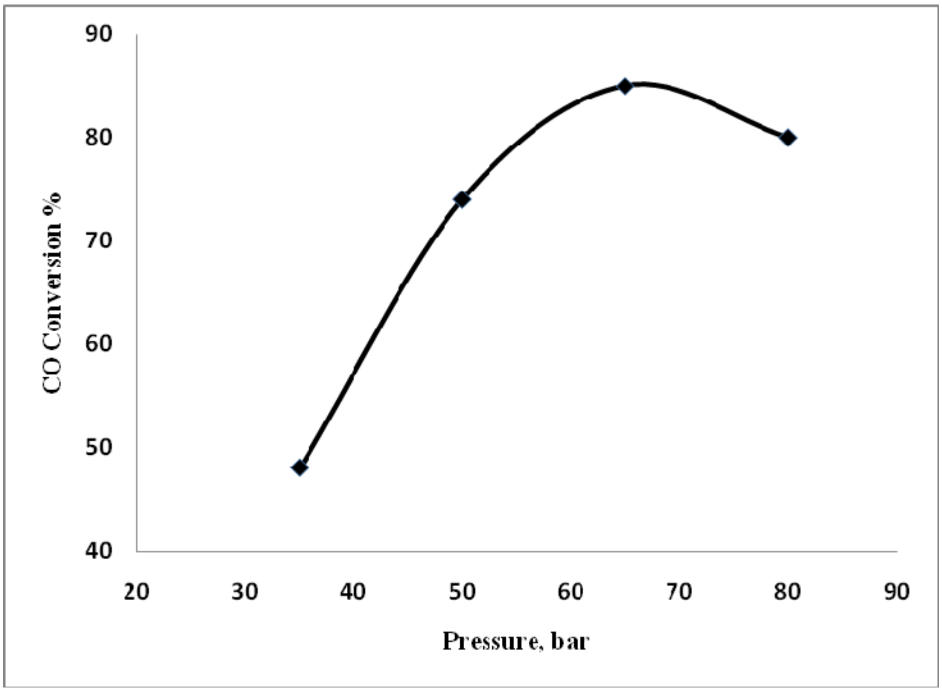


Figure 4.12: Effect of reaction pressure on CO conversion at 250 °C and syngas/hexane molar ratio of 1/3 [Elbashir, 2005].

In order to determine the optimal processing conditions, simulation models of SCF-FTS reactors are developed for a variety of reaction conditions based on the CO conversion at different pressures and temperatures, which are summarized in Figure 4.11 and 4.12. First, the pressure is fixed at 65 bar in order to investigate how the hydrocarbon production distribution changes with temperature. Then the temperature is set to be 250 °C to simulate how production distribution varies with pressure. The complexity of phase behavior under the supercritical condition leads to an increase of heavy hydrocarbon production. This makes the product distribution in the SCF-FTS reactor different from the Anderson-Schulz-Flory (ASF) model. More detailed simulation results for SCF-FTS reactors are shown in Figure 4.13 to Figure 4.16. In the first case at 65 bar, four temperatures are investigated, 230 °C, 240°C, 250 °C and 260 °C respectively as shown in Figure 4.13. With increasing temperature from the near critical point

(230°C, 240°C) to the supercritical region (240°C, 250°C), more light hydrocarbons fractions are produced. This is mainly because that temperature could dramatically affect the chain growth mechanism, which is directly related to the hydrocarbon products distributions. The production rates of gasoline and jet fuel at different temperature ranges at 65 bar were normalized and compared with the fuel production rate at 230˚C in Figure 4.14. The production rate of gasoline increases with temperature while the rate of jet fuel reaches a maximum at around 250°C. Although the gasoline production is slightly higher at 260°C, the jet fuel production rate is less than one third of the peak value. The results indicates that in the supercritical hexane solvent with fixed pressure of 65 bar, the maximum fuel production rate is achieved at 250°C. After optimizing the temperature, three pressures (35, 65 and 80 bar) are selected for simulation and comparison under 250°C, and the results are shown in Figure 4.15 and 4.16. By increasing the pressure from below critical pressure (35 bar) to critical pressure (80 bar), the product distribution profile did not change significantly. Again, figure 4.16 shows the relative fuel production rate compared to the rate at 35 bar. Clearly, both gasoline and jet fuel reach the peak production rate at 65 bar. The experimental data shows that the CO conversion peaks at 0.85 under conditions of 250°C and 65 bar. The syngas/hexane molar ratio is 1/3. The simulation results also indicated that the optimal operating conditions to maximize FT fuel production appear at 250°C and 65 bar. The total pressure could influence the bed residence time, which is defined as the volume of feed at the applied pressure passing through the volume of the catalyst bed per second, and affect the equilibrium of the FTS products [Elbashir, 2005].

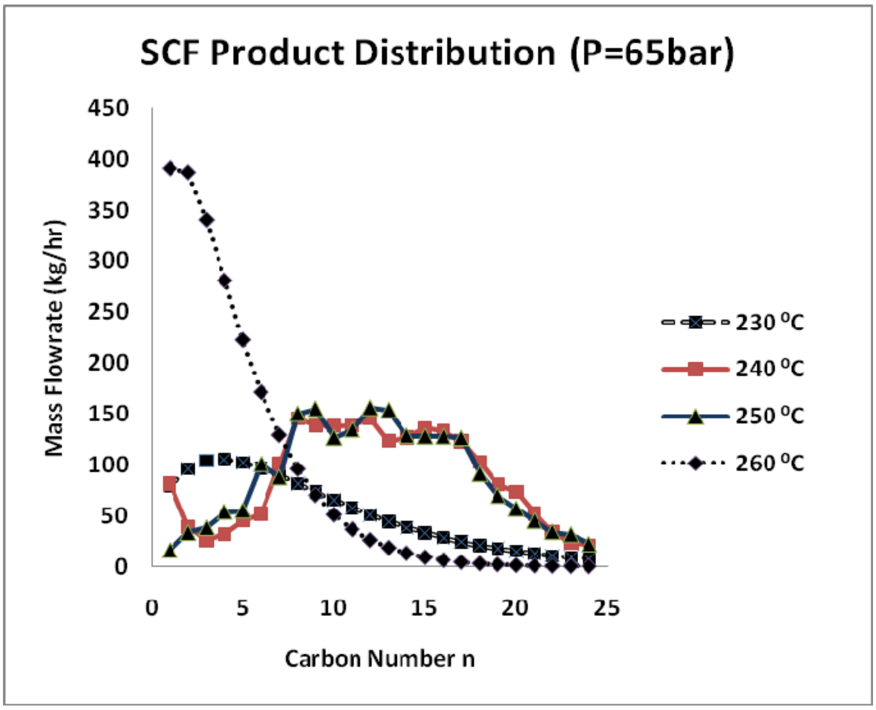


Figure 4.13: Simulation results of hydrocarbon product distribution from SCF-FTS at 65 bar. Reaction conditions; H_2/CO feed ratio of 2.17. Hexane/syngas molar ratio of 3/1

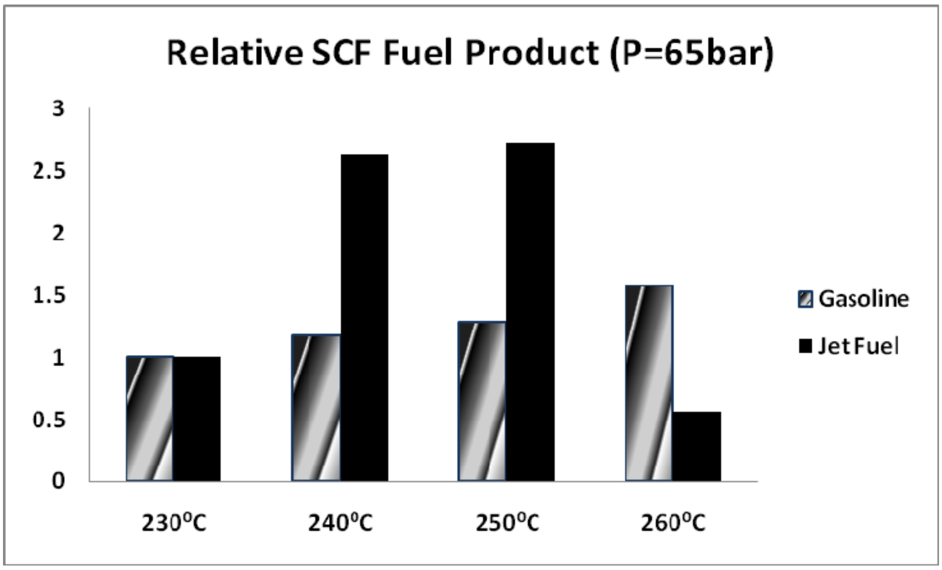


Figure 4.14: Simulation results of relative SCF fuel production at 65 bar. Reaction conditions; H_2/CO feed ratio of 2.17. Hexane/syngas molar ratio of 3/1.

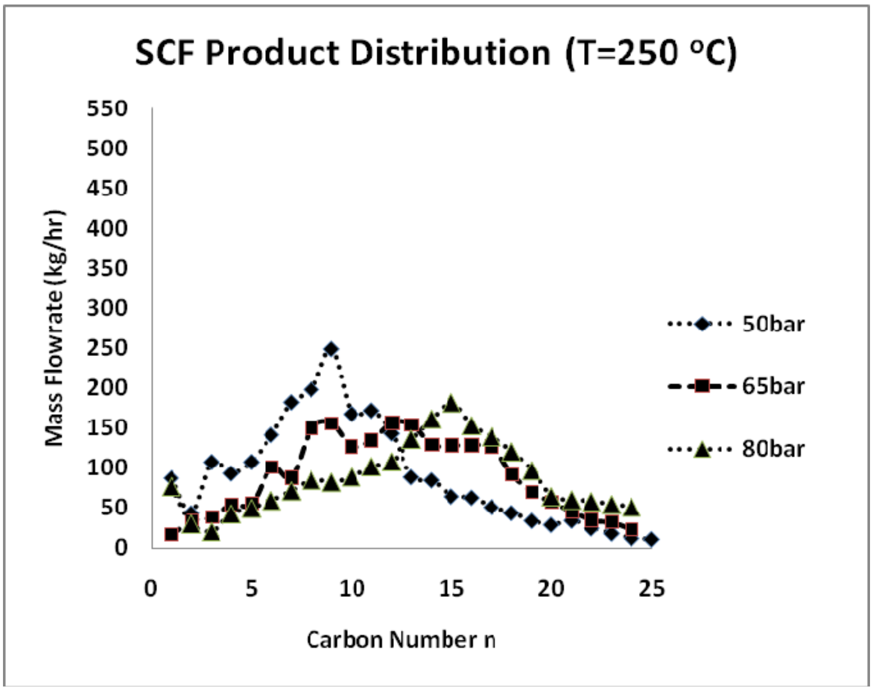


Figure 4.15: Simulation results of hydrocarbon product distribution from SCF-FTS at 250 ^{0}C. Reaction conditions; H_2/CO feed ratio of 2.17. Hexane/syngas molar ratio of 3/1.

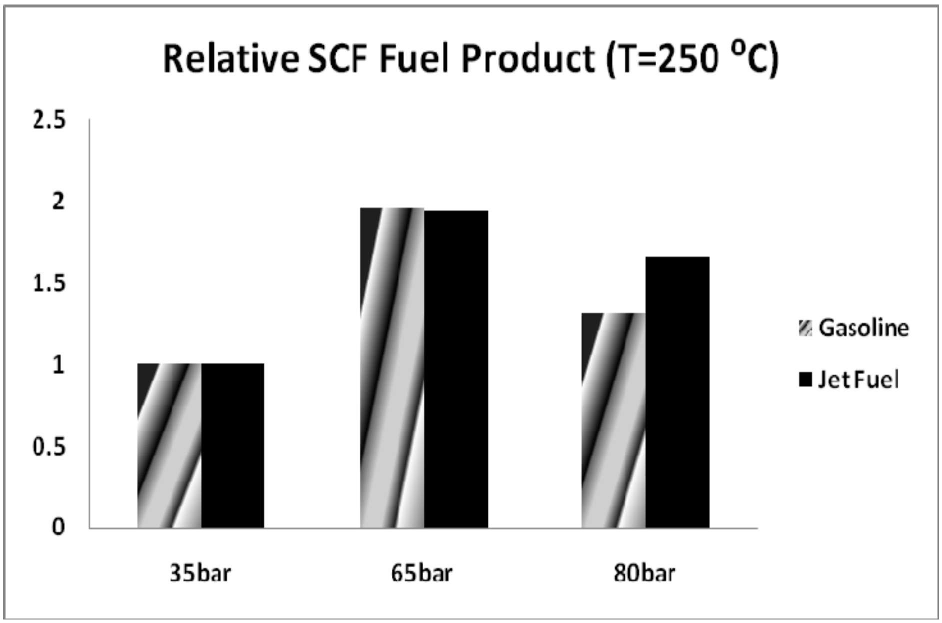


Figure 4.16: Simulation results of relative SCF fuel production at 250 ^{0}C. Reaction conditions; H_2/CO feed ratio of 2.17. Hexane/syngas molar ratio of 3/1.

4.3.2.3 Model Specification and Results

Based on literature and simulated reactor data, the SCF-FTS process was developed in Aspen Plus as shown in Figure 4.17.

- Feedstock

Syngas is fed into the SCF-FTS reactor with a H_2/CO ratio of 2.17/1. The molar flow rate is 2370 kmol/hr. This flow rate is based on the industrial fuel production scale which can be changed according to the desired fuel production rate. Hexane is used as supercritical solvent in FT reactor. It is only pumped into the system once at the beginning with a purity of 99%. Then the inert hexane stream is recycled in the system as shown in Figure 4.18.

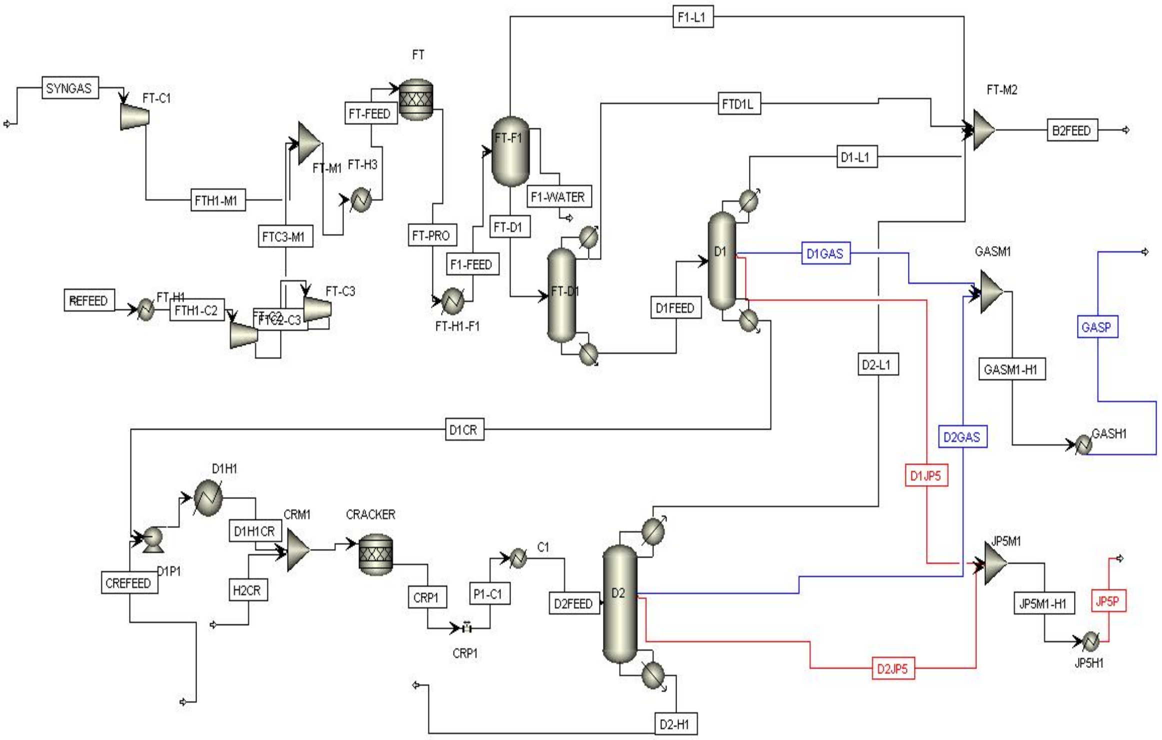


Figure 4.17: Initial SCF-FTS model in Aspen Plus

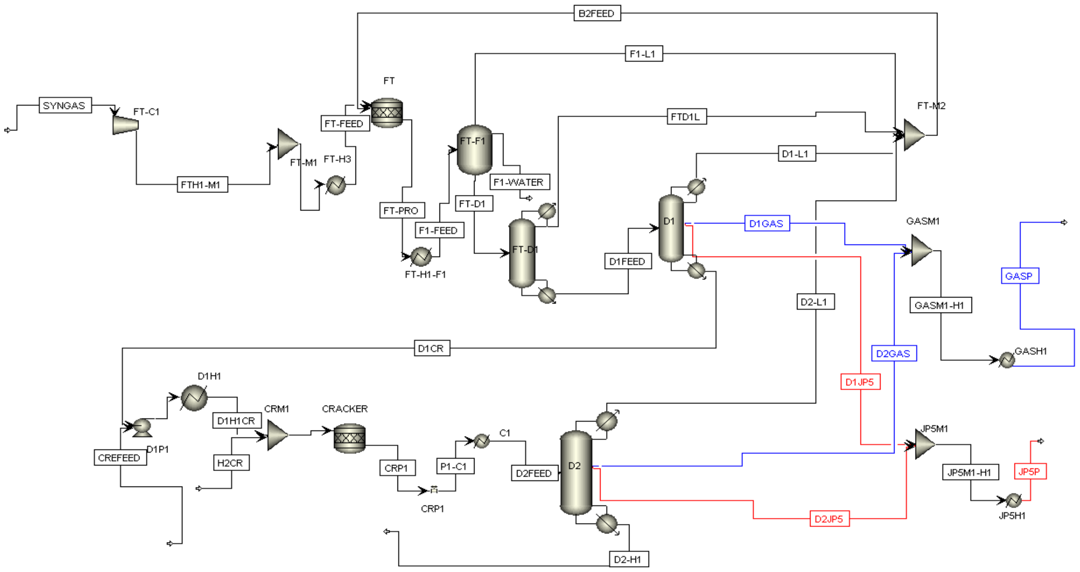


Figure 4.18: Refined SCF-FTS model in Aspen Plus

- SCF-FT synthesis

The FT reaction operates at the optimal conditions of 250 °C and 65 bar (as we have identified before) in the supercritical hexane solvent with a CO conversion of 0.85. 15% Co/Al_2O_3 is used as the catalyst [Elbashir, 2005]. The main products are paraffins, olefins and oxygenated products. In this work, only paraffins are considered as the products. Olefins and oxygenates have not been included yet. The SCF-FT reactor is modeled using a stoichiometric reactor. Detailed reactions are shown in Table 4.4 below. The overall reaction is divided into individual sub-reactions. The sum of all the individual conversions is equal to the overall CO conversion of 0.85.

Table 4.4: Detailed Stoichiometry in SCF-FT Reactor.

Stoichiometry	**Conversion**
$CO + 3 H_2 \rightarrow CH_4 + H_2O$	0.14718332
$2 CO + 5 H_2 \rightarrow C_2H_6 + 2 H_2O$	0.00504988
$3 CO + 7 H_2 \rightarrow C_3H_8 + 3 H_2O$	0.01066858
$4 CO + 9 H_2 \rightarrow C_4H_{10} + 4 H_2O$	0.01238410
$5 CO + 11 H_2 \rightarrow C_5H_{12} + 5 H_2O$	0.01757500
$6 CO + 13 H_2 \rightarrow C_6H_{14} + 6 H_2O$	0.01805530
$7 CO + 15 H_2 \rightarrow C_7H_{16} + 7 H_2O$	0.03314586
$8 CO + 17 H_2 \rightarrow C_8H_{18} + 8 H_2O$	0.02893211
$9 CO + 19 H_2 \rightarrow C_9H_{20} + 9 H_2O$	0.04958491
$10 CO + 21 H_2 \rightarrow C_{10}H_{22} + 10 H_2O$	0.05129589
$11 CO + 23 H_2 \rightarrow C_{11}H_{24} + 11 H_2O$	0.04196833
$12 CO + 25 H_2 \rightarrow C_{12}H_{26} + 12 H_2O$	0.04456514
$13 CO + 27 H_2 \rightarrow C_{13}H_{28} + 13 H_2O$	0.05179173
$14 CO + 29 H_2 \rightarrow C_{14}H_{30} + 14 H_2O$	0.05111690
$15 CO + 31 H_2 \rightarrow C_{15}H_{32} + 15 H_2O$	0.04268219
$16 CO + 33 H_2 \rightarrow C_{16}H_{34} + 16 H_2O$	0.04247476
$17 CO + 35 H_2 \rightarrow C_{17}H_{36} + 17 H_2O$	0.04252344
$18 CO + 37 H_2 \rightarrow C_{18}H_{38} + 18 H_2O$	0.04200030
$19 CO + 39 H_2 \rightarrow C_{19}H_{40} + 19 H_2O$	0.03033064
$20 CO + 41 H_2 \rightarrow C_{20}H_{42} + 20 H_2O$	0.02319241
$21 CO + 43 H_2 \rightarrow C_{21}H_{44} + 21 H_2O$	0.01897179
$22 CO + 45 H_2 \rightarrow C_{22}H_{46} + 22 H_2O$	0.01502597
$23 CO + 47 H_2 \rightarrow C_{23}H_{48} + 23 H_2O$	0.01146745
$24 CO + 49 H_2 \rightarrow C_{24}H_{50} + 24 H_2O$	0.01056270
$25 CO + 51 H_2 \rightarrow C_{25}H_{52} + 25 H_2O$	0.00745130
Overall CO Conversion	**0.85**

- Crude fractionation

In addition to the FTS products, the effluent from the FTS reactor also contains unreacted carbon monoxide, hydrogen, hexane and water. The C_{7+} products are separated by a condenser and sent to the middle distillate fractionation and cracker to produce FT fuels. The unreacted H_2, CO, and lighter paraffin products are recycled to replace the initial syngas feed.

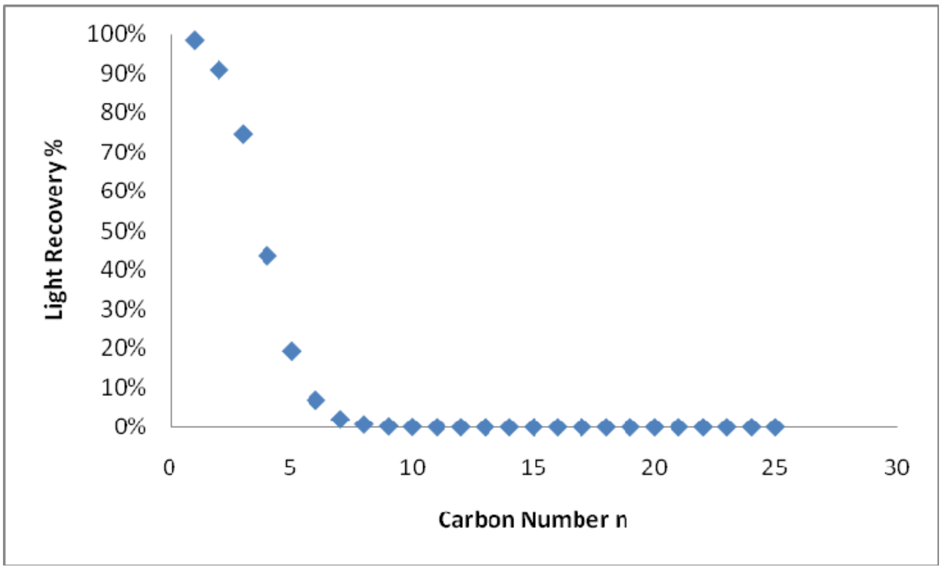


Figure 4.19: Recovery percentage of light product stream out of the condenser

After the condenser, we can obtain basically two product streams: light products, mainly containing C_1-C_5, which will be recycled as feedstock the FT reactor; and the fuel product, which will be sent to the distillation column. The fuel products C_{7+} will be further processed to gasoline and jet fuel. In order to save energy and raw materials, the hexane stream should be recycled inside the system after the initial feed, which means it should be separated with the lights. As shown in Figure 4.19, after the condenser, only 7% of hexane is recovered with the light product. Thus a hexane separation unit should be added to separate the excess hexane from the fuel products. The product stream coming out the condenser is then introduced to a hexane recovery unit. The detailed recovery data is shown in Figure 4.20. 92% of hexane is recovered into the light product stream which is recycled to the FT reactor.

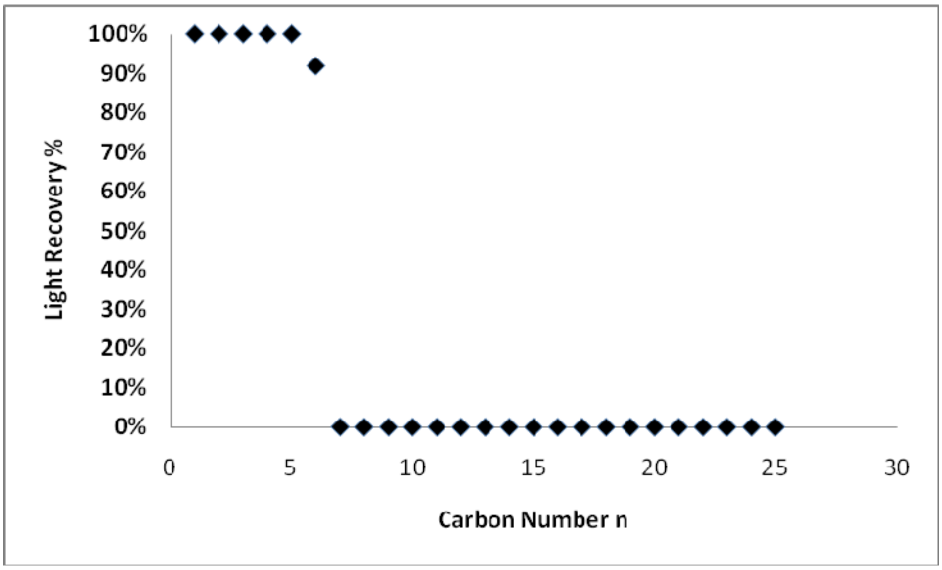


Figure 4.20: Recovery percentage of light product stream out of the hexane recovery unit

- First Distillation Column

After the lights are recycled, the fuel products are introduced into a fractionation unit. The C_5-C_9 portion is separated from the heavier products as gasoline and the C_{10}-C_{14} portion is separated as the Jet-fuel product. The C_{15+} portion is converted into smaller paraffin structures in a hydrocracking unit, which is presented by the heavy portion in figure 4.21. The C_1-C_6 portion (light in figure 4.21) is recycled as feedstock back to the FT reactor. Figure 4.21 shows the detailed mass flow rates of different product streams coming out of the distillation tower. The light product stream that is coming out of the distillation tower contains mainly the low molecular weight hydrocarbons from C_1 to C_6. This fraction is going to be sent back to FT reactor as part of the feed. The heavy (bottoms) fraction of the product stream is mostly larger than C_{13}, which will be sent to the hydrocracking unit. The gasoline product is concentrated within C_5-C_{12} range and the jet fuel product falls in the range between C_{11} and C_{14}.

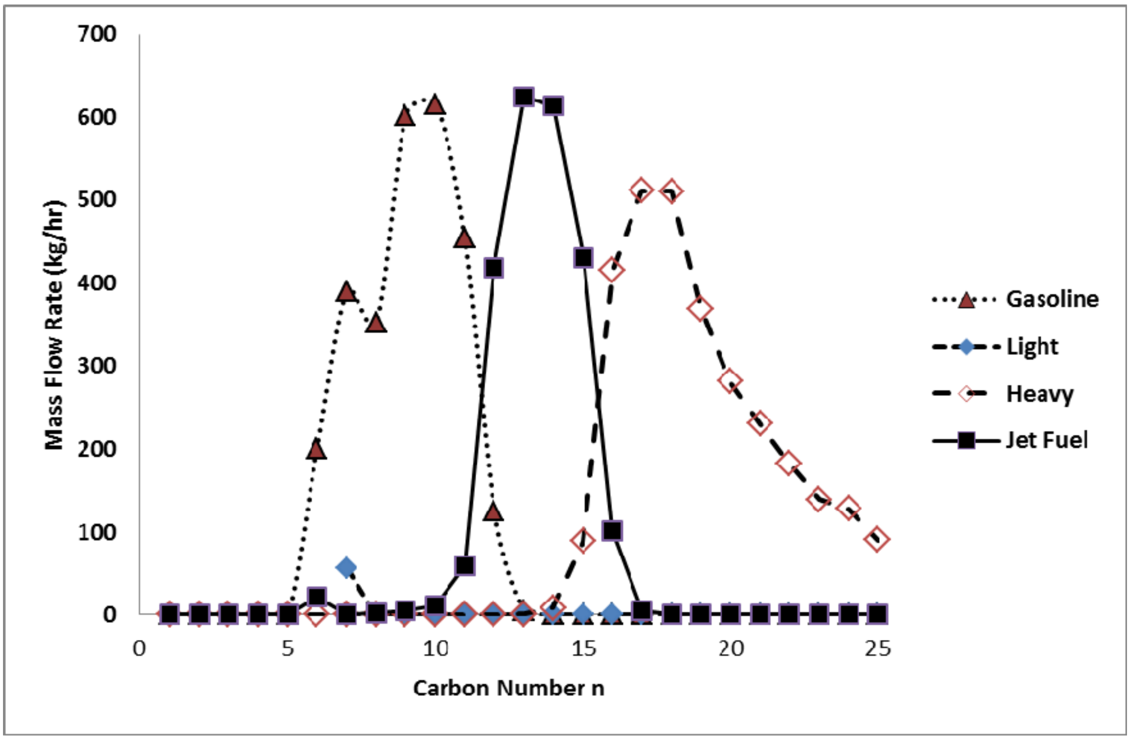


Figure 4.21: Mass flow rate of product streams out of the distillation tower

- Hydrocracker

The FTS heavy products need further hydrocracking to enhance the yield of fuel range products. Hydrogen is added to hydrogenate the products from the high molecular weight C_{15}-C_{25} to a lower paraffin fraction. A stoichiometric reactor is used to simulate the reactor with a temperature of 380 °C and pressure of 1400 psi [Ali, 2002]. Figure 4.22 shows the detailed mass flow rates coming out of the hydrocracker. The feed stream contains mainly the heavy carbon fraction from C_{15} to C_{25}. This is an important step to convert the unused heavy fraction to our desired products. However, it could also be separated as base stock for lubricant if there is a base oil plant nearby. After hydrocracking, the product stream is rich in the fuel product fractions from C_5 to C_{13} as shown in the figure below.

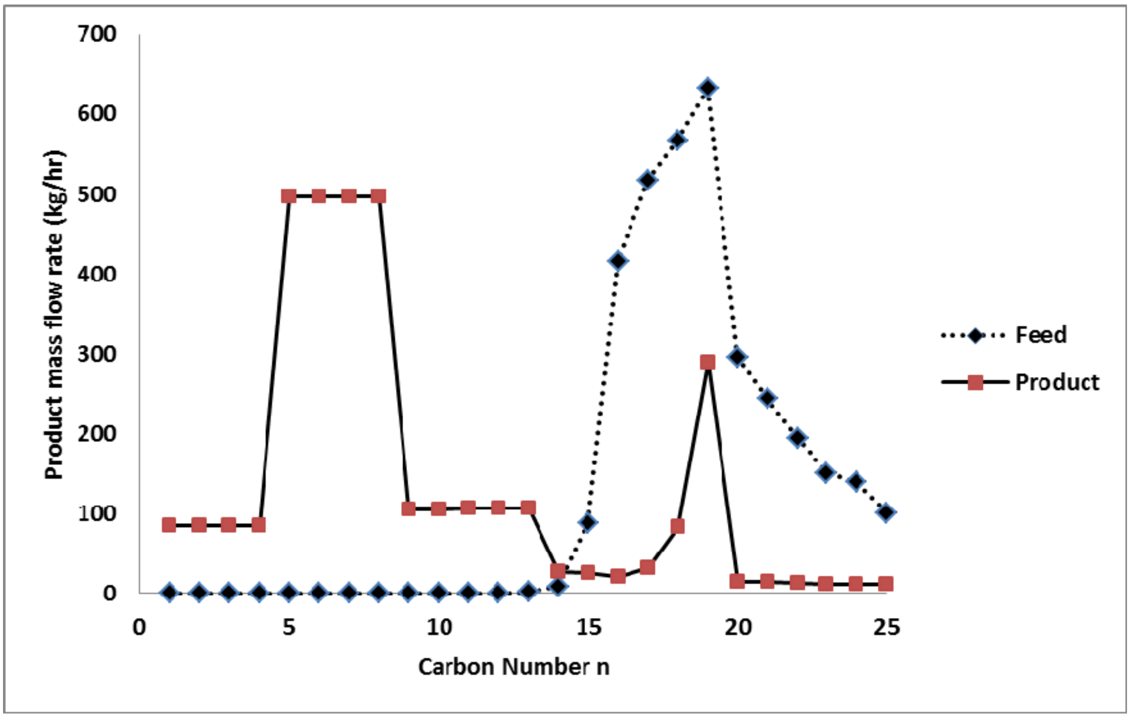


Figure 4.22: Mass flow rate of streams in and out of the hydrocracker

- Second Distillation Column

The stream coming out of the hydrocracker is then introduced to a second middle distillate fractionation unit. The hydrocracked heavy hydrocarbons are further separated to produce additional gasoline and Jet-fuel. Similar to the first distillation tower, the light portion is recycled to the FT reactor feed. The light stream coming out of the distillation tower contains mainly the light carbon fraction from C_1 to C_5, which will be sent back to the FT reactor. The heavy (bottom products) fraction is mainly larger than C_{13}, which will be recycled back to the hydrocracking unit again. The product streams are shown in Figure 4.23.

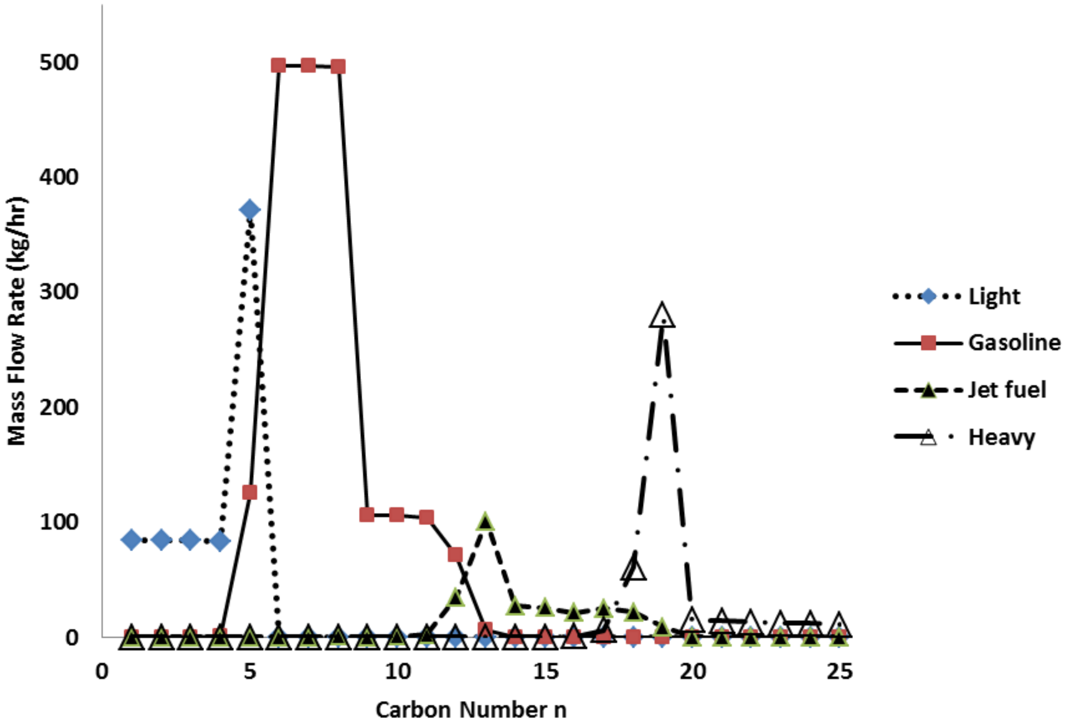


Figure 4.23: Mass flow rate of second distillation tower

4.3.2.4 SCF-FTS Fuel Production Results

SCF FT process produces a total of 7317kg/hr of fuel range products comprised of 4755 kg/hr of gasoline and 2562 kg/hr of jet fuel. Figure 4.24 shows the detailed distribution of product mass flow rate for the final products, gasoline and jet-fuel, and they are both in the appropriate carbon number range.

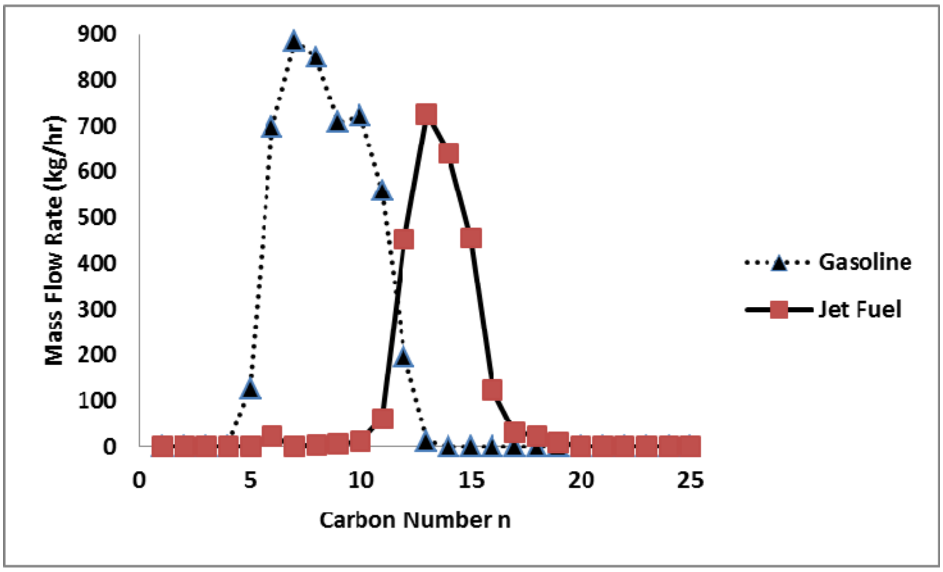


Figure 4.24: Mass flow rate distribution with different carbon numbers for gasoline and jet fuel products

4.3.3 Gas-Phase Fischer-Tropsch Process (Gas-FTS)

4.3.3.1 Process Illustration

In order to evaluate the potential of the novel supercritical FT process, a traditional gas phase FT reactor is simulated according to the experimental data from Elbashir (2005). Figure 4.25 is a simplified generic process block diagram representing the system considered here. In this process, synthesis gas produced from steam reforming is introduced into the system. The cleaned syngas is then introduced into the gas-phase FT reactor. After the FT reaction the off-gas is recycled and the liquid FTS products are treated to yield gasoline and jet fuel. The products from the reactor are introduced into a crude fractionation unit, for separation and recycling of unreacted syngas. Then the products are further refined in a distillation column to produce the desired FT fuels. An integrated cracking unit is added to hydrotreat/crack the heavy products. In this step, extra hydrogen is added to crack heavy products (C_{16}–C_{25}) back to light and middle distillates (C_1–C_{12}) for further processing. Another distillation column is introduced to recover additional gasoline and Jet-fuel. The light fraction from various processing units are fed into a reformer, where extra steam is added to react with the light hydrocarbon fraction to produce additional synthesis gas for recycle, avoiding purging a valuable stream.

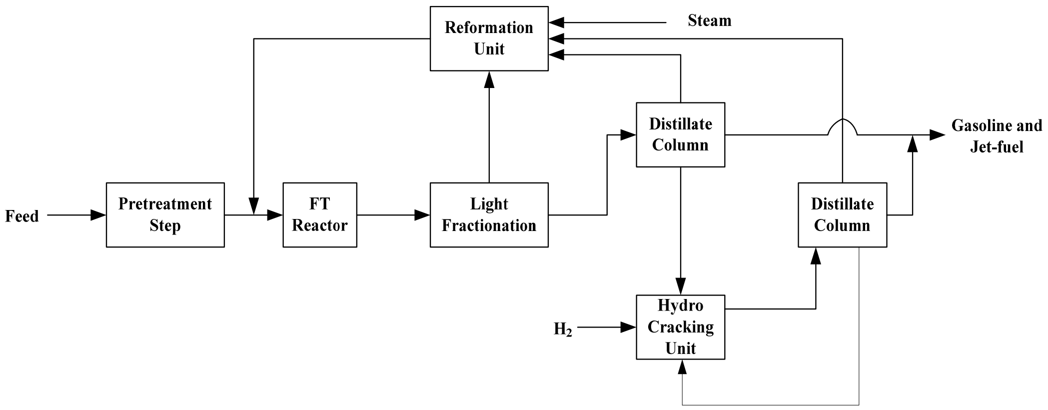


Figure 4.25: Gas-phase FT process block diagram

4.3.3.2 Model Specification and Results

Figure 4.26 shows the process model which was developed in Aspen Plus.

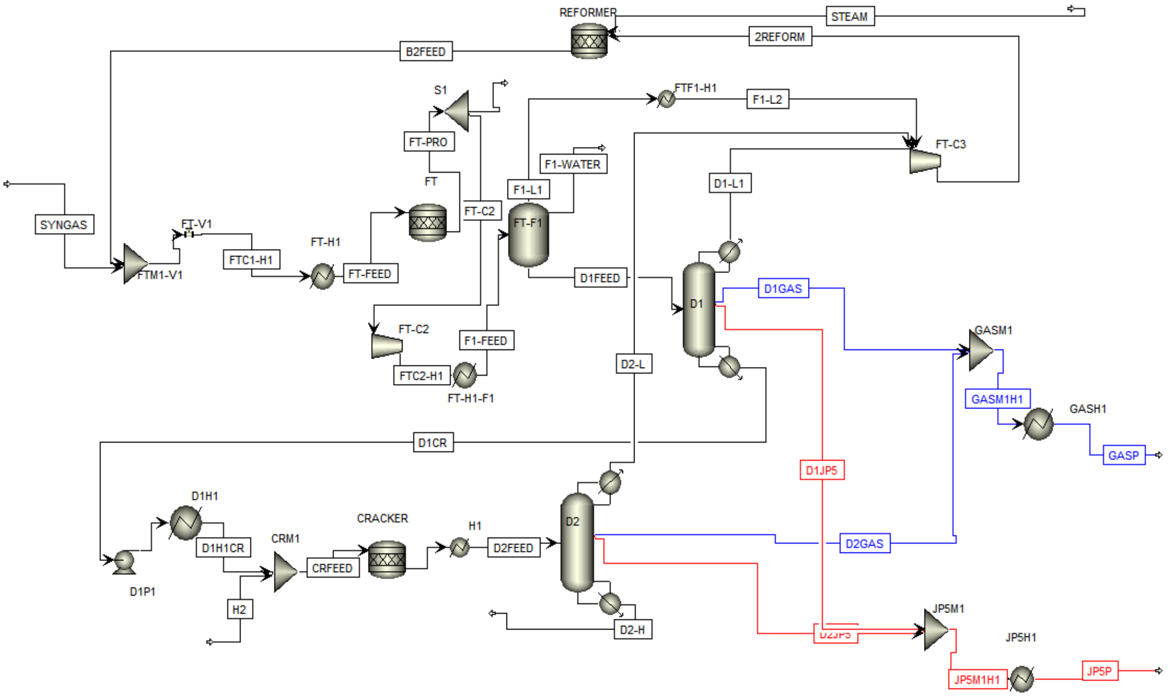


Figure 4.26: Gas-phase FTS model in Aspen Plus

- Fischer-Tropsch synthesis

The syngas feed flow rate is 2370 kmol/hr which is kept the same as in the supercritical FT model. Similarly, a multicomponent product with a wide range of hydrocarbon formed. The major products are paraffins, olefins and oxygenated products. In this work, only paraffins are considered as the products. The FT reaction operated at the same temperature of 250 °C but a different pressure of 20 bar with Co/Al_2O_3 as catalyst, because gas phase FT reactors do not require high pressure. The syngas H_2/CO ratio is still 2.17. The conversion of CO is reported to be 0.65 under these conditions [Van Der Laan, 1999]. The FT reactor is modeled as a stoichiometric reactor in Aspen Plus. Detailed reactions are shown in Table 4.5 below. The overall reaction is divided into individual sub-reactions of different hydrocarbons. The sum of all the individual conversions should be equal to the overall CO conversion of 0.65.

Table 4.5: Detailed Stoichiometry in Gas-FT Reactor.

Stoichiometry	**Conversion**
$CO + 3 H_2 \rightarrow CH_4 + H_2O$	0.15542490
$2 CO + 5 H_2 \rightarrow C_2H_6 + 2 H_2O$	0.00353901
$3 CO + 7 H_2 \rightarrow C_3H_8 + 3 H_2O$	0.01220428
$4 CO + 9 H_2 \rightarrow C_4H_{10} + 4 H_2O$	0.02010356
$5 CO + 11 H_2 \rightarrow C_5H_{12} + 5 H_2O$	0.04385817
$6 CO + 13 H_2 \rightarrow C_6H_{14} + 6 H_2O$	0.04858571
$7 CO + 15 H_2 \rightarrow C_7H_{16} + 7 H_2O$	0.04116813
$8 CO + 17 H_2 \rightarrow C_8H_{18} + 8 H_2O$	0.04170226
$9 CO + 19 H_2 \rightarrow C_9H_{20} + 9 H_2O$	0.04156033
$10 CO + 21 H_2 \rightarrow C_{10}H_{22} + 10 H_2O$	0.03700033
$11 CO + 23 H_2 \rightarrow C_{11}H_{24} + 11 H_2O$	0.03260203
$12 CO + 25 H_2 \rightarrow C_{12}H_{26} + 12 H_2O$	0.02848311
$13 CO + 27 H_2 \rightarrow C_{13}H_{28} + 13 H_2O$	0.02373892
$14 CO + 29 H_2 \rightarrow C_{14}H_{30} + 14 H_2O$	0.02130319
$15 CO + 31 H_2 \rightarrow C_{15}H_{32} + 15 H_2O$	0.01827218
$16 CO + 33 H_2 \rightarrow C_{16}H_{34} + 16 H_2O$	0.01560146
$17 CO + 35 H_2 \rightarrow C_{17}H_{36} + 17 H_2O$	0.01326815
$18 CO + 37 H_2 \rightarrow C_{18}H_{38} + 18 H_2O$	0.01124411
$19 CO + 39 H_2 \rightarrow C_{19}H_{40} + 19 H_2O$	0.00949896
$20 CO + 41 H_2 \rightarrow C_{20}H_{42} + 20 H_2O$	0.00655158
$21 CO + 43 H_2 \rightarrow C_{21}H_{44} + 21 H_2O$	0.00646039
$22 CO + 45 H_2 \rightarrow C_{22}H_{46} + 22 H_2O$	0.00589306
$23 CO + 47 H_2 \rightarrow C_{23}H_{48} + 23 H_2O$	0.00471601
$24 CO + 49 H_2 \rightarrow C_{24}H_{50} + 24 H_2O$	0.00393785
$25 CO + 51 H_2 \rightarrow C_{25}H_{52} + 25 H_2O$	0.00328232
Overall CO Conversion	**0.65**

Figure 4.27 illustrates the mass flow rate for different paraffin products in the gas phase FT reactor. Fewer C_1 to C_5 products were obtained here.

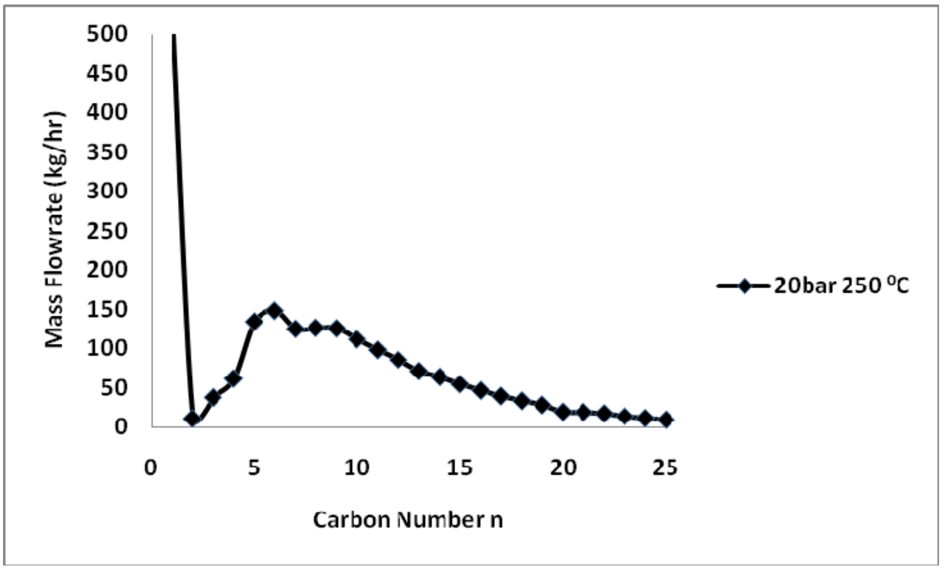


Figure 4.27: Gas phase FT reactor product distribution for different carbon numbers

- Crude fractionation

The effluent from the FTS reactor also contains unreacted carbon monoxide and hydrogen. The C_{5+} products are separated by a condenser and sent to the middle distillate fractionation and hydrocracking section, while unreacted H_2, CO, and lighter paraffin products are recycled. By combining the recycle gas with steam through a reformer, we can convert C_1-C_5 back to syngas. Figure 4.28 shows the detailed mass flow rates in and out of the condenser.

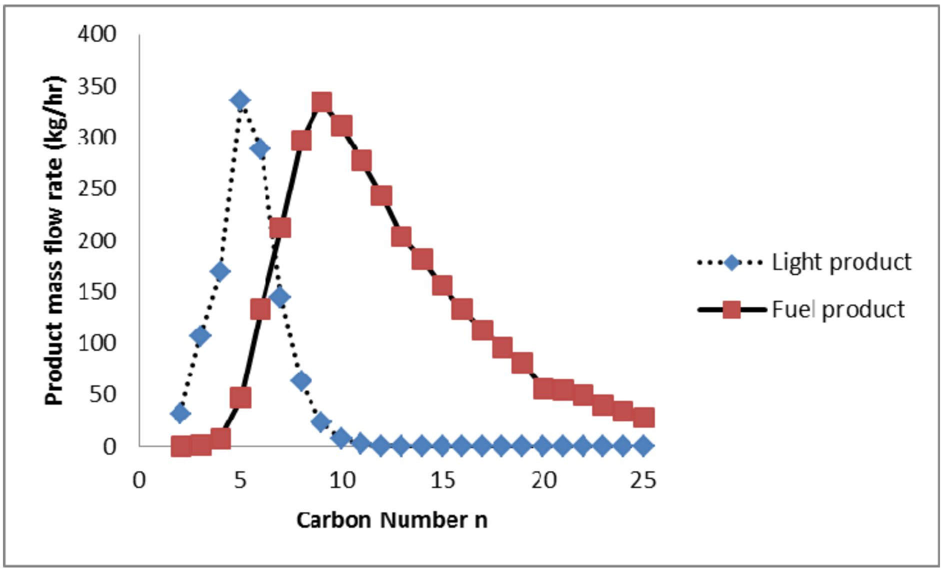


Figure 4.28: Mass flow rate of products out of the condenser

As we can see, after the condenser, we can obtain basically two product streams: light products, mainly containing C_1-C_5, which will be sent to the reformer to convert back to syngas; and the fuel product, which will be sent to the distillation step. The fuel products are mainly C_5-C_{15}, which will be further processed to gasoline and jet fuel.

- First Distillation Column

After the lights are recycled, the fuel products are introduced into a middle distillate fractionation unit. In this first distillation column, the C_5-C_{10} portion is separated from the heavier products such as gasoline and the C_{11}-C_{14} portion is separated as the Jet-fuel product. The C_{15+} portion is converted into smaller paraffins in a hydrocraking unit. Figure 4.29 shows the detailed mass flow rates out of the distillation tower. The light stream coming out of the distillation tower contains mainly the light carbon fraction from C_1 to C_5. This stream will be converted to syngas through a reformation process and recycled to the FT reactor. The heavy (bottoms) fraction is mostly larger than C_{15}, which will be introduced into a hydrocracking unit. The gasoline product is concentrated within C_5-C_{11} and the jet fuel product falls in the range between C_{11} to C_{14}.

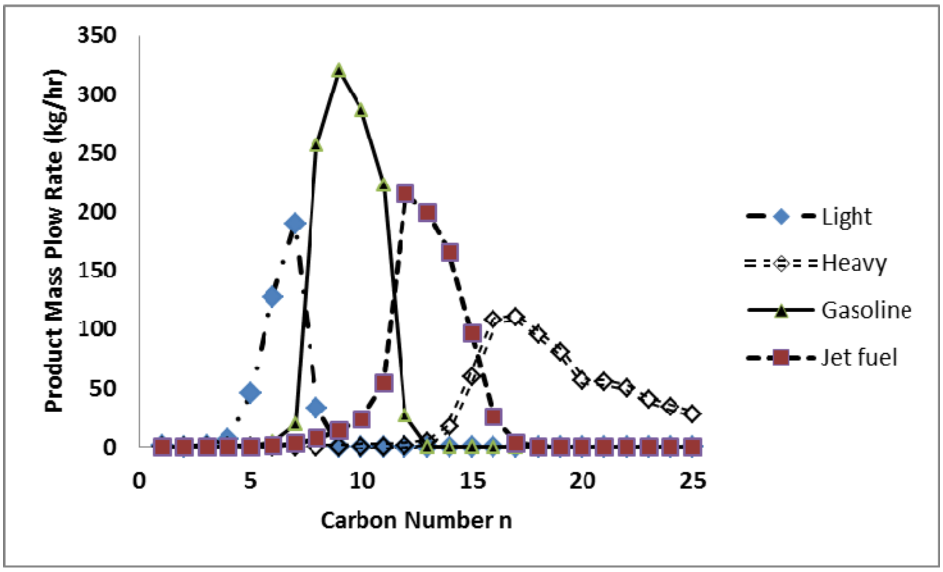


Figure 4.29: Mass flow rate out of the distillation tower

- Hydrocracker

Similarly, the FTS heavy product requires hydrocracking to increase the yield of fuel range products. Hydrogen is added to hydrogenate the stream from the high molecular weight C_{16}-C_{25} paraffin fraction. The reactor is operated at 380 °C and 1400 psi [Ali, 2002]. A stoichiometric reactor was used.

- Second Distillation Column

The stream coming out of the hydrocracker is introduced to a second distillation unit. Seen from Figure 4.30, the converted heavy hydrocarbons are further processed to produce gasoline and Jet-fuel. Similar to the first middle distillate tower, the light fraction is reformed back to syngas and recycled to the hydrocracker.

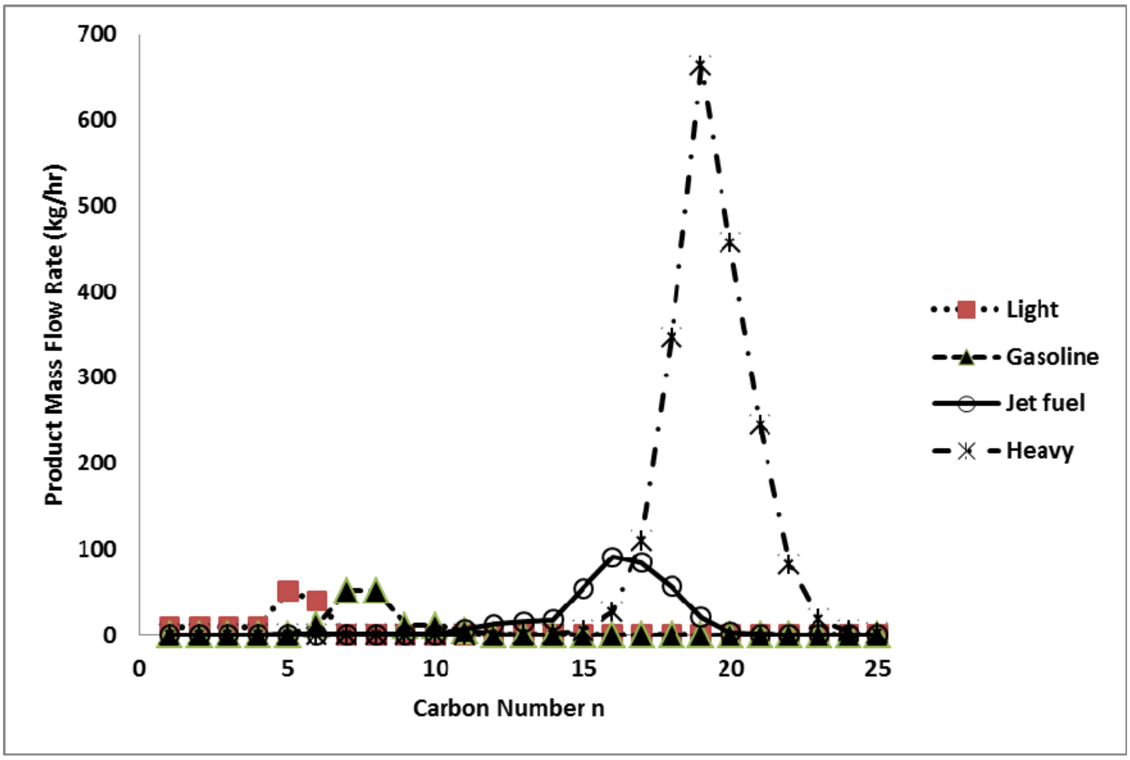


Figure 4.30: Product mass flow rate for different hydrocarbons from the second distillation column

- Reformer

To avoid costly purges in the FT system, a reformer is incorporated to convert the combined light hydrocarbon fraction from the condenser and two middle distillate units back to syngas. The reactions in the reformer are based on steam reforming data obtained at 1000 °C and 28.5 atm. All the light fractions are assumed to be converted back to syngas. A stoichiometric reactor is used to simulate the reactor. Then the syngas from the light fraction is combined with the initial syngas feed stream and fed into the FT reactor.

4.3.3.3 Gas-FTS Fuel Production Results

The gas phase FT process produces a total of 2449 kg/hr of fuel range products comprised of 1279 kg/hr of gasoline and 1170 kg/hr of jet fuel based on the same syngas feed rate. Figure 4.31 shows the detailed mass product carbon distribution for the final products, gasoline and jet-fuel.

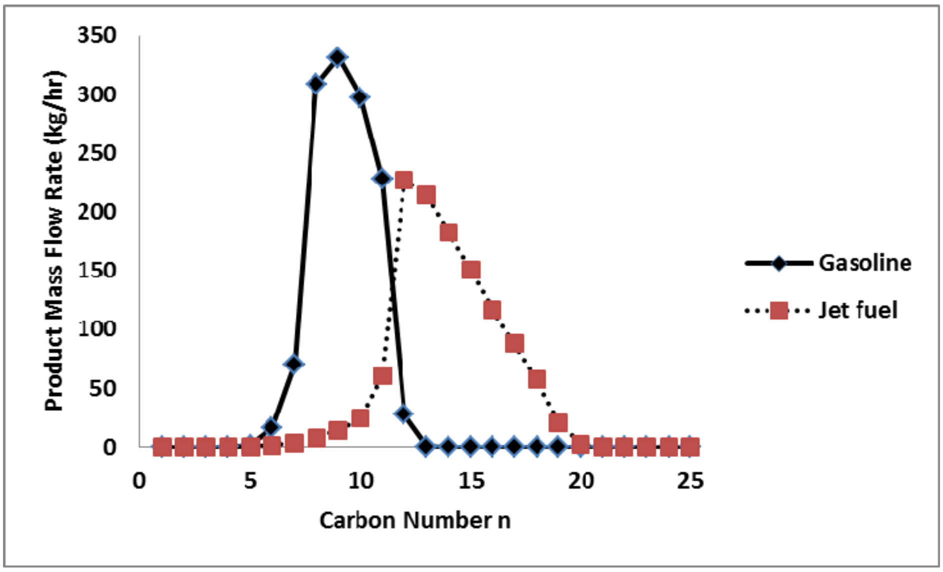


Figure 4.31: Gas phase fuel product carbon distributions

4.3.4 *Results and Discussion*

4.3.4.1 Fuel Production Cost Evaluation

Fuel production costs for both processes have been evaluated and compared. The evaluation process includes several procedures. The first step is to calculate the total equipment cost, estimated using the methods provided by Peters (2003). The utility cost is extracted from Aspen HX-Net^{TM} directly. Then the equipment and utility costs are translated into the total production cost according to the method provided by Peters *et al* (2003), which accounts for monitoring, engineering and so on.

The fixed capital investment (FCI), which has a linear relationship to the equipment cost, represents the installed process equipment with all elements that are needed for completing process operation. Working capital investment is the sum of monthly raw materials, labor supervision and maintenance. The raw materials cost is calculated based on the data from

Chemical Market Reporter2010 as follows: 0.0516 \$/mol for hexane, 0.00000828 \$/mol for water, 0.0049 \$/mol for hydrogen and 0.00202 \$/mol for syngas. The labor costs are then calculated based on work hours, processing steps, number of workers, etc. The total production cost is defined as the sum of all the raw materials, utilities, operating labor, operation supervision, service, maintenance, operating supplies, laboratory charges, overhead, administrative and distribution costs divided by the fuel production rate.

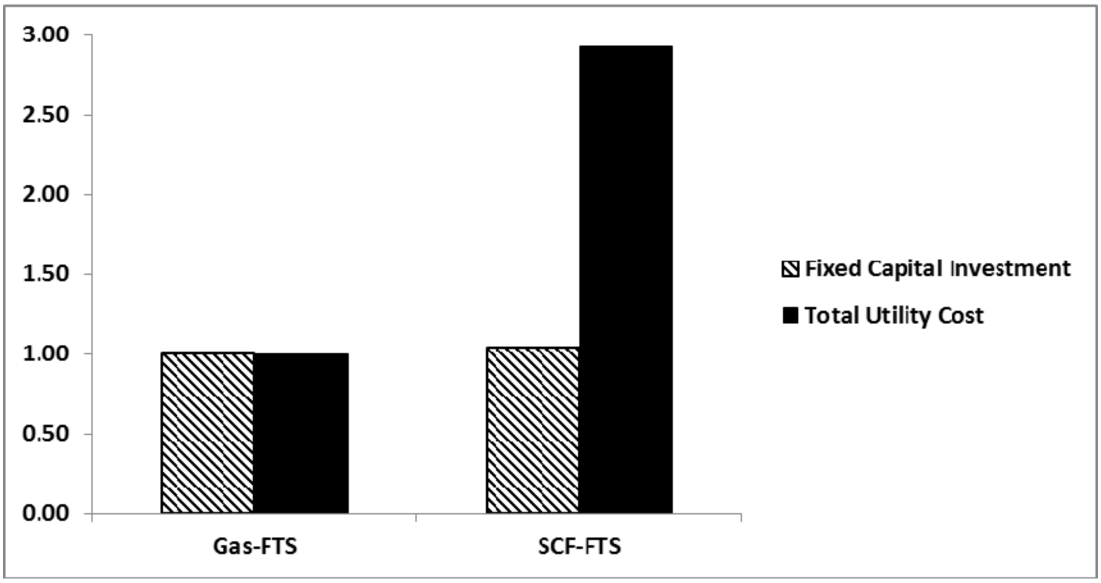


Figure 4.32: Relative cost analysis of gas phase and supercritical phase

Figure 4.32 illustrates the relative costs for fixed capital investment and total utility cost for both gas phase and supercritical phase FTS models. The fixed capital investments for both cases are on the same level. The major difference is the utility cost. Compared to the gas phase process, the utility consumption is much higher for the supercritical phase process. That is because more energy is needed to compress and heat the hexane stream to supercritical conditions and the extra unit for separating the inert solvent from the product stream increased the energy consumption. Moreover, the SCF-FTS reaction is operated at a relatively higher pressure, making it more energy intensive.

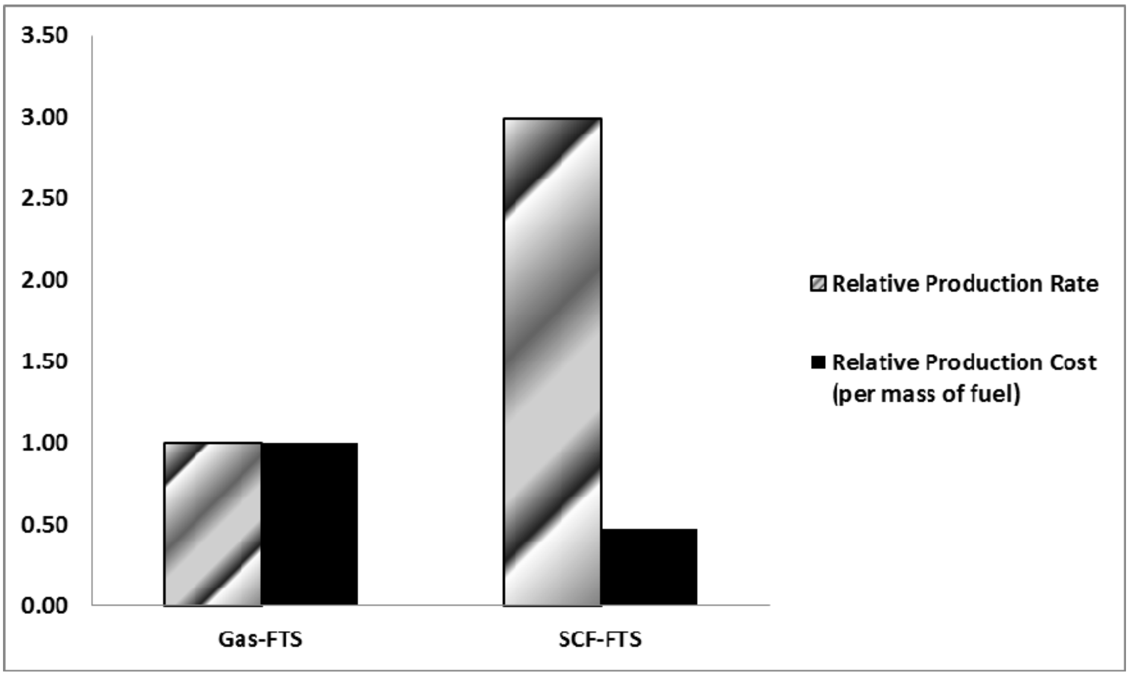


Figure 4.33: Production rate and cost comparison for different FTS processes

The total production rate and cost are normalized by setting the Gas-FTS model as baseline, which is shown in Figure 4.33. The supercritical phase process has high compressibility and desirable properties of gas-like diffusion along with liquid-like heat transfer and solubility properties, which provides better controlled FTS behavior. Therefore, with the same FT reactor feed, the fuel production rate of the SCF-FTS model is three times higher than that of the Gas-phase model. Although the SCF-FTS models has higher utility cost due to the high production rate, a much lower production cost can be observed, which is only half that of the Gas-phase process.

4.3.4.2 Environmental Performance

In order to ensure the final designs are not only optimal in economic performance but also environmentally friendly, environmental performance metrics are generated for both processes based on the WAR algorithm [Young, 2000]. The WAR algorithm looks at mass flows that are entering and leaving both the chemical process and the corresponding process that provides the energy. It calculates the environmental impact based on a weighting factor and normalized score. Environmental impact is measured through eight categories that include atmospheric and toxicological concerns, and databases are an excellent tool to decrease the work involved in determining the environmental impact of a chemical process. Figure 4.34 shows the results for both processes.

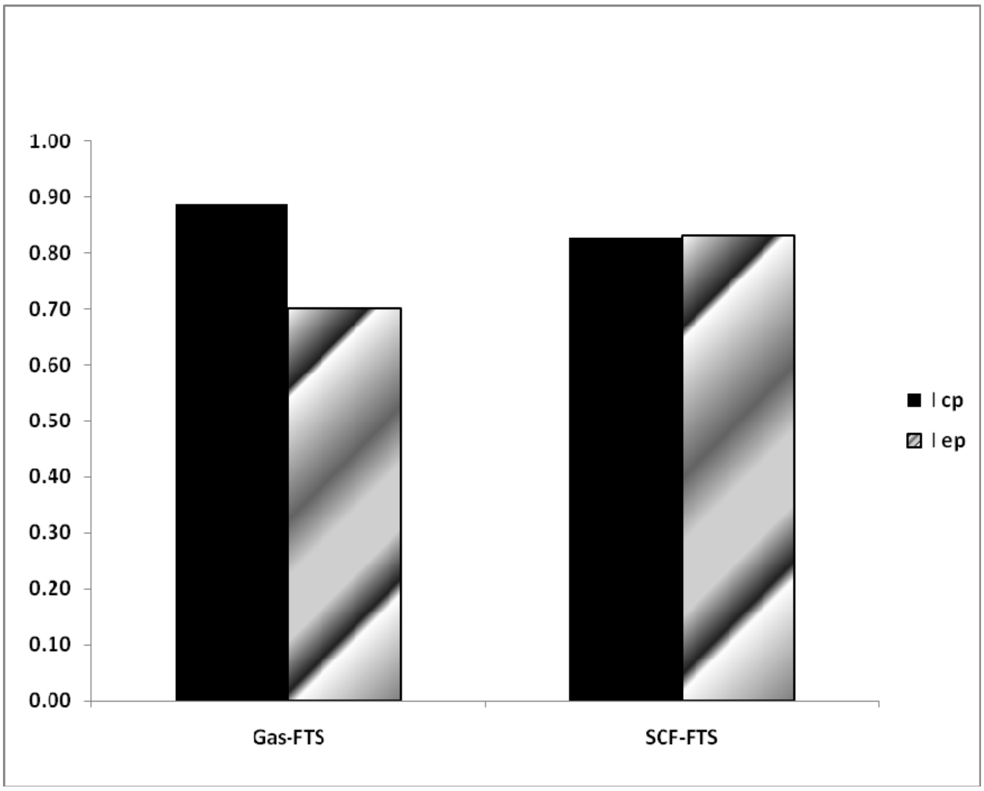


Figure 4.34: PEI analysis for large scale productions, where I cp and I ep stand for the impact of chemical processes and energy processes based on per kg product, respectively.

As we can see in figure 4.34, in terms of the impact of chemical processes, Gas-FTS has slightly more impact due to the inefficiency in the FT reaction. But SCF-FTS shows higher impact on energy processes because of the high energy demands in compression and heating as we analyzed before. In general, the overall environmental impacts of both models are very similar.

4.3.5 Conclusion

The main objective of this study was to construct and investigate the optimal flowsheet structures for gas-phase and supercritical phase Fischer-Tropsch processes. A conceptual design and corresponding ASPEN Plus simulation model was developed for the two Fischer-Tropsch (FT) fuel production processes. One great benefit of creating these models is that we can study and compare the effects of plant size, syngas conversion, and Fischer-Tropsch synthesis product distribution on the yields and cost of the plant for each Fischer-Tropsch process in the future.

The results show that although SCF-FTS is slightly more energy intensive, the production cost is much lower due to the savings in equipment, operating cost, and in particular higher production rate.

Chapter 5 Process Optimization Framework: Disjunctive-Genetic Programming

5.1 Introduction

Disjunctive-Genetic Programming (D-GP), based on the integration of Genetic Algorithm (GA) with the disjunctive formulations of the Generalised Disjunctive Programming (GDP) for the optimization of process networks, has been proposed to solve the framework. The genetic algorithm (GA) has been used as a jumping operator to the different terms of the discrete search space and for the generation of different feasible fixed configurations. This approach eliminates the need for the reformulation of the discrete/discontinuous optimization problems into direct MINLP problems, thus allowing for the solution of the original problem as a continuous optimization problem but only at each individual discrete and reduced search space. Segment-based Mutation (SBM) and Segment-based Floating Crossover (SBFC) strategies were proposed for the efficient handling of the population of chromosomes comprising the coded terms of the disjunctions.

Problems with nonlinear functions and discontinuities in the objective and/or constraint space can be found in many synthesis problems in process systems engineering. It has been shown that modeling these nonlinear optimization problems using disjunctions for the expression of discrete decisions which conditions the selection of process units (including variable intervals and cost functions) among various alternatives, can be very beneficial in the handling of discontinuities [Mussati, 2008; Vecchietti, 2003; Turkay, 1996b]. Turkay and Grossmann (1996a, 1996b, 1998) proposed Generalised Disjunctive Programming (GDP), a generalization of the

Disjunctive Programming by Balas (1985), as an efficient alternative to Mixed Integer Non-Linear Programming (MINLP) in problems that contain a combination of discrete and continuous objective functions and constraints. In GDP, problems are modelled with Boolean and continuous variables for the optimization of a given objective function subject to different types of constraints. GDP represents discrete decisions in the continuous space with disjunctions and constraints in the discrete space with logic propositions.

In their works, Grossmann and Lee (2003) used the GDP approach to model, among various benchmark problems they presented, a process network synthesis problem which was originally modelled via MINLP by Duran and Grossmann (1986a). Coupled with the convex hull formulation of this problem [Turkay, 1998], they were able to achieve, as in all the benchmark problems they analyzed, a global optimal solution in a reduced number of search nodes. This solution method, however, resulted in a higher number of variables and additional constraint equations as a result of the partitioning of the original variables into the number of terms necessary for each disjunction. An important difference between GDP and MINLP for the solution of discrete/continuous optimization problems is that GDP facilitates the representation of discrete decisions through the combination of algebraic and logic equations, while MINLP is based wholly on algebraic equations and inequalities. Further examples of the application of GDP to different classes of process synthesis problems are available in literature [Mussati, 2008; Farkas, 2005; Oldenburg, 2005; Caballero, 2004].

As in all optimization problems, finding a set of solutions that can guarantee convergence and lead to the globally optimal solution is an important and non-trivial task, especially when nonlinear equality constraints and non-convex functions are involved. This can be further worsened by the presence of discrete decisions which could lead to infeasible solutions if not explicitly modelled and adequately handled using appropriate algorithms. An infeasible or even suboptimal solution in the discrete or binary space will never lead to an optimal solution of the synthesis problem. Many solution strategies have been proposed for the solution of discrete/continuous optimization problems modelled either as an original MINLP problem, or as reformulations of GDP problems. These strategies, now termed as standard methods, among others include the Branch and Bond (B&B) method [Dakin, 1965; Garfinkel, 1972; Gupta, 1985; Stubbs, 1999], the Outer Approximation (OA) method [Duran, 1986b], the Logic-based OA method [Bergamini, 2005], the Outer Approximation with Equality Relaxation and Augmented Penalty method (OA/ER/AP) by Viswanathan and Grossmann (1990), and the LP-NLP based Branch and Bond method [Quesada, 1995]. However, the formulation of these models could be very difficult and time consuming. Current techniques for the solution of GDP problems reformulated to logic based MINLP problems involve the iterative solution of MILP master problems and NLP sub-problems with fixed configurations. At the beginning of the MILP-NLP iterative procedure, an initial NLP problem is solved, where the integrity conditions of the propositional logical statements (represented by Boolean variables with values True or False, or 1 or 0, to denote the existence or non-existence of a unit, equipment, or process), are relaxed, and the information about the obtained solution is used for the construction of the MILP master problem. Though this approach has been widely used, the choice of good initial points of the optimization variables still remains an important factor to consider [Noronha, 1997; Manninen, 1998]. Furthermore, for the solution of the MILP master problem, cumulative information about the linearization of the constraint and objective functions at the earlier NLP iteration solution points, as well as feasibility (or integer) cuts (Emhamed, 2005; Maravelias, 2004) are needed. As the number of iterations is increased, the dimensionality and complexity of this master problem increase, making the optimization problem very difficult to converge, and leading to possible generation of local solutions which may not be optimal, or even infeasible solutions (configurations) in this MILP space, unless an alternative robust and efficient evolutionary, purely deterministic, or a hybrid deterministic-stochastic search algorithm is used.

Evolutionary search methods, of which the most widely used is the Genetic Algorithm (GA), originally initiated by Holland (1975), has been known to be less susceptible to ending in local optimal solutions in optimization problems, yielding very good solutions even with discontinuous objective and/or constraint functions. The use of GA in chemical engineering applications has been consolidated in several published works [Androulakis, 1991; Coello, 2000; Deb, 2000; Michalewicz, 1996]. In many of these works, the evolutionary search method solutions have been found in some cases to outperform those obtained through traditional deterministic approaches, among other factors, by exhibiting robustness through the use of the objective function information and not derivatives, and due to the ease at which they handle discrete and integer variables as well as non-smooth and non-continuous functions. Yet, the overall applicability of these algorithms to constrained problems remains an active research focus, especially taking into consideration the fact that they may exhibit slow convergence and may have difficulties finding the optimal solution to a problem with very small feasibility space. However, promising results are being obtained in joint heuristic and evolutionary (deterministic and stochastic) approaches to the efficient solution of engineering processes. Lewin et al. (1998a, 1998b) synthesized cost-optimal heat exchanger networks using stochastic optimization approaches. In their work, Cai et al. (2001) applied a combined GA-Linear Programming (LP) approach to the solution of a number of network management models, obtaining very satisfactory results.

The following work is based on the integration of the GA with the disjunctive representation of discrete/continuous optimization problems. The strategy involves the decoupling of the disjunctions and the propositional logic from the overall disjunctive formulation to the GA space where these constraints are treated before being returned as active terms with satisfied logic to the resulting NLP space. The population of disjunctive terms, corresponding to the different process superstructures or configurations, are manipulated by the genetic operators in an evolutionary manner in order to obtain the best NLP solution. The implication of this is the final solution of an optimization problem with smooth nonlinear constraints and objectives confined within a reduced search space corresponding to specific active terms of a set of disjunctions, as determined by the GA. An advantage of this approach, as will be seen, is that, apart from the fact that the dimensionality of the optimization problem can be considerably reduced due to the reduction in the total number of constraint equations (only common and active disjunctive terms equations are analysed at each NLP call), only feasible superstructures are generated. As such, the resulting problems can be easily solved using widely available direct NLP methods such as the reduced-gradient or other deterministic methods.

5.2 Disjunctive formulation of discrete/continuous optimization problems

In general discrete/continuous optimization problems can be represented by disjunctions, Boolean variables, and propositional logical statements, as given by Problem A below [Turkay, 1996b; Lee, 2000]:

$$
\begin{aligned}
&\min Z = \sum_{k \in K} c_k + f(x) \\
&s.t. \quad r(x) \le 0 \\
&\qquad\ \ s(x) = 0 \\
&\qquad \bigvee_{j \in J_k} \begin{bmatrix} Y_{jk} \\ g_{jk}(x) \le 0 \\ h_{jk}(x) = 0 \\ c_k = \lambda_{jk} \end{bmatrix}, k \in K \\
&\qquad\ \ \Omega(Y) = True \\
&\qquad\ \ x \ge 0,\ c_k \ge 0, \\
&\qquad\ \ x \in R^n \\
&\qquad\ \ c \in R^m \\
&\qquad\ \ Y_{jk} \in \{true,\ false\} \qquad (A)
\end{aligned}
$$

In this representation, the continuous variable is represented by x. The disjunction $k \in K$ consists of a number of terms $j \in J_k$ inter-separated by the logical OR operator. Each term of a disjunction comprises a Boolean variable, represented by Y_{jk}, sets of inequality and equality constraints, and a cost variable c_k, which consists of fixed charges denoted by λ_{jk}. Here these disjunctions may represent a process, process unit, or equipment such as heat exchangers, pumps, reactors, and distillation columns. The terms of the disjunctions may represent the different configurations of these units or processes, such as types of distillation column, areas of reactor, or different processing routes. The logic proposition, expressed in the conjunctive normal form and in terms of the Boolean variables, is given by $\Omega(Y) = True$. This implies that at least one term of a disjunction interconnected by the OR operator must be true. If Y_{jk} is true, then the constraint equations as well as the cost functions of the corresponding *j* term are enforced; otherwise they are ignored. The function *r(x)* represents sets of constraint equations that are common to all alternatives, and they hold independent of the discrete decisions.

Different approaches have been used for the solution of the discrete/continuous optimization problem presented in Problem A. Current programming approaches involve the reformulation of the Big M-Outer Approximation formulation and the convex hull formulation as proposed by Turkay and Grossmann (1996a), smooth approximation, piecewise linear approximation, and the direct NLP approach. It should be noted, however, that the direct NLP approach, being the most trivial of all the approaches, may lead to unreliable results if the discontinuities are not effectively defined [Turkay, 1996b]. In this chapter, it is shown that discontinuities in the cost and constraint functions modelled as disjunctions can be effectively handled through decoupling from the traditional optimization model and handling within a GA framework, thus allowing for the efficient solution of large scale combinatorial discrete functions and reduced NLP problems using available deterministic algorithms.

5.3 Genetic algorithms

Genetic algorithms (GAs) belong to the group of stochastic evolutionary search methods that are analogous to the natural evolution process [Michakewicz, 1992; Goldberg, 1989]. GAs can encode highly complex individuals and the gradual transformation (evolution) of these individuals through collective learning processes to the global optimal solution. Since evolutionary methods do not use any information about function derivatives, this has made GA methods more attractive in cases where conventional deterministic approaches fail. The individual in the GA contains sets of parameters which represent potential candidate solutions to the optimization problem.

Generally, genetic algorithms involve five different components: the representation of individuals in terms of chromosomes which encodes possible solution alternatives, an evaluation function which may correspond to the objective function of the optimization problem, rating of these individuals according to their current fitness using the evaluation function, alteration of parent individuals to reproduce children, and the genetic parameters. These genetic parameters define the performance of the GA and include the size of the population, the number of generations, the selection procedure, the mutation rate, the crossover type and rate. Of these, the crossover parameters and procedures greatly affect the evolutionary process since they define the reproduction process of offspring to subsequent generations.

The GA first creates a pre-specified population size of randomly generated chromosomes, which could be random values of a set of variables, or different configurations of a process network. This is followed by calculation of the fitness of these individual chromosomes using a fitness or objective function. The population of chromosomes with their corresponding fitness value are sorted in order to identify individual chromosomes which will not only take part in the reproduction of children through the crossover operations, but also when specified, pass over to the next generation without alteration (elitism). These chromosomes are called parents, and are usually those within the highest score range according to the fitness function.

For the crossover operation, pairs of parents are selected at random, and this is followed by the swapping of parts of the components of one parent chromosome to the other. As a result, the generated offspring (child) contains structures from two high-ranking parents. In order to guarantee the diversity of the genetic algorithm and to avoid the algorithm getting entangled in local optimum solutions through loss of potential feasible structures, mutation is performed. This is basically the random alternation of the components of a chromosome. The parent selection, crossover and mutation form the process called reproduction. The whole process is repeated a number of times which corresponds to the number of generations, until a convergence criterion is met. Different convergence criteria have been developed and proposed for GAs [Leboreiro, 2004;

Reeves, 1997]. In this work, the termination of the genetic algorithm is based on the attainment of the maximum specified number of generations.

5.4 The D-GP concept for optimization problems with discontinuous functions

The basic idea behind the D-GP approach involves the decoupling of the disjunctive terms, represented by the Boolean variables as well as the proposition logic-based constraints formed by these variables, to the genetic algorithmic space where they are encoded into chromosomes with specific structures corresponding to potential superstructure solution alternatives. In a typical solution framework such as the Big M -OA approach [Williams, 1999], the reformulation of optimization problems with discontinuous functions modelled with disjunctions would involve the conversion of the Boolean variables to binary and logical proposition into simple linear equations, leading to MINLP problems which in turn could be solved using an iterative MILP-NLP scheme as shown in figure 5.1. An important feature of our proposed approach is that no MINLP reformulation of the disjunctive representation is needed. Terms of the disjunctions only need to be identified, well defined, and coded into strings or chromosomes. To facilitate the adaptation of GA for efficient handling of the class of generated chromosomes, special operators for segment-based crossover and mutation are proposed. Furthermore, we apply the all-feasible populations approach, consisting of the creation and use of chromosomes that always satisfy the logical constraints [Odjo, 2008; Yuan, 2009]. The basic steps of the D-GP framework are depicted in figure 5.2.

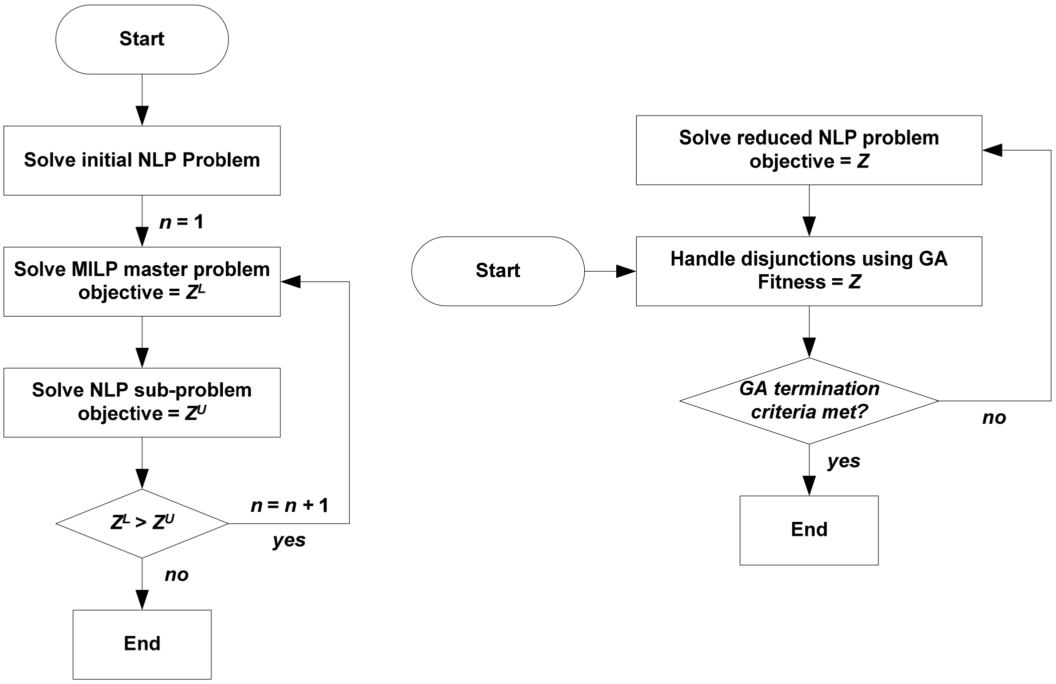


Figure 5.1: (left) MILP-NLP iterative solution approach, and (right) the GA-NLP framework

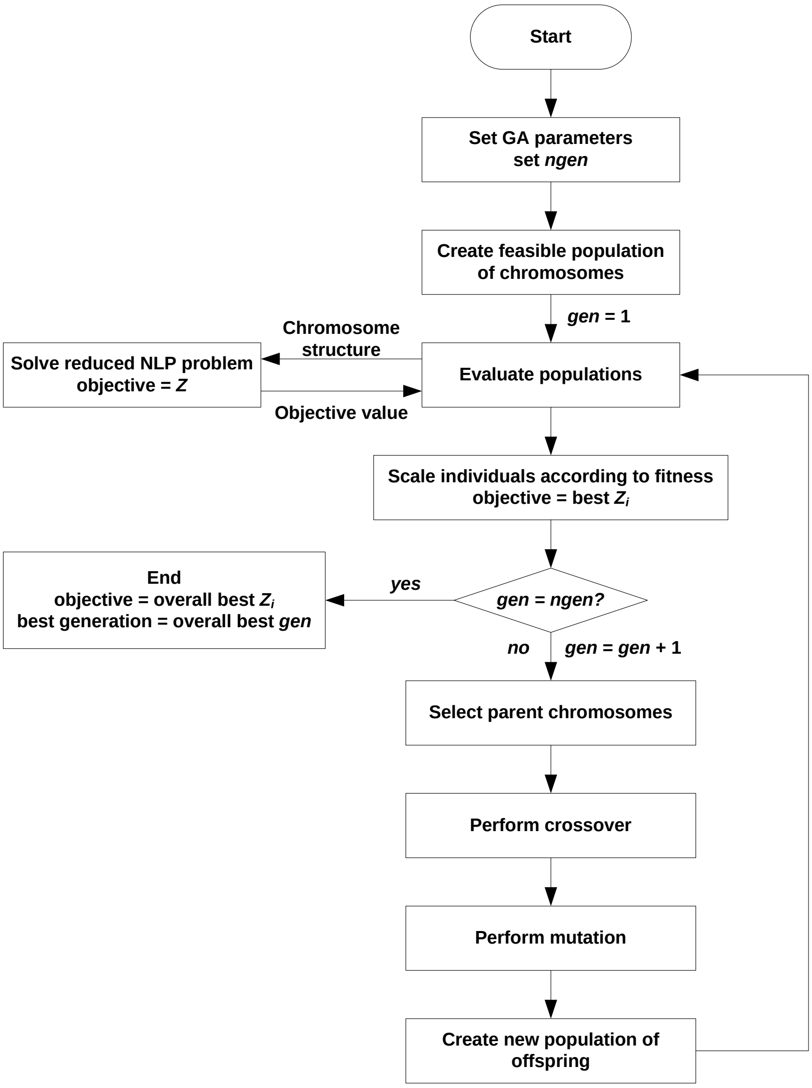


Figure 5.2: The D-GP solution framework

5.4.1 Real codification of the disjunctive terms

Given a set of disjunctions d_k, where $k \in K$ each with terms t_j, and where $j \in J_k$ as represented in problem A; a chromosome $i \in P$, where P is a population whose size is defined by a pre-specified value npop (number of population) will have the following basic parameters:

$$L = \sum_j \sum_k t_{jk} + 2 \qquad \text{(Eqn. 5.1)}$$

$$S = \sum_k d_k + 1 \qquad \text{(Eqn. 5.2)}$$

Here, L and S are the length (total number of genes) and the total number of segments, respectively, of a chromosome. In this work, real-coded chromosomes [García-Martínez, 2008] are adopted instead of binary codifications which have been shown to exhibit poor performance when dealing with chromosomes with large L values [Chang, 2006; Achiche, 2004]. Each chromosome has been codified such that each gene takes a real numerical but random value of the Boolean variables (0, 1). It is worth noting that a segment sq, where $q=1 \ldots S$, of a chromosome i will have a length $l_s = \sum_j t_j, \quad \forall q = k$.

In each chromosome, two special genes, corresponding to the constant at the right hand side of Eq. 5.1, store information about the performance of that particular chromosome, namely the termination criteria at each NLP call and the GA fitness value, which invariably equals the objective function value of the reduced NLP problem that used the structure of that chromosome as the fixed configuration. The numerical values of these two genes (hereby known as the performance segment, corresponding to the constant of Eq. 5.2), play the most important role in the scaling of individuals of the population and in child breeding during crossover and mutation operations.

5.4.2 Creation of the initial population: Population of feasible chromosomes

A basic and important step in the application of GA to the solution of optimization problems is the creation of a population of random individuals, in our case, *P*, with a fixed number of members *npop*. This population typically corresponds to the search space of the optimization problem (e.g. *npop* numbers of randomly generated temperature or pressure values between a specified lower and upper limit). This is particularly trivial if the feasible region of the problem is as large as the search space. However, synthesis problems with a large number of variables give rise to huge combinatorial problems such as different candidate flowsheet configurations for a process with a large number of units and process streams. When this is coupled with the existence of a narrow feasibility region due to different specifications and restrictions, the traditional approach of generating the individuals within the optimization search space might lead to slow convergence and even sub-optimal solutions. Therefore, in this work, a population of feasible chromosomes approach is adopted. The basic idea behind this approach is portrayed in figure. 5.3 and will be explained in detail in the example involving the synthesis of a simple heat exchanger network with cost functions defined over multiple areas of the equipment. As will be seen, the important aspect of this approach is that infeasible chromosomes have been eliminated from the initial population before the GA fitness function evaluation stage, in contrast to the traditional approach where feasibility constraints defined by the logic propositions and embedded as linear algebraic equations were satisfied during the GA fitness function evaluation.

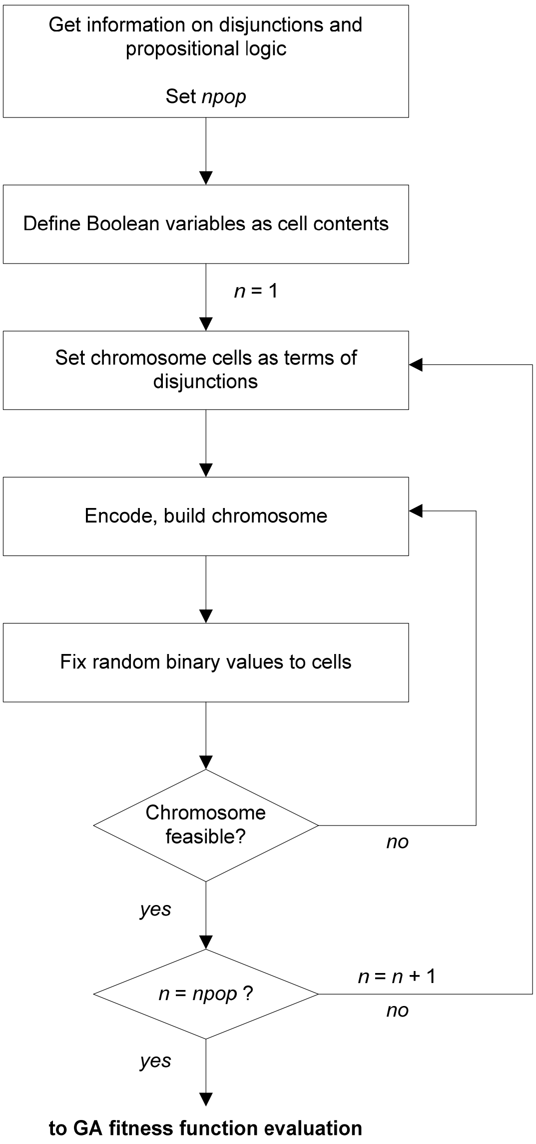
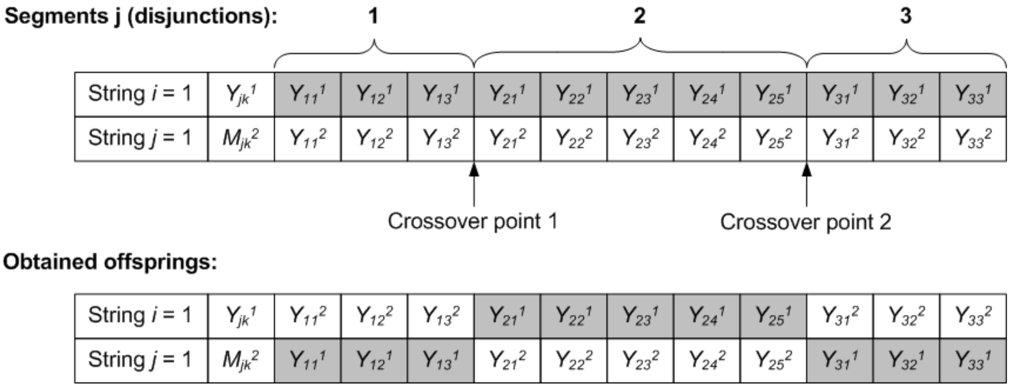


Figure 5.3: Generation of populations of feasible chromosomes

5.4.3 Segment-based Floating Crossover Operation Strategy

In order to not only conserve parts of the feasible configuration from the parents to the offspring, but also to achieve less disruptive chromosomes, the crossover operation strategy employed in this work involved the selection of two strings (parent chromosomes) with consistent identification and exchange of identical segments of the parents. The number of identical segments in a parent string or chromosome is dependent not on the size of the optimization problem, but on the number of disjunctions in the synthesis problem, as the genes in each segment would represent the terms of the disjunctions. The rules governing the crossing over of the identical segments involve the selection and direct inter-exchange of the bulk of those segments, but not the individual genes within the segments. Consider a network synthesis problem expressed in disjunctive form with 3 sets of disjunctions, two of which carry three terms each, and one with 5 terms (Problem B). The chromosomal codification (without the performance segment) of these disjunctions will be given by the parent strings in figure 5.4. The numbers of segments for crossover and their position were chosen at random. Segments in the parent string or chromosome comprising only two genes could be crossed over using the linear crossover operation proposed by Tang et al. (1998). In this study, such segments were not modified in order to increase the feasible configurations of the obtained offspring.

$$
\begin{aligned}
&\min \quad Z = f(x) \\
&s.t. \\
&\begin{bmatrix} Y_{11} \\ \ldots\ldots \end{bmatrix} \vee \begin{bmatrix} Y_{12} \\ \ldots\ldots \end{bmatrix} \vee \begin{bmatrix} Y_{13} \\ \ldots\ldots \end{bmatrix} \\
&\begin{bmatrix} Y_{21} \\ \ldots\ldots \end{bmatrix} \vee \begin{bmatrix} Y_{22} \\ \ldots\ldots \end{bmatrix} \vee \begin{bmatrix} Y_{23} \\ \ldots\ldots \end{bmatrix} \vee \begin{bmatrix} Y_{24} \\ \ldots\ldots \end{bmatrix} \vee \begin{bmatrix} Y_{25} \\ \ldots\ldots \end{bmatrix} \\
&\begin{bmatrix} Y_{31} \\ \ldots\ldots \end{bmatrix} \vee \begin{bmatrix} Y_{32} \\ \ldots\ldots \end{bmatrix} \vee \begin{bmatrix} Y_{33} \\ \ldots\ldots \end{bmatrix} \\
&\Omega(Y_{jk}) = TRUE \\
&Y_{jk} = \{TRUE, FALSE\} \\
&Y_{11} \vee Y_{12} \vee Y_{13} \\
&Y_{21} \vee Y_{22} \vee Y_{23} \vee Y_{24} \vee Y_{25} \\
&Y_{31} \vee Y_{32} \vee Y_{33} \qquad\qquad\qquad\qquad\qquad\qquad (B)
\end{aligned}
$$



String i = 1	Y_{jk}^1	Y_{11}^1	Y_{12}^1	Y_{13}^1	Y_{21}^1	Y_{22}^1	Y_{23}^1	Y_{24}^1	Y_{25}^1	Y_{31}^1	Y_{32}^1	Y_{33}^1
String j = 1	M_{jk}^2	Y_{11}^2	Y_{12}^2	Y_{13}^2	Y_{21}^2	Y_{22}^2	Y_{23}^2	Y_{24}^2	Y_{25}^2	Y_{31}^2	Y_{32}^2	Y_{33}^2

String i = 1	Y_{jk}^1	Y_{11}^2	Y_{12}^2	Y_{13}^2	Y_{21}^1	Y_{22}^1	Y_{23}^1	Y_{24}^1	Y_{25}^1	Y_{31}^2	Y_{32}^2	Y_{33}^2
String j = 1	M_{jk}^2	Y_{11}^1	Y_{12}^1	Y_{13}^1	Y_{21}^2	Y_{22}^2	Y_{23}^2	Y_{24}^2	Y_{25}^2	Y_{31}^1	Y_{32}^1	Y_{33}^1

Figure 5.4: Adopted crossover operation strategy for the D-GP approach

5.4.4 Segment based mutation

Mutation, carried out at random on any bit of a string (gene) of the population, often leads to infeasible configurations. This can be improved, however, if the operator is modified by incorporating specific information on desired mutation routes. For example, rather than executing mutations on individual genes, mutations were performed on segments of specific size and position in the string, corresponding to individual disjunctions and the order in which they are placed, respectively. It is worth noting that the length of each segment (or the number of genes within) corresponds to the number of terms in each disjunction. In this work, this leads to the creation of mutant genes, which can be considered sets of disjunctions of the current problem with different configurations of propositional logic. Consider the set of disjunctions in Problem B. The propositional logic constraints in this equation imply that only one of the terms of each disjunction must hold (that is $Y_{jk} = 1$), while the remaining terms are false (that is $Y_{jk} = 0$ for any $Y_{jk} \neq 1$). Consider the parent string *i=1* in figure 5.4. If the current numerical configuration of this chromosome is assumed to be given as the parent string in figure 5.5a, an example of a traditional mutation operation would involve random replacement of one or more genes in the chromosome, which may potentially lead to infeasible mutated strings. Instead, in this work, sets of mutant genes were created and randomly chosen to replace segments with equal length in the parent chromosome. Segments to be replaced were also selected randomly, and in this way, diversity of the next population was guaranteed without loss of feasibility.

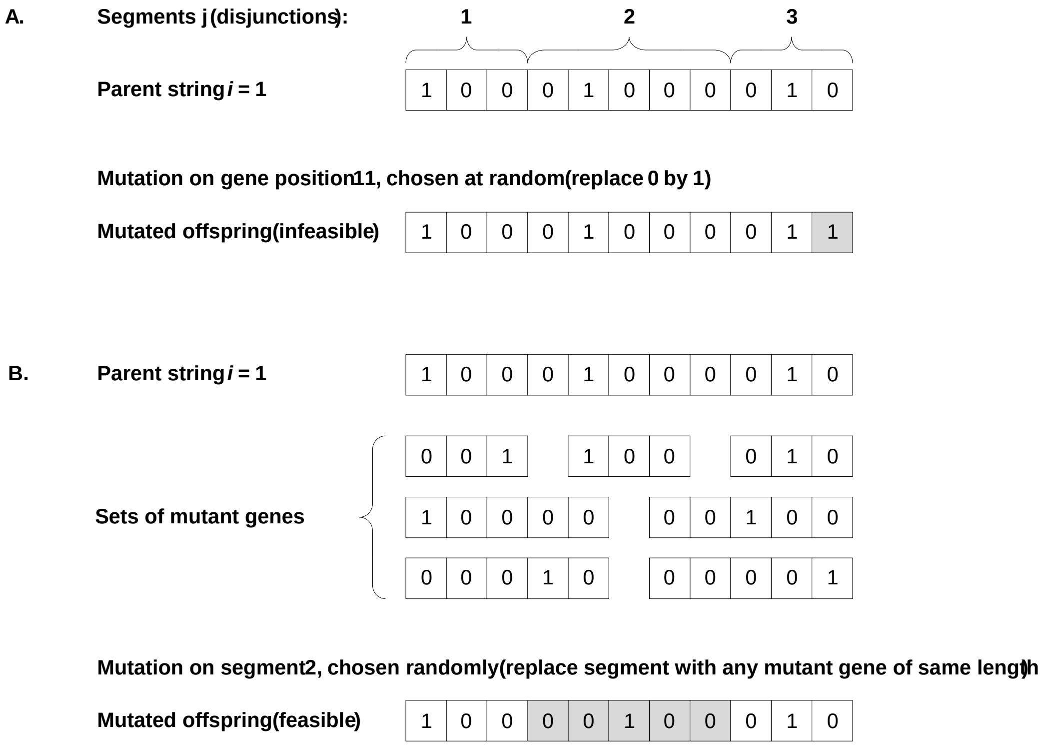


Figure 5.5: (a) Traditional mutation with infeasible offspring, and (b) proposed segment based mutation with mutant genes

5.5 Application of the D-GP approach to process synthesis problems.

The efficacy and the applicability of the D-GP approach was tested on a number of small and medium scale optimization problems with discrete/continuous functions. Example 1 is used for illustrative purposes, where the proposed different GA operators are further elaborated.

5.5.1 Example 1: The 3 heat exchanger network

The following example was taken from Turkay and Grossman (1996a), though with a slight modification for ease of demonstration and simulation in a modular simulator environment as given by [Caballero, 2006; Caballero, 2007]. The heat exchanger network consists of a tubular heat exchanger, a heater, and a cooler (E101, E102, and E103 respectively), interconnected as shown in figure 5.6. Specifically, the problem involves the optimization of process models with discontinuous cost functions and fixed charges defined over different area regions of the heat exchangers. More details on this problem can be found in Turkay and Grossman (1996b).

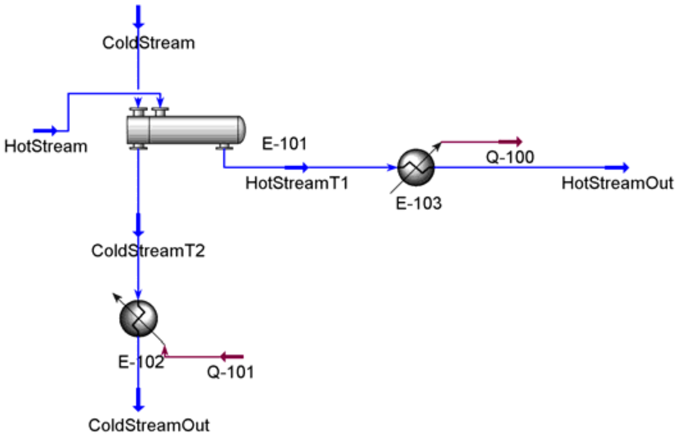


Figure 5.6: A HYSYS representation of the 3 heat exchanger network

The problem was simulated using HYSYS®, and expressed in disjunctive form as given in Problem C, and it was sought to minimize the total cost and select the corresponding heat exchangers based on the optimised values of their areas.

$$
\begin{aligned}
&\min \quad Z = \sum_{j \in J} CU_j + \sum_{k \in K} IC_k \\
&s.t. \\
&\begin{bmatrix} Y_{k,1} \\ IC_k = 2750 A_k^{0.6} + 3000 \\ 0 \le A_k \le 10 \end{bmatrix} \vee \begin{bmatrix} Y_{k,2} \\ IC_k = 1500 A_k^{0.6} + 15000 \\ 10 \le A_k \le 25 \end{bmatrix} \vee \begin{bmatrix} Y_{k,3} \\ IC_k = 600 A_k^{0.6} + 46500 \\ 25 \le A_k \le 50 \end{bmatrix} \\
&A_k \ge 0 \quad \forall i \in I = \{1..3\} \\
&k \in K = \{k \mid heat\ exchangers\} \\
&i \in I = \{i \mid heat\ exchanger\ areas\} \\
&j \in J = \{j \mid Service\ streams\} \\
&Y_{i,k} = \{TRUE, FALSE\} \qquad\qquad (C)
\end{aligned}
$$

In this formulation, *CU* and *IC* represent the utility and the investment costs of the whole process respectively. The solution of this problem using the D-GP as proposed in this work involves the decoupling of the logical propositional constraints from the general optimization model, and consequent generation, in a genetic algorithmic framework, of feasible configurations that satisfy these logical constraints. For illustration purposes, the above problem has been explicitly represented in Problem D below.

A chromosome template was defined, consisting of 11 genes with four distinct segments (figure 5.7). The first three segments correspond to the disjunctions, and the 9 genes they contain correspond to the terms of these disjunctions. The last segment, common to all chromosomes, contains two genes which store information on the performance of the particular chromosome, namely the NLP termination criteria and objective function, respectively. It should be noted, that the propositional logic relations were defined and satisfied at the genetic algorithmic population generation stage using a drag and drop method. Logical constraints were satisfied through the comparison of each randomly generated segment with a set of predefined conditions in the form of simple linear equations. To create a chromosome, an empty string is chosen, and the genes were selected randomly with real values 0 and 1. If the created chromosome satisfies the logical propositional constraints, it is chosen, else it is dropped (that is, the chromosome is illegal), and a new combination is chosen until the logical constraints are satisfied. No penalization is applied for illegal chromosomes. By this means, *npop* always feasible populations were generated.

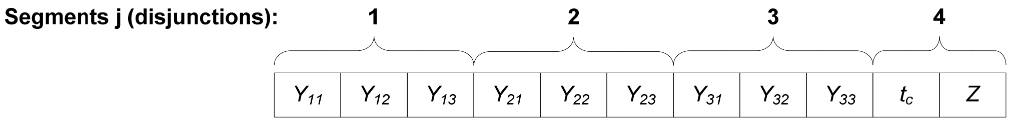


Figure 5.7: Chromosome structure for the 3 heat exchanger network problem

In some optimization problems, the number of unequal strings that satisfies the propositional logic constraints might be small; thus if a high value of *npop* is chosen, the population will contain traces of identical chromosomes. Although this factor will not affect the optimal value of the optimization problem, it will increase the computational time taken to get to that optimum.

$$
\begin{array}{l}
\min \quad Z = C_s Q_{Heater} + C_w Q_{cooler} + IC_1 + IC_2 + IC_3 \\
s.t. \\
h(A_1, u) = 0 \\
\begin{bmatrix} Y_{1,1} \\ IC_1 = 2750 A_1^{0.6} + 3000 \\ 0 \le A_1 \le 10 \end{bmatrix} \vee \begin{bmatrix} Y_{1,2} \\ IC_1 = 1500 A_1^{0.6} + 15000 \\ 10 \le A_1 \le 25 \end{bmatrix} \vee \begin{bmatrix} Y_{1,3} \\ IC_1 = 600 A_1^{0.6} + 46500 \\ 25 \le A_1 \le 50 \end{bmatrix} \\
\begin{bmatrix} Y_{2,1} \\ IC_2 = 2750 A_2^{0.6} + 3000 \\ 0 \le A_2 \le 10 \end{bmatrix} \vee \begin{bmatrix} Y_{2,2} \\ IC_2 = 1500 A_2^{0.6} + 15000 \\ 10 \le A_2 \le 25 \end{bmatrix} \vee \begin{bmatrix} Y_{2,3} \\ IC_2 = 600 A_2^{0.6} + 46500 \\ 25 \le A_2 \le 50 \end{bmatrix} \\
\begin{bmatrix} Y_{3,1} \\ IC_3 = 2750 A_3^{0.6} + 3000 \\ 0 \le A_3 \le 10 \end{bmatrix} \vee \begin{bmatrix} Y_{3,2} \\ IC_3 = 1500 A_3^{0.6} + 15000 \\ 10 \le A_3 \le 25 \end{bmatrix} \vee \begin{bmatrix} Y_{3,3} \\ IC_3 = 600 A_3^{0.6} + 46500 \\ 25 \le A_3 \le 50 \end{bmatrix} \\
Y_{11}, Y_{12}, Y_{13} = \{0, 1\}; \quad \forall A_1 \ge 0 \\
Y_{21}, Y_{22}, Y_{23} = \{0, 1\}; \quad \forall A_2 \ge 0 \\
Y_{31}, Y_{32}, Y_{33} = \{0, 1\}; \quad \forall A_3 \ge 0 \\
Y_{11} \vee Y_{12} \vee Y_{13} = TRUE \\
Y_{21} \vee Y_{22} \vee Y_{23} = TRUE \\
Y_{31} \vee Y_{32} \vee Y_{33} = TRUE \\
IC_1, IC_2, IC_3 \ge 0
\end{array}
\qquad (D)
$$

In the representation as given by Problem D, $h_1(A_1, u) = 0$ represents the energy balance, material balance, and other unit operation equations performed by the simulator, Q_{Heater} and Q_{Cooler} are the total heat exchanged in kilowatt between the hot (steam) and cold (water) utility streams respectively, and C_s and C_w are their respective costs in \$/kW per year. The GA parameters included the *npop* set to 25 and number of generations *ngen* set to 25. Crossover fraction was 0.8 and mutation fraction was 0.1. The fitness function of the GA corresponds to the returned optimal value of the reduced NLP sub-problem with fixed configurations corresponding to the generated feasible strings (chromosomes). The Matlab® *fmincon* functionality from the Matlab Optimization Toolbox, which solves nonlinear constrained optimization problems using gradient based methods, was used to solve the reduced NLP problem. Chromosomes that return infeasible reduced NLP solutions (that is $t_c = -1$) were penalized with a fixed weighting factor rendering these chromosomes less competitive in the next population selection, crossover and mutation process. The GA termination criteria was based on the attainment of the maximum specified number of generations (*ngen*).

Table 5.1 shows the GA parameter and solution summary from solving the three heat exchanger problem. Since different solutions may be obtained when GA is executed, even with the same parameters, the D-GP sequence was executed five times in this example. In almost all runs, the optimal objective value of $125,600 per year was obtained at the first generation. However, when a population of 10 chromosomes were chosen and the number of generations set to 10, the D-GP found the same optimal solution, but at a slightly higher generation count on average than when *npop* was fixed at 25 (figure 5.8). As can be seen from Table 5.1, even Run 3 returned a string with a sub-optimal value of $137,930 per year as solution at the third generation, after which no improvement in the objective value was obtained. GAs are more effective while using an optimal combination of the GA parameters, which in turn depends on the problem complexity, dimension, and type.

Table 5.1: Solution Summary of the 3 Heat Exchanger Network Using Proposed D-GP.

GA parameters		**D-GP Performance**			
Property	Value	Runs	Optimal Generation	Objective Value ($1000/year)	Optimal Chromosome
		npop = 25 *ngen* = 25			
Crossover fraction	0.8	1	1	125.60	010010001(+1)(125.60)
Mutation fraction	0.1	2	2	125.60	010010001(+1)(125.60)
Selection type:	Tournament	3	1	125.60	010010001(+1)(125.60)
		4	1	125.60	010010001(+1)(125.60)
		5	1	125.60	010010001(+1)(125.60)
		npop = 10 *ngen* = 10			
		1	1	125.60	010010001(+1)(125.60)
		2	2	125.60	010010001(+1)(125.60)
		3	3	137.93	010001001(+1)(137.93)
		4	1	125.60	010010001(+1)(125.60)
		5	2	125.60	010010001(+1)(125.60)

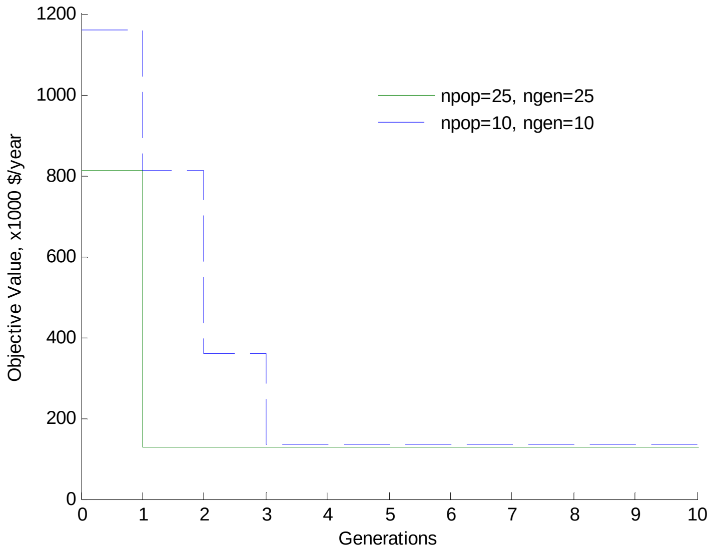


Figure 5.8: Best and worst objective values with two different values of the GA generation and population

Table 5.2 and figure 5.9 show a comparison of the reduced NLP model parameters of the D-GP and the NLP sub-problems (with fixed structures) of the MINLP reformulation of the GDP technique as proposed by Turkay and Grossman (1996a). The NLP sub-problem of the GDP formulation found an objective function which was almost 20% worse than that found by the D-GP. A clear reduction in the total number of constraint equations as well as variables of the NLP problem can be observed using this proposed approach. This is because, at each GA-NLP iteration only the constraints of the active terms of the disjunctions (which correspond to the configuration of each chromosome) were solved, leading to a reduced search space and dimensionality of the NLP problem. Thus, the reduced NLP problem of the optimal chromosome structure is given in Problem E, with constraint functions which are continuous in their respective variables.

$$
\begin{aligned}
&\min \quad Z = C_s Q_{Heater} + C_w Q_{cooler} + IC_1 + IC_2 + IC_3 \\
&s.t. \\
&h(A_1, u) = 0 \\
&IC_1 = 1500 A_1^{0.6} + 15000 \\
&IC_2 = 1500 A_2^{0.6} + 15000 \\
&IC_3 = 600 A_3^{0.6} + 46500 \\
&10 \le A_1 \le 25 \\
&10 \le A_2 \le 25 \\
&25 \le A_3 \le 50 \\
&IC_1, IC_2, IC_3 \ge 0 \\
&A_1, A_2, A_3 \ge 0 \qquad (E)
\end{aligned}
$$

Table 5.2: Model Parameters of the Reduced NLP Problem of the D-GP Approach and Comparison with the NLP Sub-problem of the MINLP Reformulation of the GDP Formulation of the Problem Using the Outer Approximation (OA) Algorithm Coupled with the Big-M Transformation.

Model parameters		**Formulations**	
		D-GP	**GDP-OA**
Objective value, \$1000/year		125.60	150.32
Total investment cost, \$1000/year		75.99	100.36
Total utility cost, \$1000/year		49.61	50.16
Optimal areas, m^2: Heat exchanger		25	24.95
	Heater	26.18	21.94
	Cooler	30.28	28.07
Number of variables		4	15
Total number of equations		12	39
Constraints:	Nonlinear	6	36
	Linear	6	3
Number of bonds		6	15

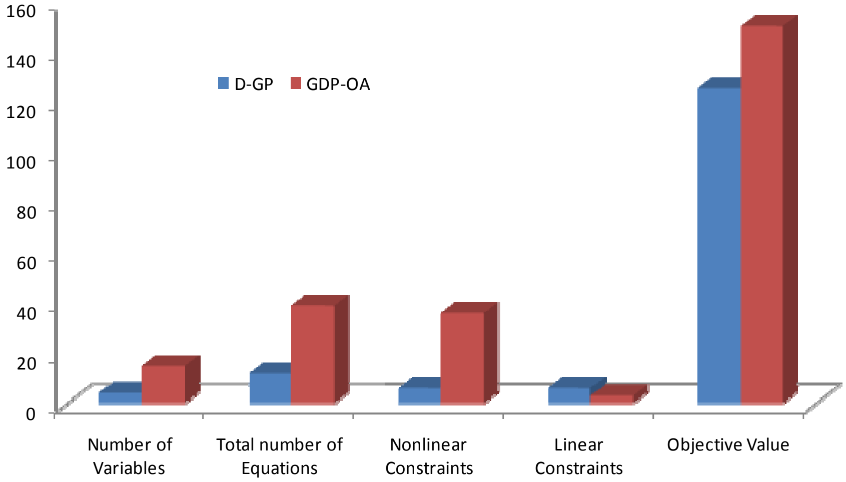


Figure 5.9: Comparison of the reduced NLP model parameters of D-GP with those of the NLP subproblem of the MINLP formulation of the 3 heat exchanger network

5.5.1.1 Mixed vs. all-feasible initial population

Here, the efficacy of the feasible population strategy adopted for the D-GP approach is shown by comparing results obtained from a mixed initial population. For the case of the mixed population type, the initial populations consisted of randomly created chromosomes which were not subjected to feasibility tests at the creation stage. As a result, this population contains strings which may not satisfy the propositional logic constraints. The feasibility tests on these chromosomes were embedded into the GA fitness function before the reduced NLP problem call. In the fitness function, infeasible chromosomes were penalised with large fixed weight factors, returning a fitness value large enough to render the corresponding chromosome less competitive for selection in subsequent reproduction operations. Infeasible strings at this stage were simply returned and the next member of the population evaluated. If a string satisfied the propositional logic constraints, the NLP problem was solved with fixed configurations corresponding to the chromosome structure. The GA fitness takes the value of the returned objective function of the reduced NLP problem, and this information, coupled with the corresponding termination state, was returned and stored for the next generation population creation using the different specified GA operators.

Poor performances were obtained using the mixed population approach, as can be seen in Table 5.3, which shows the objective values of 10 different runs of the D-GP with GA parameters *npop* and *ngen* being 25 each. Only 30% of the total runs carried out were capable of finding the optimal objective value and configuration. An important factor to consider in this approach is that in some problems, only a small fraction of the population (those which meet the logic constraints) of each generation passes on to the NLP space. This consequently increases not only the mean fitness value of the population members of a particular generation due to the accumulation of large penalty weights on the infeasible strings, but also the number of generations needed to find the global objective value. This can be seen in figure 5.10, which shows the evolution of the GA fitness function value with the generations (for the best run, Run 3 in Table 5.3), as compared to the case with feasible initial populations. As can be seen in this figure, the mean fitness value (objective value) of the population, that has undergone feasibility tests during the population creation stage was significantly lower than the population which comprised both feasible and infeasible chromosomes. Similarly, in the earlier case, the total number of iterations needed to attain the optimal solutions was smaller, which highlights the strength of the feasible initial population in the execution of this D-GP approach.

Table 5.3: Performance of the D-GP with Mixed Initial Population Through Repetitive Runs.

Runs	Objective Value	Generation	Optimal String Structure
1	809.86	2	010001100(-1)(809.86)
2	125.60	2	010010001(1)(125.60)
3	125.60	1	010010001(1)(125.60)
4	135.90	2	010010001(1)(135.90)
5	125.60	7	010010001(1)(125.60)
6	656.02	5	001100100(-1)(656.02)
7	934.87	2	010100001(-1)(934.87)
8	925.70	3	100100100(-1)(925.70)
9	809.86	2	010001100(-1)(809.86)
10	809.87	1	010001100(-1)(809.86)

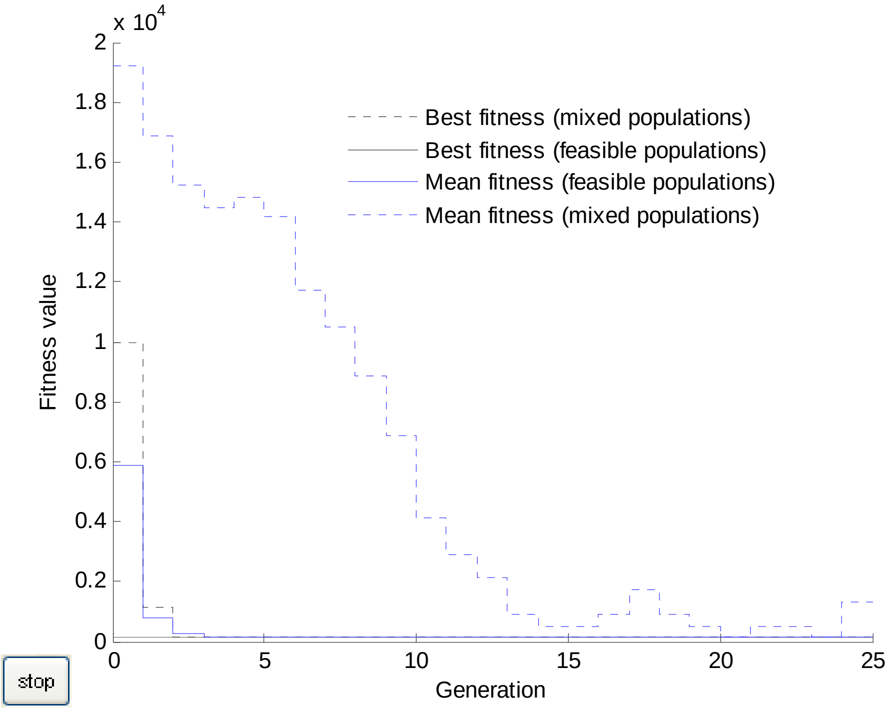


Figure 5.10: Evolution of the GA fitness function value with the generations for best performance (Run 3)

5.5.2 Example 2: Process network synthesis

In this example, which was taken from Lee and Grossmann (2000) and was originally proposed by Duran and Grossmann (1986a), it was sought to determine the most profitable flowsheet configuration involving the possible selection of 8 processes from the network presented in figure 5.11. This model has been originally formulated as an MINLP and later as a GDP problem [Turkay, 1996a]. The D-GP model took advantage of the original disjunctive formulation of the problem (Problem F) for the chromosome structure definition and codification within a GA framework. In this example, each chromosome contained 10 genes, with the first eight containing the information on the activation or non-activation of a certain term of each disjunction. Following similar procedures and with GA parameters as in Example 1, the GA returned a chromosome with the structure 01010101(+1)(68.009) at the first generation, from which it can be seen that the optimal flowsheet configuration involved the selection of units 2, 4, 6 and 8, with an optimal objective value of 68.01. This implies that the chromosome with the optimal flowsheet configuration was among the initial parent population of feasible chromosomes generated during the first population creation. Several runs were performed and the generation containing the worst optimal objective value was the third generation. The obtained optimal value and configuration agree well with the values obtained in other works [Duran, 1986a; Turkay, 1996a]. This same problem was reformulated from the GDP [Lee, 2000] to the MINLP and iteratively solved between the NLP sub-problems and the MILP master problems using GAMS [Brooke, 1992] NLP (SNOPT7) and LP (Cplex) solvers respectively. Similarly to Example 1 involving the 3 heat exchanger network, a notable decrease was observed in the dimensions of the reduced NLP problem in the proposed D-GP method. In Table 5.4, it can be seen that the reduced

NLP problem of the D-GP approach has been simplified by the existence of fewer nonlinear constraints than in the case of NLP subproblems developed from the MINLP method.

Table 5.4: Comparison of NLP model parameters of D-GP with GAMS SNOPT7 output.

Model parameters	**Formulations**	
	Reduced NLP (D-GP)	**NLP (GAMS SNOPT7), MINLP**
Objective value ($1000/year)	68.01	68.01
Number of variables	33	34
Total number of equations	38	61
Constraints: Nonlinear	10	10
Linear	28	51
Number of bonds	33	34

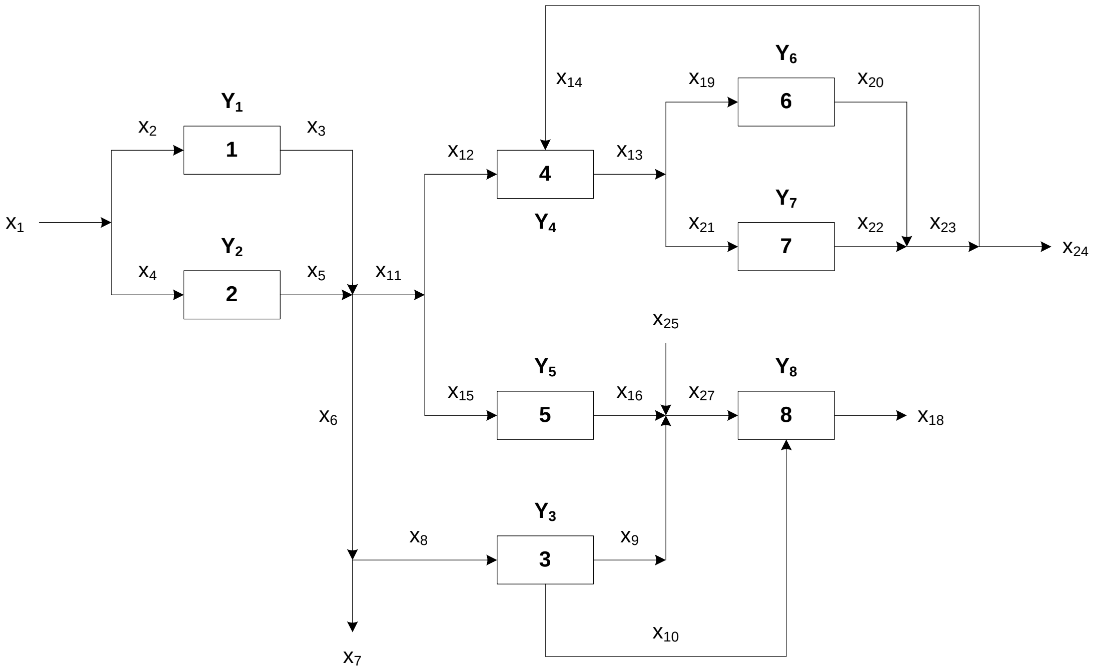


Figure 5.11: Superstructure for process network synthesis example

$$\min Z = \sum_{k=1}^{8} c_k + a^T x + 122$$

$s.t.$

$x_1 - x_2 - x_4 = 0, \qquad x_6 - x_7 - x_8 = 0,$

$x_3 + x_5 - x_6 - x_{11} = 0, \qquad x_{13} - x_{19} - x_{21} = 0,$

$x_{17} - x_9 - x_{16} - x_{25} = 0, \qquad x_{11} - x_{12} - x_{15} = 0,$

$x_{23} - x_{20} - x_{22} = 0, \qquad x_{23} - x_{14} - x_{24} = 0,$

$x_{10} - 0.8x_{17} \le 0, \qquad x_{10} - 0.4x_{17} \ge 0,$

$x_{12} - 5x_{14} \le 0, \qquad x_{10} - 2x_{14} \ge 0,$

$$\begin{bmatrix} Y_1 \\ \exp(x_3) - 1 - x_2 = 0 \\ c_1 = 5 \end{bmatrix} \vee \begin{bmatrix} \neg Y_1 \\ x_3 = x_2 = 0 \\ c_1 = 0 \end{bmatrix}$$

$$\begin{bmatrix} Y_{21} \\ \exp(x_5/1.2) - 1 - x_4 = 0 \\ c_2 = 8 \end{bmatrix} \vee \begin{bmatrix} \neg Y_2 \\ x_4 = x_5 = 0 \\ c_1 = 0 \end{bmatrix}$$

$$\begin{bmatrix} Y_3 \\ 1.5x_9 - x_8 + x_{10} = 0 \\ c_3 = 6 \end{bmatrix} \vee \begin{bmatrix} \neg Y_3 \\ x_9 = 0, \quad x_8 = x_{10} \\ c_3 = 0 \end{bmatrix}$$

$$\begin{bmatrix} Y_4 \\ 1.25(x_{12} + x_{14}) - x_{13} = 0 \\ c_4 = 10 \end{bmatrix} \vee \begin{bmatrix} \neg Y_4 \\ x_{12} = x_{13} = x_{14} = 0 \\ c_4 = 0 \end{bmatrix}$$

$$\begin{bmatrix} Y_5 \\ x_{15} - 2x_{16} = 0 \\ c_5 = 6 \end{bmatrix} \vee \begin{bmatrix} \neg Y_5 \\ x_{15} = x_{16} = 0 \\ c_5 = 0 \end{bmatrix}$$

$$\begin{bmatrix} Y_6 \\ \exp(x_{20}/1.5) - 1 - x_{19} = 0 \\ c_6 = 7 \end{bmatrix} \vee \begin{bmatrix} \neg Y_1 \\ x_{19} = x_{20} = 0 \\ c_6 = 0 \end{bmatrix}$$

$$\begin{bmatrix} Y_7 \\ \exp(x_{22}) - 1 - x_{21} = 0 \\ c_7 = 4 \end{bmatrix} \vee \begin{bmatrix} \neg Y_1 \\ x_{19} = x_{20} = 0 \\ c_7 = 0 \end{bmatrix}$$

$$\begin{bmatrix} Y_1 \\ \exp(x_{18}) - 1 - x_{10} - x_{17} = 0 \\ c_8 = 5 \end{bmatrix} \vee \begin{bmatrix} \neg Y_1 \\ x_{10} = x_{17} = x_{18} = 0 \\ c_8 = 0 \end{bmatrix}$$

$$\begin{aligned} a^T = [&0, 1, -10, 1, -15, 0, 0, 0, -40, 15, 0, 0, 0, -40, 15, \\ &0, 0, 0, 15, 0, 0, 80, -65, 25, -60, 35, -80, 0, 0, -35] \end{aligned}$$

$$x_j, c_k \geq 0, \quad Y_k \in \{true, fase\}, \quad k = 1,2,...8; \quad j = 1,2,...25.$$

Logic Propositions:

$Y_1 \Rightarrow Y_3 \vee Y_4 \vee Y_5$

$Y_2 \Rightarrow Y_3 \vee Y_4 \vee Y_5$

$Y_3 \Rightarrow Y_1 \vee Y_2$

$Y_3 \Rightarrow Y_8$

$Y_4 \Rightarrow Y_1 \vee Y_2$

$Y_4 \Rightarrow Y_6 \vee Y_7$

$Y_5 \Rightarrow Y_1 \vee Y_2$

$Y_5 \Rightarrow Y_8$

$Y_6 \Rightarrow Y_4$

$Y_7 \Rightarrow Y_4$

$Y_8 \Rightarrow Y_3 \vee Y_5 \vee (\neg Y_3 \wedge \neg Y_5)$

Specifications:

$Y_1 \veebar Y_2$

$Y_4 \veebar Y_5$

$Y_4 \veebar Y_7$ (F)

5.5.3 Example 3: Jobshop scheduling

The application of the D-GP methodology was further tested for the solution of a scheduling problem (Problem G) with discontinuous constraints (linear functions) representing the boundaries of the feasible region. The objective is the minimization of the makespan given a set of three jobs and three stages, expressed in disjunctive terms. Details of this problem can be found in the original work [Lee, 2000]. The obtained results demonstrate the ease with which the D-GP method tackles process synthesis problems of this nature.

The GA number of generations and number of populations were each set to 25, and the optimal solution provided by the D-GP yielded a chromosome at the second GA generation (figure 5.12), with the configuration 011001(1)(11), corresponding to Y_1=*FALSE*, Y_2=*TRUE*, and Y_3=*FALSE*. The optimal values for the variables x_1, x_2, and x_3 were 3, 0, and 1 correspondingly. This is clearly in agreement with the optimal solutions found in Lee and Grossmann (2000), though no comparison could be made on the performance of the method employed by those authors and the D-GP approach since both involved the use of different solution frameworks.

$$
\begin{array}{l}
\min \quad Z = T \\
s.t. \\
T \geq x_1 + 8 \\
T \geq x_1 + 5 \\
T \geq x_3 + 6 \\
\begin{bmatrix} Y_1 \\ x_1 - x_3 + 5 \leq 0 \end{bmatrix} \vee \begin{bmatrix} \neg Y_1 \\ x_3 - x_1 + 2 \leq 0 \end{bmatrix} \\
\begin{bmatrix} Y_2 \\ x_2 - x_3 + 1 \leq 0 \end{bmatrix} \vee \begin{bmatrix} \neg Y_2 \\ x_3 - x_2 + 6 \leq 0 \end{bmatrix} \\
\begin{bmatrix} Y_3 \\ x_1 - x_2 + 5 \leq 0 \end{bmatrix} \vee \begin{bmatrix} \neg Y_3 \\ x_2 - x_1 \leq 0 \end{bmatrix} \\
T, x_1, x_1, x_1, \geq 0 \\
Y_k \in \{TRUE, FALSE\}, \quad k = 1,2,3.
\end{array}
\qquad \text{(G)}
$$

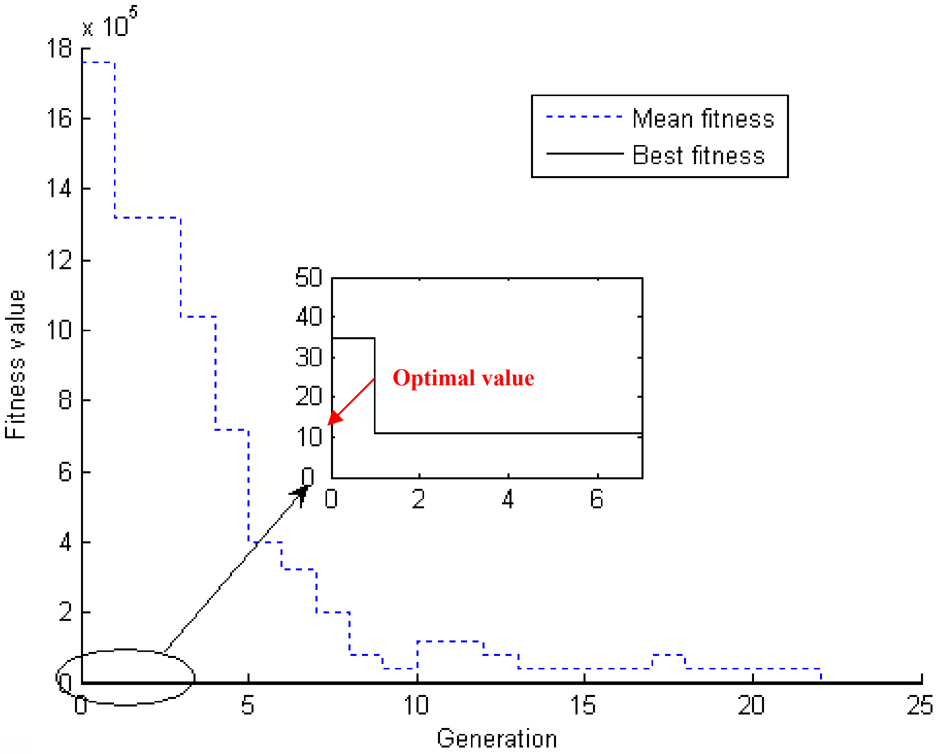


Figure 5.12: Optimal value and generation for the jobshop schedule problem

5.5.4 Example 4: Biorefinery Optimal Product Allocation (BOPA)

The applicability of the D-GP approach to chemical engineering process synthesis is further demonstrated through its application to the identification of the optimal set of products and the best route for producing them, given a set of bio-resources and finite production paths with performance criteria. Details of this problem can be found in the works of Sammons et al. (2007, 2008). The superstructure of the different production paths is given in figure 5.13. The BOPA problem was first expressed in terms of disjunctions with propositional logic, from which information about the GA chromosome structure was extracted. An interesting feature of this problem is the existence of process sub-routes, giving rise to embedded disjunctions as shown in Problem H. Analogous to the previous examples, the length of the chromosome equals the total number of disjunctions in the formulation plus 2, where the information on the termination criteria and objective function values of the individual chromosome is stored. In this example, the number of segments in a chromosome equals 4, with segment 3 embedding two sub-segments. Following similar procedures as elaborated earlier, populations of feasible chromosomes were generated in the GA framework, followed by the solution of the reduced NLP problem with fixed configuration (information which is passed on to this non-linear optimization space from the information contained in the GA generated chromosomes).

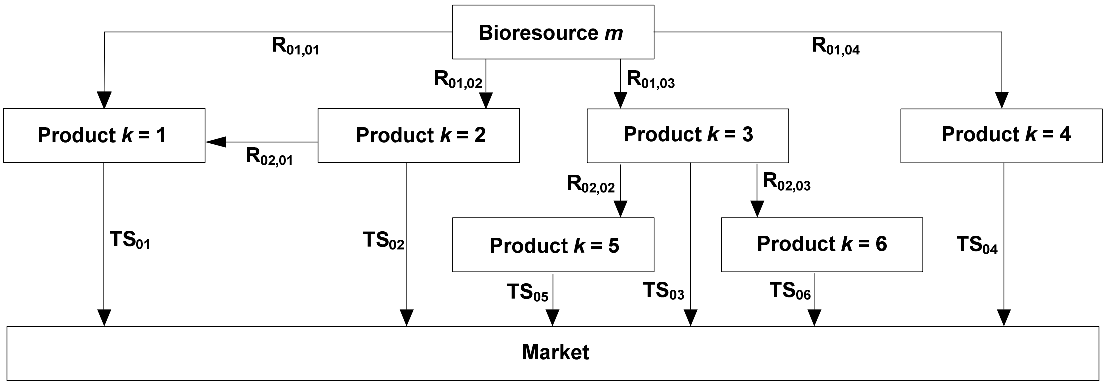


Figure 5.13: Superstructure of the general biorefinery model (Sammons et al., 2006)

The optimal configuration and parameter values of the BOPA problem obtained using the D-GP approach are shown in figure 5.14. The optimal objective value was \$16,277.00 with routes leading to the production of products 1, 2, 4, 5 and 6 being selected. In the optimal configuration, route 1 was not selected; however, 130 units of product 1 are being produced and sold to the market due to the feasibility of production sub-route R02,01 as shown figure 5.14.

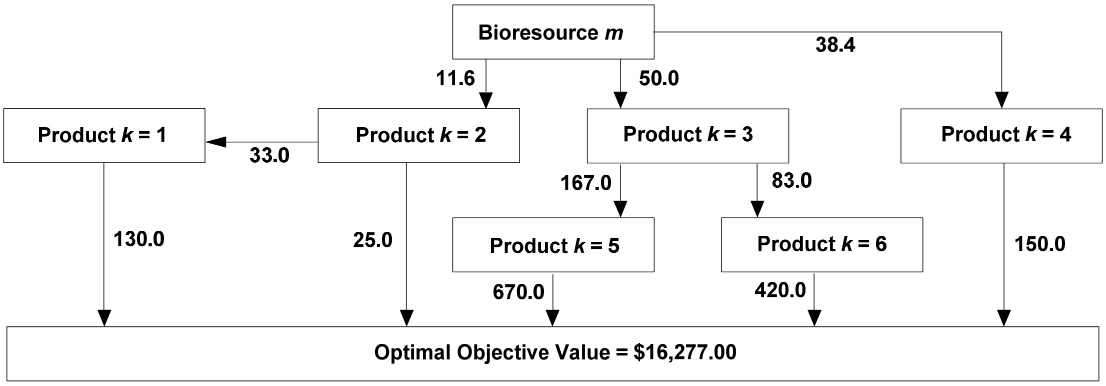


Figure 5.14: Optimal superstructure and flow parameters for the general BOPA problem

It is also worth noting that although production path 3 was selected, no part of product 3 being processed from this route was sold to the market since the D-GP approach determined that it was more profitable to further reprocess this product through routes $R_{02,02}$ and $R_{02,03}$. For the attainment of this feasible configuration and optimal value, the optimization model included a total of 40 constraint equations from which 13 are nonlinear.

$$Max\ profit = \sum_{i=1}^{6} \mathrm{Rev}_i - \sum C - BC$$

s.t.

$$\begin{bmatrix} Y_{R_1} \\ PC = 3 \\ PR = 5 \\ TS_1^* = PR * \gamma_1 * m \\ C_1 = PC\ * \gamma_1 * m \\ TC_1 = 0.35 * \gamma_1 * m \\ 0 \le \gamma_1 \le 1 \end{bmatrix} \vee \begin{bmatrix} \neg Y_{R_1} \\ PC = 0 \\ PR = 0 \\ TS_1^* = 0 \\ C_1 = 0 \\ TC_1 = 0 \\ \gamma_1 = 0 \end{bmatrix}$$

$$
\left[\begin{array}{l}
\qquad\qquad\qquad\qquad Y_{R_2} \\
\left[\begin{array}{l}
\qquad\quad Y_{R_2^{'}} \\
PC = 2 \\
PR = 4 \\
TS_2^{'} = PR * (\gamma_2^{'} * TS_2^{'}) \\
C_2^{'} = PC * (\gamma_2^{'} * TS_2^{'}) \\
TC_2^{'} = 0.68 * (\gamma_2^{'} * TS_2^{'}) \\
0 \le \gamma_2^{'} \le 1
\end{array}\right]
\vee
\left[\begin{array}{l}
\quad \neg Y_{R_2^{'}} \\
PC = 0 \\
PR = 0 \\
TS_2^{'} = 0 \\
C_2^{'} = 0 \\
TC_2^{'} = 0 \\
\gamma_2^{'} = 0
\end{array}\right] \\
\\
PC = 3 \\
PR = 5 \\
TS_2^{*} = PR * (\gamma_2 * m) \\
TS_2 = (1 - \gamma_2^{'}) * TS_2^{*} \\
C_2 = PC * (\gamma_2 * m) \\
TC_2 = 0.55 * (\gamma_2 * m)^2 \\
0 \le \gamma_2 \le 1
\end{array}\right]
\vee
\left[\begin{array}{l}
\quad \neg Y_{R_2} \\
\\
PC = 0 \\
PR = 0 \\
TS_2^{'} = 0 \\
C_2^{'} = 0 \\
TC_2^{'} = 0 \\
\gamma_2^{'} = 0 \\
\\
\\
TS_2 = 0 \\
TS_2 = 0 \\
C_2 = 0 \\
TC_2 = 0 \\
\gamma_2 = 0 \\
\\
\end{array}\right]
$$

$$
\left[\begin{array}{l}
\qquad\qquad\qquad Y_{R_3} \\
\left[\begin{array}{l}
\qquad Y_{R_3'} \\
PC = 2 \\
PR = 4 \\
TS_5 = PR * (\gamma_3' * TS_3^*) \\
C_3' = PC * (\gamma_3' * TS_3^*) \\
TC_3' = 0.89 * (\gamma_3' * TS_3^*) \\
0 \le \gamma_3' \le 1
\end{array}\right]
\vee
\left[\begin{array}{l}
\neg Y_{R_3'} \\
PC = 0 \\
PR = 0 \\
TS_5 = 0 \\
C_3' = 0 \\
TC_3' = 0 \\
\gamma_3' = 0
\end{array}\right] \\
\left[\begin{array}{l}
\qquad Y_{R_3''} \\
PC = 5 \\
PR = 5 \\
TS_6 = PR * (\gamma_3'' * TS_3^*) \\
C_3'' = PC * (\gamma_3'' * TS_3^*) \\
TC_3'' = 0.78 * (\gamma_3'' * TS_3^*) \\
0 \le \gamma_3'' \le 1
\end{array}\right]
\vee
\left[\begin{array}{l}
\neg Y_{R_3''} \\
PC = 0 \\
PR = 0 \\
TS_6 = 0 \\
C_5 = 0 \\
TC_3'' = 0 \\
\gamma_3'' = 0
\end{array}\right] \\
PC = 3 \\
PR = 5 \\
TS_3^* = PR * (\gamma_3 * m) \\
TS_3 = \gamma_3''' * TS_3^* \\
C_3 = PC * (\gamma_3 * m) \\
TC_3 = 0.82 * (\gamma_3 * m)^{0.5} \\
0 \le \gamma_3 \le 1 \\
0 \le \gamma_3''' \le 1 \\
\gamma_3' + \gamma_3'' + \gamma_3''' = 1
\end{array}\right]
\vee
\left[\begin{array}{l}
\neg Y_{R_3} \\
PC = 0 \\
PR = 0 \\
TS_3 = 0 \\
TS_5 = 0 \\
TS_6 = 0 \\
C_3' = 0 \\
C_3'' = 0 \\
C_3 = 0 \\
TC_3' = 0 \\
TC_3'' = 0 \\
TC_3 = 0 \\
\gamma_3' = 0 \\
\gamma_3'' = 0 \\
\gamma_3''' = 0 \\
\gamma_3 = 0
\end{array}\right]
$$

$$\begin{bmatrix} Y_{R_4} \\ PC = 5 \\ PR = 4 \\ TS_4 = PR * \gamma_4 * m \\ C_4 = PC * \gamma_4 * m \\ TC_4 = 0.9 * \gamma_4 * m \\ 0 \le \gamma_4 \le 1 \end{bmatrix} \vee \begin{bmatrix} \neg Y_{R_4} \\ PC = 0 \\ PR = 0 \\ TS_4 = 0 \\ C_4 = 0 \\ TC_4 = 0 \\ \gamma_4 = 0 \end{bmatrix}$$

General equations:

$$\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4 = 1$$
$$TS_1 = TS_1^* + TS_2^'$$
$$P_1 = 11; \quad P_2 = 50; \quad P_3 = 16; \quad P_4 = 10; \quad P_5 = 15; \quad P_6 = 8;$$
$$BP = 1; \quad m = 100;$$
$$\mathrm{Rev}_1 = P_1 * TS_1$$
$$\mathrm{Rev}_2 = P_2 * TS_2$$
$$\mathrm{Rev}_3 = P_3 * TS_3$$
$$\mathrm{Rev}_4 = P_4 * TS_4$$
$$\mathrm{Rev}_5 = P_5 * TS_5$$
$$\mathrm{Rev}_6 = P_6 * TS_6$$
$$BC = m * BP$$

$$\left.\begin{matrix} Y_1, & \neg Y_1 \\ Y_2, & \neg Y_2 \\ Y_3, & \neg Y_3 \\ Y_4, & \neg Y_4 \\ Y_2^', & \neg Y_2^' \\ Y_3^', & \neg Y_3^' \\ Y_3^{''}, & \neg Y_3^{''} \end{matrix}\right\} = \{0, 1\}; \quad \forall\, TC_1, C_1 \ge 0$$

$$\forall\, TC_1, TC_2, TC_3,\; TC_4, TC_2^{'}, TC_3^{'}, TC_3^{''} \geq 0$$

$$\forall\, C_1, C_2, C_3, C_4, C_2^{'}, C_3^{'}, C_3^{''} \geq 0$$

$$\left.\begin{array}{l} Y_1 \vee \neg Y_1 \\ Y_2 \vee \neg Y_2 \\ Y_3 \vee \neg Y_3 \\ Y_4 \vee \neg Y_4 \\ Y_2^{'} \vee \neg Y_2^{'} \\ Y_3^{'} \vee \neg Y_3^{'} \\ Y_3^{''} \vee \neg Y_3^{''} \end{array}\right\} = TRUE$$

$$TS_1, TS_2, TS_3,\; TS_4, TS_5, TS_6 \geq 0 \qquad (H)$$

Where:

PC_n	Processing Costs of given route n per unit input; $n = \{1 \ldots 7\}$
PR_n	Production rates for given route n
TS_k	To Sell (final output to market); $k = \{1 \ldots 6\}$
TC_n	Total Cost (total equipment and processing cost)
C_n	Cost (Cost of production, cost of processing resource through specific route)
m	Raw material input quantity (feed)
P_k	Price of product
BP	Biomass Price per mass unit
BC	Total Biomass Cost
Rev_k	Revenues from obtained products

5.6 Summary

This chapter has presented a joint disjunctive-genetic algorithm (D-GP) representation approach to synthesis of process networks involving discrete/discontinuous functions, or where the selection of different equipment, units, or processes are involved, given a set of alternatives. Special modified GA operators were presented to better handle the proposed solution approach, and it was found that the generation of feasible populations yields better results as compared to the case when the population is composed of randomly generated individuals that underwent feasibility testing at the fitness function evaluation stage. An interesting feature of the D-GP approach is that it eliminates the need for the reformulation of the GDP problems into direct MINLP problems, thus allowing the solution of the original problem as a continuous optimization problem but only at each individual discrete and reduced search space. The effectiveness of the D-GP has been shown in different chemical engineering problems, and in all the examples studied, no more than five generations of the genetic algorithm were needed to find the optimal solution. An important contribution of this paper is based on the use of the evolutionary approach as an alternative to the efficient handling of discontinuities in optimization problems while simultaneously applying deterministic approaches to handle the continuous functions.

Chapter 6 Conclusions and Future Directions

6.1 Conclusions

The work presented in this dissertation pertains to research in the areas of process synthesis, integration and optimization of novel fuel production. It specifically targets developing a methodology to design simulation models based on the analysis of the experimental or literature data and includes the considerations of environmental and economic metrics.

Based on the methodology, the case studies successfully compared the reformation strategies based on the impact of utility requirements, energy integration potential, equipment costs, and raw material costs on the total production cost. Two specific applications were evaluated for the reformation strategies: hydrogen production and the Fischer-Tropsch (FT) process. In this work, simulation models were first developed for different fuel production schemes and then environmental and economic analyses were performed for each process. Several fuel reformation strategies were considered and four different fuel sources in the hydrogen production models and two different FT synthesis approaches were evaluated. Since the reformation kinetics are very complex, a systematic approach using simplified reaction stoichiometry was developed. The economic analysis was performed for each reformation strategy and reforming fuel, allowing for the determination of the most economical way to obtain the desired fuel product.

The success of alternative fuels such as hydrogen and FT fuels is largely dependent on cost competitiveness with other transportation fuels. Currently, the price cannot beat gasoline from the traditional refinery processes. The development of alternative fuel infrastructure (i.e. hydrogen stations) and transportation could be even more expensive. Therefore, the ability to produce alternative fuels in a cost-effective way is only the first of many challenges that need to be addressed, although it is a very important step in our decision-making process. The implementation of an alternative energy infrastructure will require enormous investments in new production and distribution systems.

As previously mentioned, it is apparent that the current technologies for producing hydrogen from liquid fuels are not attractive if evaluated only on the production costs. However, it would be much more competitive if hydrogen could be efficiently generated from electrolysis of water with the use of solar energy, but this technology is still under development and is dependent on the improvement of the solar cell panels. Moreover, besides cost, benefits such as storage, transportability, etc. will need to be quantified for all types of fuels in order to better compare the technologies. From this study, dry reforming appears to be a potential alternative to the current technique in terms of cost and performance.

The other case study was focused on developing generic process simulation models of traditional gas-phase Fischer-Tropsch Synthesis (FTS) process and novel supercritical-phase FTS process in collaboration with our colleagues at Auburn University. FTS is an attractive pathway to convert carbonaceous feedstock into synthetic hydrocarbon fuels that are directly compatible with existing infrastructure. The results show that the novel FTS process by using supercritical fluid could produce more fuels than the gas phase FTS process and only has half of the production cost with similar/lower environmental impact.

A joint disjunctive-genetic algorithm (D-GP) representation approach was proposed in the optimization step. Special modified GA operators were presented to better handle the proposed solution approach, and it was found that the generation of feasible populations yields better results as compared to the case when the population is composed of randomly generated individuals that underwent feasibility testing at the fitness function evaluation stage. An interesting feature of the D-GP approach is that it eliminates the need for the reformulation of the GDP problems into direct MINLP problems, thus allowing the solution of the original problem as a continuous optimization problem but only at each individual discrete and reduced search space. The effectiveness of the D-GP has been shown in different chemical engineering problems, and in all the examples studied, no more than five generations of the genetic algorithm were needed to find the optimal solution.

6.2 Future Directions

In the FT case study, it should be noticed that the environmental performance is not included in the optimization step. Economic and environmental evaluations are made separately. So far, no standards exist for environmental metrics, and thus the choice of appropriate metrics is quite difficult.

Besides developing more complex, detailed models for current fossil fuel processing, research into alternative fuels which are environmentally friendly appears promising. The reforming of bio-derived fuels, such as ethanol, bio-diesel and di-methyl-ether (DME) are considered to be excellent types of future alternative fuel. Bio-derived fuels have energy densities comparable to other hydrocarbon fuels and are renewable, unlike fossil fuels [Gerhartz, 2003].

Seeing that one of the major challenges of the future fuel energy economy is the cost, more reformation models such as the production of olefins and FT fuels to perform the cost analysis of the different reforming strategies in the final step need to be generated and investigated. Various reforming fuels should be evaluated in order to develop a relationship between raw material and production cost and to make sure the process system is achieving the highest fuel production levels for the lowest raw material cost. By evaluating alternative fuels and strategies we can obtain more information on how to produce them in a cost effective, environmentally friendly manner for various applications. Currently, the cost of production for alternative transportation fuels is not competitive with conventional fuels and technologies. Further research is needed to significantly reduce the capital equipment, operational, and maintenance costs to improve the efficiency of alternative fuel production technologies such as hydrogen production.

Syngas production was not included in the analysis of the Fischer-Tropsch processes. The next step in the modeling of the FT processes will combine the results from the hydrogen production studies with the FT process models to evaluate the best syngas production schemes for FT fuel production. Process design under uncertainty could potentially avoid design related issue such as suboptimal decisions, overdesign or underdesign at an early design stage. Uncertainty analysis should also be included in the model to make analysis of scaling up to industrial levels more accurate and fit for global analysis.

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