PROCESS DESIGN AND OPTIMIZATION OF BIOREFINING PATHWAYS

A Dissertation

by

BUPING BAO

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2012

Major Subject: Chemical Engineering

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Approved by:

Co-Chairs of Committee,	Mahmoud El-Halwagi
	Nimir Elbashir
Committee Members,	M. Sam Mannan
	Christine Ehlig-Economides
Head of Department,	Charles Glover

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ABSTRACT

Process Design and Optimization of Biorefining Pathways. (May 2012)

Buping Bao, B.S., Zhejiang University;

M.S., Texas A&M University

Co-Chairs of Advisory Committee: Dr. Mahmoud El-Halwagi
Dr. Nimir Elbashir

Synthesis and screening of technology alternatives is a key process-development activity in the process industries. Recently, this has become particularly important for the conceptual design of biorefineries. A structural representation (referred to as the chemical species/conversion operator) is introduced. It is used to track individual chemicals while allowing for the processing of multiple chemicals in processing technologies. The representation is used to embed potential configurations of interest. An optimization approach is developed to screen and determine optimum network configurations for various technology pathways using simple data.

The design of separation systems is an essential component in the design of biorefineries and hydrocarbon processing facilities. This work introduces methodical techniques for the synthesis and selection of separation networks. A shortcut method is developed for the separation of intermediates and products in biorefineries. The optimal allocation of conversion technologies and recycle design is determined in conjunction with the selection of the separation systems. The work also investigates the selection of separation systems for gas-to-liquid (GTL) technologies using supercritical Fischer-Tropsch synthesis. The task of the separation network is to exploit the pressure profile of the process, the availability of the solvent as a process product, and the techno-economic advantages of recovering and recycling the solvent. Case studies are solved to illustrate the effectiveness of the various techniques developed in this work.

The result shows 1, the optimal pathway based on minimum payback period for cost efficiency is pathway through alcohol fermentation and oligomerized to gasoline as 11.7 years with 1620 tonne/day of feedstock. When the capacity is increased to 120,000 BPD of gasoline production, the payback period will be reduced to 3.4 years. 2, from the proposed separation configuration, the solvent is recovered 99% from the FT products, while not affecting the heavier components recovery and light gas recovery, and 99% of waster is recycled. The SCF-FT case is competitive with the traditional FT case with similar ROI 0.2. 3, The proposed process has comparable major parts cost with typical GTL process and the capital investment per BPD is within the range of existing GTL plant.

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Particularly, I would give special thanks to Dr Arturo Jiménez-Gutiérrez, Dr Jose Maria Ponce-Ortega , Dr Denny Ng , Douglas Tay, and Ammar Alkhawaldeh for the BTL optimization research. Their insightful advices and solid experiences provided me a broader view of research, and make my research life more meaningful.

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NOMENCLATURE

ASF	Anderson-Schulz-Flory Equation
ASU	Air Separation Unit
ATR	Autothermal Reactor
BPD	Barrels Per Day
CFB	Circulating Fluidized Bed
FCI	Fixed Capital Investment
F-T	Fischer Tropsch
GTL	Gas to Liquid
HEN	Heat Exchange Network
HP	High Pressure
HTFT	High Temperature Fischer Tropsch
IGCC	Integrated Gasification Combined Cycle
LNG	Liquefied Natural Gas
LP	Low Pressure
LPG	Liquefied Petroleum Gas
LTFT	Low Temperature Fischer Tropsch
MEN	Mass Exchange Network
MILP	Mixed Integer Linear Program
POX	Partial Oxidation
ROI	Return on Investment

SCFD	Standard Cubic Feet per Day
SMDS	Shell Middle Distillate Synthesis
SMR	Steam Methane Reforming
SPD	Slurry-Phase Distillate Process
TAC	Total Annualized Cost
TCI	Total Capital Investment
TEHL	Table of Exchangeable Heat Loads
TID	Temperature Interval Diagram
WGS	Water Gas Shift
$a_{g,i}$	Parameter To Get Annualized Cost For The Different Capacity
$AFC_{g,i}$	Annualized Fixed Cost Of Technology g_i In Layer i
$AOC_{g,i}$	Annualized Operating Cost Of Technology g_i In Layer i
c	Index For Chemical Species
$C^{Feedstock}$	Cost Of The Feedstock
$c_{g_i}^{\lim}$	Index For The Limiting Component Of g_i
$C^{Product}$	Selling Price Of The Product
d_{g_i}	Design Variable Of g_i
E	Binary Variable For The Route Selected
$F_{c,i}$	Flowrate Of Chemical Species c In Chemical-Species Layers i
$F_{c,i+1}$	Flowrate Of Chemical Species c In Chemical-Species Layers i+1
$F^{Feedstock}$	Flowrate Of The Feedstock

$F^{in}_{g_i,i,c}$	Flowrate Of Chemical Species c Entering Conversion Operator g_i In Layer i
$F^{out}_{g_i,i,c}$	Flowrates Of Chemical Species c Leaving Conversion Operator g_i In Layer i
$F_{p,NP}$	Flowrate Of The Desired Product Leaving The Last Chemical-Species Layer
$FC_{g,\ i}$	Capacity Flowrate Of Annual Cost Found In Literature With Technology g_i
$Frac_{k,i,c_i}$	Products Fraction
g_i	Index For A Conversion-Operator Layer
i	Index For A Chemical-Conversion Or A Conversion-Operator Layer
MinFrac	Limit For The Concentration Of A Given Stream
MinProdFlow	Limit For The Product Flow
NC	Total Number Of Candidate Chemical Species
NCASE	Set For The Number Of Cases
NP	Total Number Of Chemical-Conversion Layers Or Index Corresponding To The Product Layer
OperCost	Operational Cost For Technology
O_{g_i}	Operating Variable Of g_i
PP	Pay Back Period

$r_{g_i,c,i}$	Rate Of Formation/Depletion Of Chemical Species c In Conversion Operator g_i
$TAC_{g_i,i}$	Total Annualized Cost Of Conversion Operator g_i In Layer, i
$TAFC$	Total Annualized Fixed Cost
$TAOC$	Total Annualized Operating Cost
$y_{g_i,i,c}$	Yield Of Component c In Conversion Operator g_i
$\Omega_{g_i,i}$	Functional Expression For Total Annualized Cost Of Conversion Operator g_i In Layer i
$\psi_{g_i,i}$	Performance Model For Conversion Operator g_i In Layer i
$\upsilon_{g_i,c,i}$	Stoichiometric Or Another Coefficient For Compound c In Conversion Operator g_i

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1. INTRODUCTION AND LITERATURE REVIEW

1.1 Overview and Background

Over half of U.S. oil consumption is imported each year, equaling to approximately 10 MMbbl/day of fuels, of which 2/3 is used for transportation fuels, bringing an about annual 300 billion $ of US economy cost (Spath et al., 2005). When burning these fuels, 2.1 billion metric tons of CO_2 / year will be released to environment as pollution (assuming 20 pounds of CO_2 / gallon) (Jones et al., 1999; Hamelinck and Fajj, 2002). This puts both economy and environmental pressures on traditional fossil fuels, and engenders trend for renewable fuel resources for sustainable operation.

Biomass to liquid (BTL) refineries are among the promising choices for the sustainable processing. Conventional biorefineries are only concerned with the particular process pathway, design, or feedstock/product selection, without broadening the view to the systematic design and process configuration, nor applying for multiple task/scale/numerous technologies optimization of the process. This work will take into consideration the process integration techniques to globally optimize the biorefinery pathways and eliminate the limitations mentioned above.

The systematic approach to optimize a biomass to liquid process is to integrate the

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This dissertation follows the style and format of Chemical Engineering Science.

biorefinery process from process synthesis and process analysis (shown in Figure 1.1). Process synthesis will generate alternative pathways, establish performance targets, and provide holistic insights for the design. While process analysis will incorporate simulation and mathematic models to produce input/output relations, compare performance and operating conditions, and screen the alternative designs from the process synthesis to finally reach the optimal biorefinery pathways and designs.

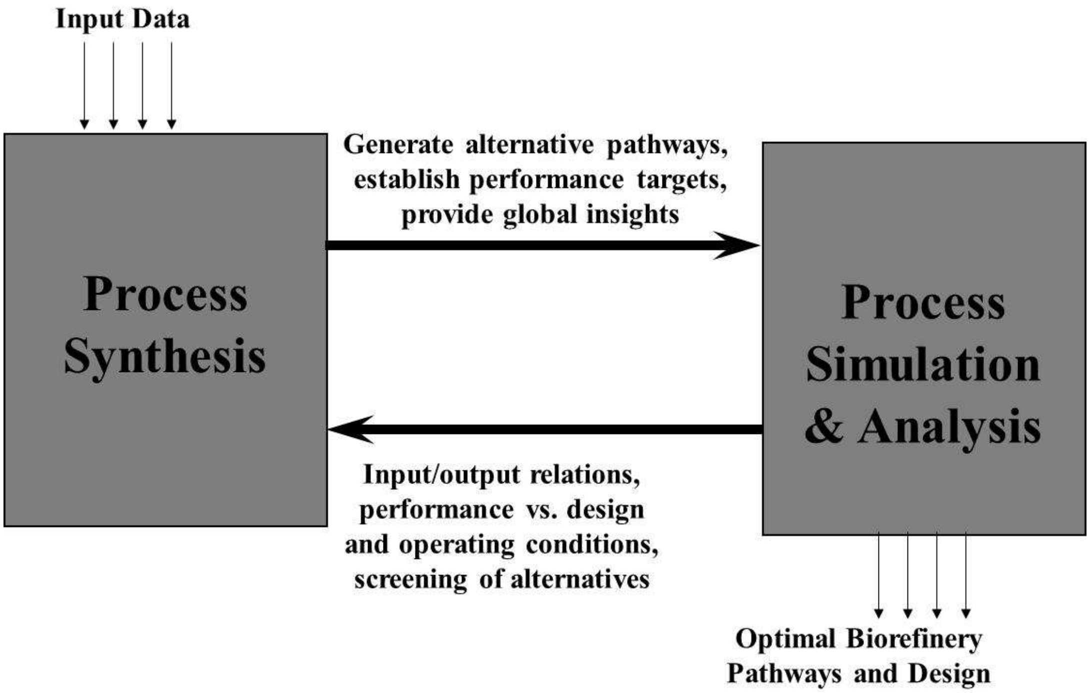


Figure 1.1. The Design Approach for Biorefinery Processes

This dissertation presents the approaches and applications of process optimization and integration for a XTL refinery pathway selection and design. It provides a systematic framework for conceptual designing and optimizing the technology route for producing value added chemicals and fuels from biomass or natural resources. The first section covers the background and technologies introduction for the problem in the disseration, including the Fischer-Tropsch technology, the biorefinery overview, the biomass feedstock treatment and GHG analysis. The second section introduces the approaches and methodologies for the problem solution, including process synthesis and problem analysis. The third section focuses on developing the systematic way for biorefinery pathway optimization, followed by section four for the continuing work on the conversion technology integrated with material interception network to further optimize the biorefinery pathway system. The fifth section detailed the aforementioned pathway by exploring the unit operation and process design. The scope of the techniques covered in the approach ranges from the mass integration, heat integration, and property integration, including mathematical programming, graphical approach, separation and recycle methods. Process simulation, economic evaluation, greenhouse gas life cycle analysis and other analysis measures will be conducted to evaluate the potential and optimizing opportunities for the illustrated cases.

1.2 BTL Technology Introduction

Biomass feedstock treatment technology could be categorized into thermochemical conversions and biochemical conversions. Thermochemical conversion typically uses high temperature and pressure to improve conversion efficiencies. Therefore the feedstock need to be less moisturized and could range wide. Thermochemical conversion technologies include:

Combustion utilizes excess oxidizer to convert fuels by 100% to produce heat, CO_2, H_2O, ash and other incomplete reaction products at high temperatures between 1500 and 3000 ºF. The process will not generate useful intermediate such as fuel gases or liquids. The heat efficiency is dependent on the furnace design, operating conditions, feedstocks, and system configuration (Hackett et al., 2004).

Gasification is a process that generally uses oxidation or indirect heating to produce mainly fuel gases including synthesis gas, methane, and other light hydrocarbons depending on the process operations (Hackett et al., 2004). It also uses air or oxygen as input to produce oils, tars, char as additional output as well. Gasification can be applied in processes like methanol production, Fischer-Tropsch (FT) process, etc.

Pyrolysis typically refers to gasification similar processes that don't include air or oxygen as an input. It produces pyrolysis oils rich in oxygenated hydrocarbons that can be directly used or upgraded to higher quality chemicals, fuels as primary products. It also produces gases and solids. Refining of pyrolysis oils will generate stable and easy handling value added chemicals. In addition to the thermal degrading of the solid biomass, there are catalytic cracking technologies that involves catalysts to increase product selectivity and embedding favorable groups to the products, such as volatility or solubility (Hackett et al., 2004). The reaction design could include Circulating Fluidized Bed Pyrolysis, Bubbling Fluidized Bed Pyrolysis, Rotating Cone, Entrained Flow Pyrolysis, Ablative pyrolysis, Moving Bed or Auger Pyrolysis (Bridgewater 2007). The produced pyrolysis oil is a “dark brown, free-flowing, unstable liquid with about 25% water that cannot be easily separated” (Oasmaa and Kuoppala, 2003, Diebold, 2000). It’s immiscible with traditional hydrocarbon fuels (Bridgewater, 2007). To utilize the pyoil, it could be converted to high quality fuel by removing the oxygen via hydrotreating process.

Liquefaction requires lower temperatures but higher pressures. It has high conversion to liquid fuels.

Biochemical conversion doesn’t care the moisture of the feedstock and operates at mild temperatures. And it will give higher selectivity to products but has lower conversions. Biochemical conversion technologies include:

Fermentation generally uses yeast or bacteria to function without oxygen to produce ethanol, acids, and other chemicals from cellulosic feedstocks. Cellulosic in biomass, need pretreatment such as acid treatment, enzymatic, or hydrolysis to decompose cellulose and hemicellulose to easy fermented molecules. Lignin is not viable for fermentation but could be reactant for thermochemical conversion. Anaerobic digestion is also classified as one of the particular fermentation.

Anaerobic digestion is a fermentation technique occurring mostly in waste water treatment, sludge degradation, and landfills. It operates at anaerobic conditions and produces biogas that includes methane and carbon dioxide as main products, and also moisture, H2S, siloxane as by products. Technologies to separate methane from biogas cover the following methods: scrubbing, pressure swing absorption (PSA), Selexol (polyethylene glycol ether), membrane separation, and cryogenic separation (Lynd 1996).

Aerobic conversion has higher conversion rate than anaerobic processes, but not tends to produce value added gases. It usually takes place at sludge orwaste water treatment processes (Wooley et al., 1999).

Boerrigter (2006) indicated in the report that total capital cost of BTL plants is usually 60% higher than GTL plant with same scale and technologies through FT conversions, due to the following reasons: 1, extensive solid handling and treatment for the feedstocks, 2, 50% more oxygen input is demanded for BTL resulting in lager ASU capacity, 3, additional application of Rectisol unit is installed to remove impurities and clean syngas. Boerrigter (2006) concluded the same conclusion that lager capacities will favor more economical production is given from this assessment. The cost calculation approach is following the way Boerrigter (2006) did, and it referenced the ORYX GTL (34,000 BPD) with TCI of 1100 MM$.

The notion of first generation biofuels is liquid biofuels like ethanol from sugar plant, oil from oil crops, biodiesel from esterification. Their low fuel qualities, low environmental efficiency (50% avoided CO2 emission compared to 80% of the second generation), and low production capacity due to specific feedstock crops production lead to the necessity to utilize other biofuels from the second generation. The second generation biofuels are produced from lingo-cellulose feedstock and has high quality fuels with as high as 70% BTL efficiency (Boerrigter, 2006).

These BTL design studies introduced a basis for identifying the status of alternative conversion technologies for producing biofuels. These studies also helped understand technical barriers for the design and cost improvement potential.

1.3 Feedstock Introduction and Pretreatment

Different feedstock has wide range of compositions and hence various handling and converting technologies. The feedstock characteristic and compositions will also affect the following processing designs, conversion rate, capital cost, and choices of fuel types. There are biomass feedstock such as municipal solid waste (MSW), algae, energy crop, plantation waste, farm residuals, landfill gas, etc.

There are microalgae and cyanobacteria (blue green algae) which can be cultivated either by photoautotrophic (which needs light to grow) in ponds, or by heterotrophic methods (which doesn’t need light and need carbon source to grow). Another category of algae called macroalgae (or seaweed) has different cultivation requirement of open off-shore or coastal facilities. Therefore waste water, CO2, sugar waste streams could serve as the nutrient source for algae grow. The difficulty with technology handling algae lies in the large water amount existing in it. The government investment in algae development adds to $180M in 2010 (Hamelinck and Fajj, 2002).

Morello and Pate (2010) shows a variety of technologies that could be applied to convert algae into value added chemicals (shown in Figure 1.2). The advantage of using algae to produce fuels include:1, it occupies less land, 2, it has high production and easy culture (Micro Algae of 700 - 7000 vs. Corn 18 vs. Soybeans 48 gallon of oil/acre/yr), 3, it doesn’t compete with food crops, 4, it can potentially recycle waste and CO_2, 5. It could reduce demand on fresh water. The factors that will affect the efficiency of the process include: 1, algae species will choose different processing decision and cultivation resources, 2, algae cultivation will determine different facility and scale 3, algal harvesting and processing will determine different technologies and result in different conversion rate (Morello and Pate, 2010).

Harvesting of algae is conducted by flocculation, centrifugation of biomass, and solvent extraction. Since algae is high moisturized, the cost for extraction will be three times higher as usual for soybean extraction. The residual biomass will be used for anaerobic digestion and C rich products will be recycled back to the pond. Early cost analysis for large-scale microalgae production in the 1970s and during the 1980s showed that the biological conversion accounts for the most cost factor and open pond designs seem to be the most cost effective technology for algae production (160 barrels of crude oil/ha/yr) (Benemann et al., 1978). Without major improvements in culture patterns, economic activity, alternative design, material handling, there will be long term for looking for new algae utilization techniques.

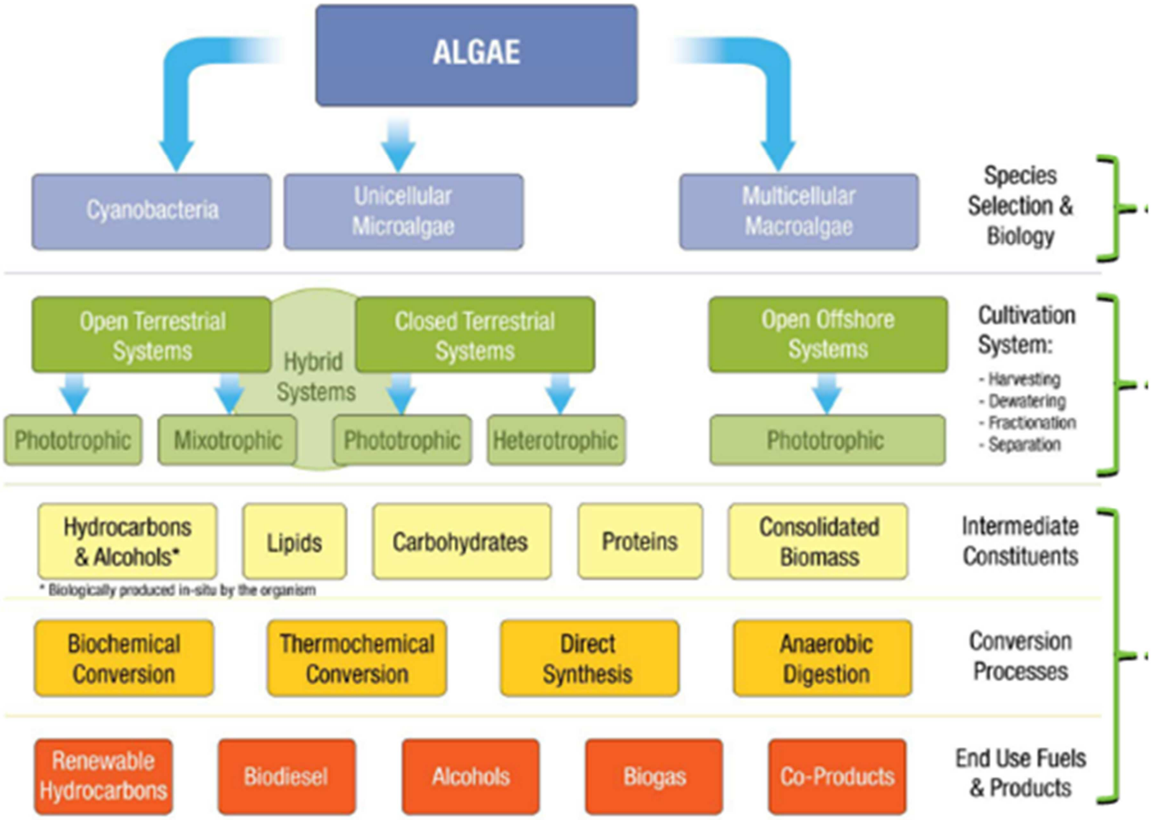
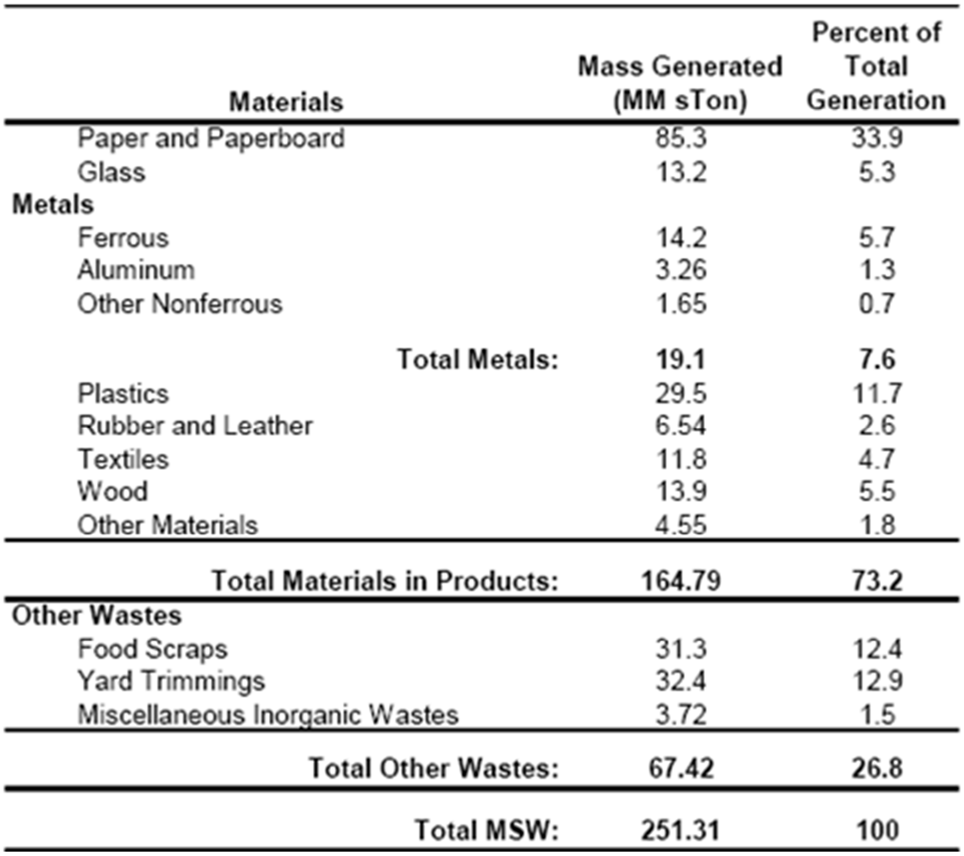


Figure 1.2. The Various Pathway to Produce Fuels and Chemicals from Algae (Morello and Pate, 2010)

“MSW is defined as household waste, commercial solid waste, nonhazardous sludge, conditionally exempt, small quantity hazardous waste, and industrial solid waste. It includes food waste, residential rubbish, commercial and industrial wastes, and construction and demolition debris.”(Williams, 2007) United States Environmental Protection Agency (EPA) reports that in 2006 the national MSW amount was more than 251 MM tons per year, and 45% was treated by recycling, composting, and energy generation. If all the MSW was converted to fuels, more than 310,000 bbl per day of liquid fuels (about 1.4% of U.S. transportation fuels) would be produced. And this accounted for an 544 MM metric tons/yr of CO_2 emissions reduction through MSW treating (Ivannova, et al, 2008; Stinson et al, 1995; Tong, et al, 1990; Ham, et al, 1993; Baldwin et al, 1998; Department of the Environment, 1995; Micales and Skog, 1997). It will retain a lot of heating value from recovering MSW. To pretreat MSW, it’s better to convert it to refuse derived fuel (RDF) first, where size is greatly reduced, characteristics and composition of the material are improved (lower pollutant, easier handling, less air combustion, homogeneous composition), and heating value is increased by approaches of screening, sorting, and pelletization. After this step, 75%– 85% of MSW is processed to RDF and 80%–90% of the heating value is recovered (Jones et al., 2009).

Lab experiments were tested and compositions of MSW were analyzed from the work (Table 1.1). MSW is majority cellulose, hemicellulose and lignin composed. The lignin is not viable to degrade. Elements like S, Cl, F, As and P are volatile and will poison the catalysts for later synthesis processing steps (Baldwin et al., 1998), and elements like Cd and Hg are also difficult to remove and increase catalyst burden (Figure 1.3).

Table 1.1. The Composition of MSW Anlaysis (Valkenburg et al, 2008)



Materials	**Mass Generated (MM sTon)**	**Percent of Total Generation**
Paper and Paperboard	85.3	33.9
Glass	13.2	5.3
Metals		
Ferrous	14.2	5.7
Aluminum	3.26	1.3
Other Nonferrous	1.65	0.7
Total Metals:	**19.1**	**7.6**
Plastics	29.5	11.7
Rubber and Leather	6.54	2.6
Textiles	11.8	4.7
Wood	13.9	5.5
Other Materials	4.55	1.8
Total Materials in Products:	**164.79**	**73.2**
Other Wastes		
Food Scraps	31.3	12.4
Yard Trimmings	32.4	12.9
Miscellaneous Inorganic Wastes	3.72	1.5
Total Other Wastes:	**67.42**	**26.8**
Total MSW:	**251.31**	**100**

Government will apply tipping fee of about $24.06 per ton in the south to $70.06 per ton in the Northeast (Repa, 2005) for treating MSW. The pretreatment steps include (Phyllis, 2008): removing non-grindables such as metal and glass, drying and milling, and finally sent to gasifier (Shown in Figure 1.4).

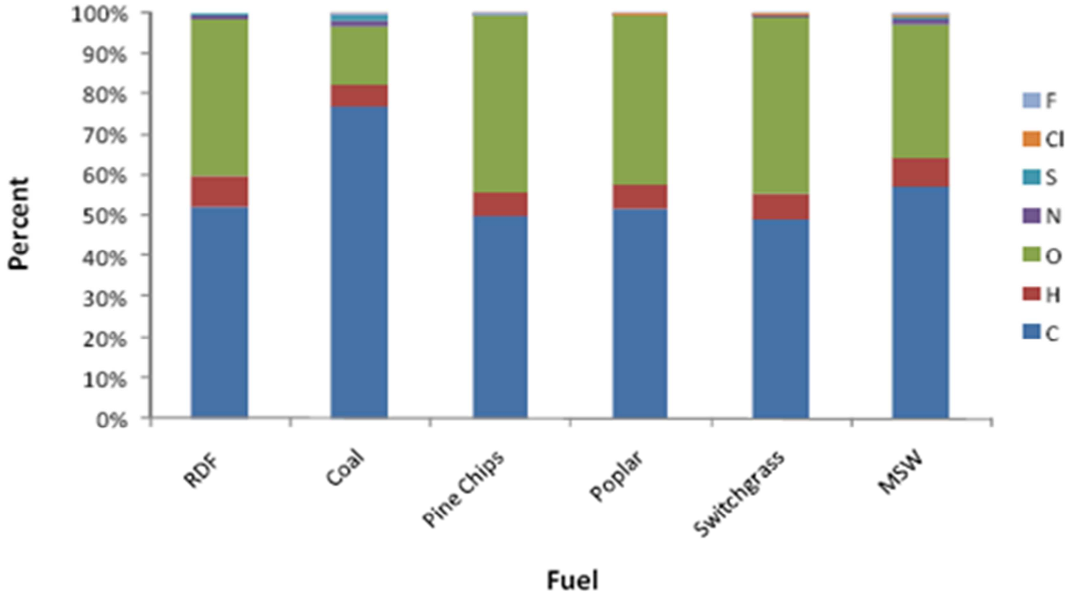


Figure 1.3. Elemental Analysis of MSW and Other Biomass Feedstock (Valkenburg et al, 2010)

Biomass pretreatment includes torrefaction and flash pyrolysis for bioslorry producing (Wooley et al., 1999). Syngas treatment and conditioning includes: syngas cooling, water gas shift, CO2 treatment, and impurities removal. The gasification for biomass has advantages of high efficiency conversion to bio syngas. In addition, it could support wide range of scalability, and has flexibility to run on coals as back-up fuel.

Besides the operational and technology performance effect for the BTL process, the feasibility and opportunity of biomass refinery is also concerned with the following constraints, difficulty of feedstock handling and pretreatment, impact of feedstock crop production and price, impact of scale, impact of feedstock transportation, etc.

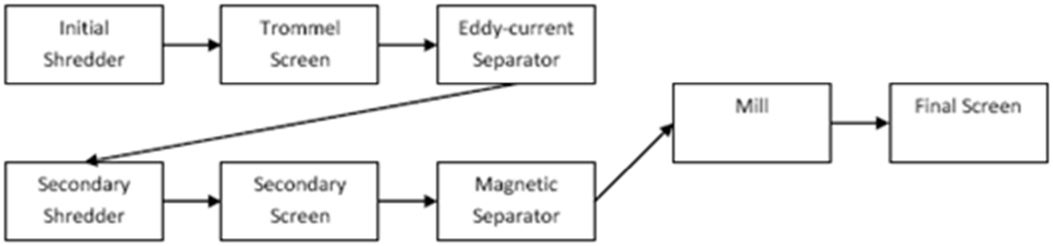


Figure 1.4. The Pretreatment for MSW Process (Valkenburg et al, 2010)

2. METHODOLOGY AND APPROACH

2.1 Overview of the Process Design Approach

The framework in this biorefinery process design work involves material treatment, mass recycle, heat retrofitting, and so on. These emphasize the use of process integration approach and picture the design from holistic view without exhausting in the separate unit detailing.

The design and optimization of chemical and industrial processes is targeted to improve the performance of the following items: raw material conservation, waste output reduction, energy efficiency increase, yield and product quality enhancement, capital cost reduction, safety emphasis, and process flexibility and debottlenecking (El-Halwagi, 2006). The development of process integration has led to a systematic and fundamental framework that could incorporate widely-applicable techniques and address the process design problems. This can be categorized into process synthesis techniques and process analysis techniques.

The traditional process design and improve approaches typically cover: 1, Adopting old designs, that is to solve similar problems based on experiences of earlier developed methods. 2, Using heuristics, that is to solve certain types of problems with general-applicable experience-generated knowledge and methods. 3, By brainstorming, that is to list only a few generic alternatives for the problem designs and screen from them through optimizing techniques. (El-Halwagi, 2006) While these approaches suggest a good platform for generating various alternatives for the process, they didn’t identify the internal challenges for the problem and didn’t take it as an integrated system, thus leaving a few limitations for obtaining the optimum solution. These limitations include: 1, Only a few of the existing process alternatives could be suggested, and the real optimum solutions maybe neglected. 2, They’re time and cost consuming for evaluating each alternative. 3, They didn’t really diagnose the root causes of the bottleneck of the process problems. 4, Since they’re derived from experiences and existing knowledge, the application will be limited and incompatible with the real case. 5, With the above listed reasons, it’s usually not getting the optimum target for the designs. (El-Halwagi, 2006)

In order to treat the root causes of the problems and generate an effective and sustainable framework, it’s necessary to perform a process integration technique. “Process integration is a holistic approach to process design, retrofitting, and operation which emphasizes the unity of the process.” (El-Halwagi, 1997) Process integration has been classified into mass integration and heat integration (discussed in later sections).

Process synthesis presents a configuration that combines separate elements and interconnects them in a systematic way. These elements include the parameters, equipments, and structures of the process. By having the inputs and outputs for a process, it’s able to generate an optimum flowsheet for the process design (shown in Figure 2.1).

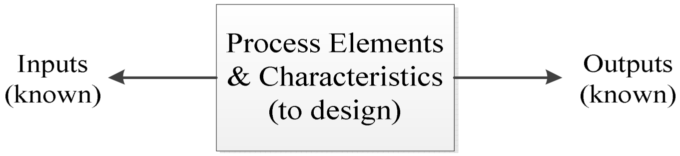


Figure 2.1. Process Synthesis Representation (El-Halwagi, 2006)

In contrast to process synthesis, process analysis aims at evaluating and predicting the performance outputs of a process design with known inputs and flowsheet details (shown in Figure 2.2). This analysis could be carried out by computer aided software, mathematical formulation, and empirical models.

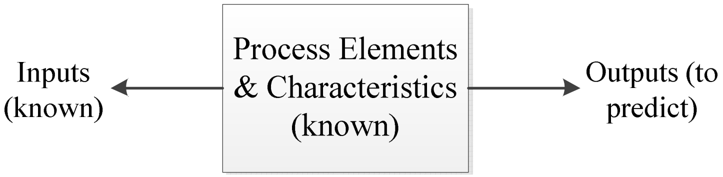


Figure 2.2. Process Analysis Representation (El-Halwagi, 2006)

The process integration is performed in the following steps: 1, data generation, to gather necessary data or models with known conditions to develop strategies for problem solving. 2, targeting, to set up the goals to be achieved and to identify the idealistic goal ahead of detailed design as a useful insight. 3, performing process synthesis, to generate design alternatives framework that could be embedded possible configurations and to select the optimum solutions using optimizing techniques. 4, performing process analysis, to assess and validate the behavior of the generated alternatives.

2.2 Methodology on Mass and Energy Integration

Mass integration provides a systematic and fundamental way to identify the optimal mass segregation, mixing and generation strategies throughout the chemical processes, the performance of which will affect the characteristics of those streams. The main elements in the mass integration are the sinks and sources. They could accept species or generate species according to the design specifications and therefore influence the streams operations. There are many tools to conduct mass integration, like graphical strategies, mathematical models, and optimization softwares.

Mass integration requires firstly to target the mass potential of the strategy. This includes the determination of for example (El-Halwagi, 2006):

- To what extent the mass amount could be recycled?
- How should the mass streams be segregated and split?
- What is the minimum waste that could be discharged?
- What is the minimum fresh feed amount?
- How should the optimum mixing fraction be?
- What unit should be proper streams assigned to?
- Should the units be replaced or added?
- How should the units be operated and conditions controlled?

With source and sink graphical techniques, the optimum target could be reached for mass recycle problems (shown in Figure 2.3). The steps follows: 1, rank the sinks and sources in ascending order of compositions, 2, plot the sink and source with the load of impurity vesus flowrate. Each sink is connected from the arrow of the previous sink with superposition arrow starting from the sink with lowest composition. The same is applied to sources. The fresh feed and the waste discharge are represented by the rate of the flowrate of the starting and the end between the sink and source composite curves. After that, the source composite curve could be moved horizontally until touched by the sink composite curve. The touch point is represented as the pinch point. This means, at this point, the minimum waste charge and minimum fresh feed is achieved. The flowrate amount passed between the pinch is reduced. Thus, the recycle extent, the waste flowrate, the feed flowrate could be reduced by this amount. The thumb rule applied here is that, there should be no fresh feed to sink above the pinch, no waste from the source below the pinch, and no flowrate passed in the pinch (El-Halwagi, 2006).

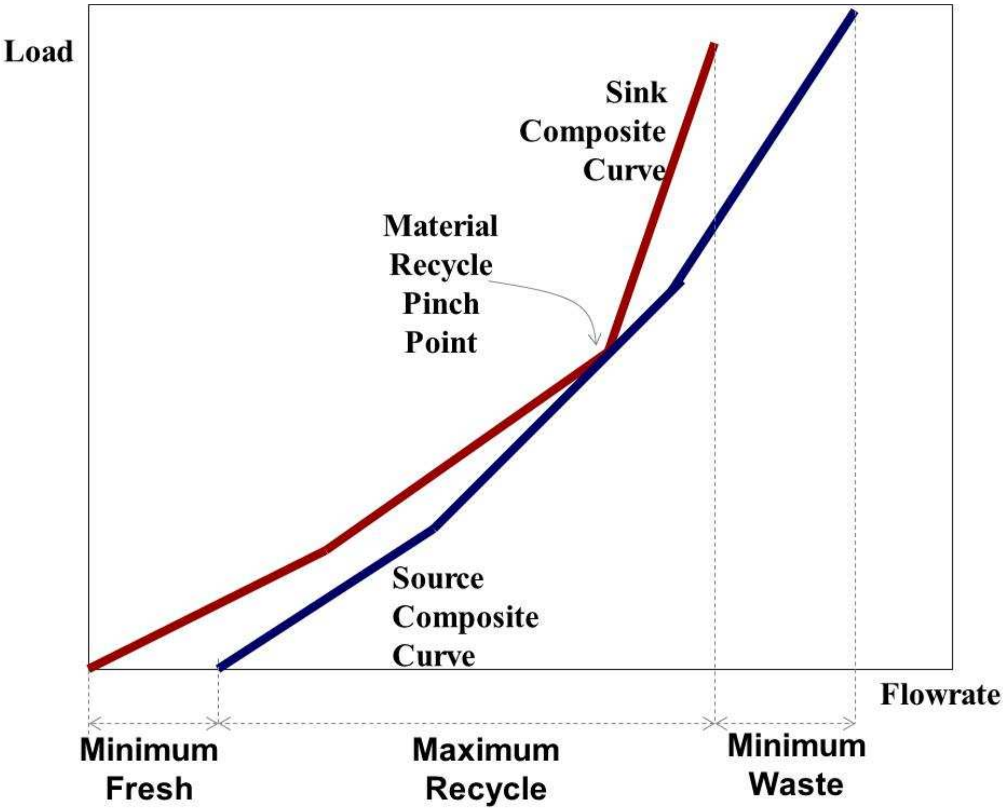


Figure 2.3. Sink and Source Composite Diagram for Material Recycle Pinch Analysis (El-Halwagi, 2006)

Another important strategy to obtain the target is by including interception systems. Interception generally takes charge of the process streams' properties such as species composition, flowrate, to make them suitable for sink designs by adding new equipment along with related materials. One particular case is the separation system for the species allocation.

While it's helpful and beneficial to apply the visual tools for these problems, it's still necessary to employ algebraic methods when it meets the cases of numerous process units or multiple task identification. In a mass synthesis network, a mathematical programming technique could be utilized to determine a sustainable process mass design.

In a source interception sink network, the formulation can be expressed as this way. Sources can be segregated into fractions and sent to interception units to separate unwanted species, and treated streams can be mixed according to the requirement of each sink and fed into the sinks. The sinks could be controlled for the design and operating purpose. It is desired to determine the minimum cost for the interception network, and at the same time the optimum allocation of the splitting and mixing of the streams between the sinks and sources could be determined. The representation is shown in Figure 2.4. To solve it in a global linear optimization perspective, the interception network could be adjusted using assumptions that each interceptor is discretized into a few interceptors for each split streams to feed in. Each interceptor is fixed with the separation efficiency.

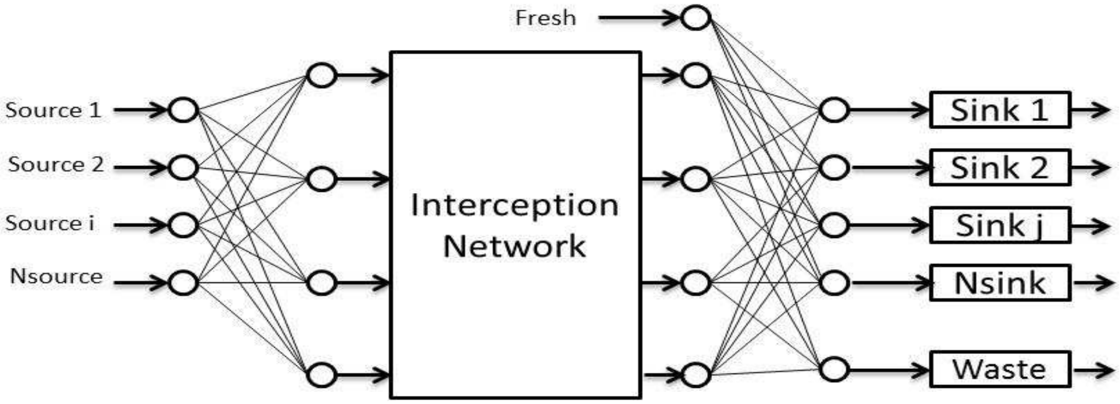


Figure 2.4. Representation of Source Interception Sink Network (El-Halwagi, 2006)

The objective is to decide the minimum cost for the system, including the cost of the intetceptors and the cost of the fresh feed cost and waste cost (El-Halwagi, 2006).

Minimize total annualized cost = $C_{Fresh} \sum_{j=1}^{N_{sinks}} Fresh_j + \sum_{u=1}^{NU_{int}} C_u \times \alpha_u \times w_u \times y_u^{in} + C_{waste} \times waste$

Subject to the constraints of:

Each source i is split into streams for each interceptor u

$$F_i = \sum_{u \in U_i} w_u \quad i = 1,2, \ldots N_{sinks}$$

The unwanted species removal in the uth interceptor is

$$y_u^{out} = (1 - \alpha_u) \times y_u^{in} \quad u = 1,2, \ldots NU$$

The streams coming out of each interceptor u is split to waste and different sinks

$$w_u = \sum_{u=1}^{NU} g_{u,j} + g_{u,waste} \quad u = 1, \ldots NU$$

The flowrate for each sink j is mixed by streams from fresh feed and streams from interceptors

$$G_j = Fresh_j + \sum_{u=1}^{NU} g_{u,j} \quad j = 1, \ldots N_{sinks}$$

Material balance for each sink j when mixing

$$G_j \times z_j^{in} = Fresh_j \times y_{fresh} + \sum_{u=1}^{NU} g_{u,j} \times y_u^{out} \quad j = 1,2, \ldots N_{sinks}$$

The material composition requirement for each sink j

$$z_j^{min} \leq z_j^{in} \leq z_j^{max} \quad j = 1,2, \ldots N_{sinks}$$

The total waste is mixed by the streams from unused flows

$$waste = \sum_{u=1}^{NU} g_{u,j,waste}$$

where

α_u is the separation efficiency of the interceptor u

C_u is the cost of the interceptor u

C_{Fresh} is the fresh feed cost

C_{waste} is the waste treatment cost

$Fresh$ is the flowrate of fresh feed

$waste$ is the flowrate of waste stream

y_u^{in} is the composition from each source to unit u

w_u is the flowrate to each unit u

$g_{u,j}$ is the flowrate coming out of each unit u to different sink j

G_j is the flowrate into each sink j

F_i is the flowrate of each source i

z_j^{in} is the composition of streams into each sink j

Synthesis of heat exchange network will significantly reduce the complex of the external utility tasks and increase the heat efficiency for the process. In a typical process, there will be a variety of hot streams need to be cooled and cold streams to be heated. This introduces a lot of duty for external utilty usage. Before the external utility is applied, it is possible to transfer heat from hot streams to cold streams according to thermodynamic rules. This is what heat integration does (shown in Figure 2.5) to simultaneously improve the energy efficiency in the process while achieving the optimal system configuration in this regard.

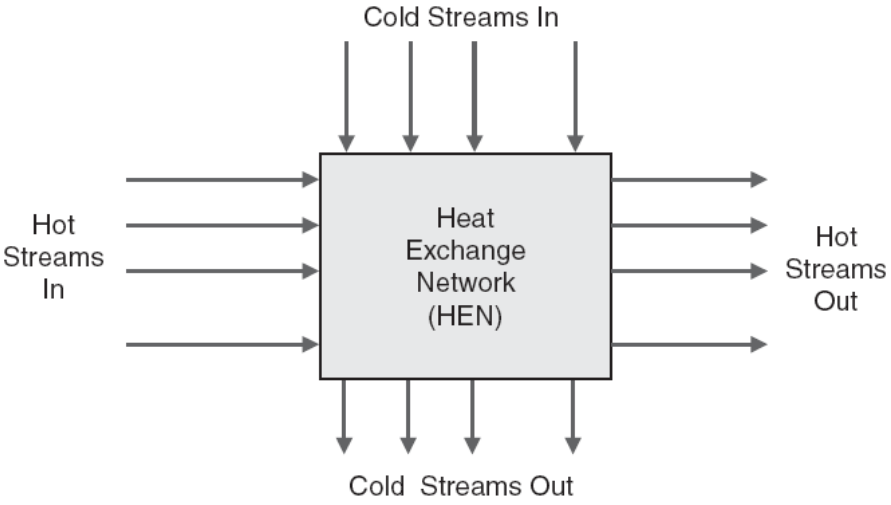


Figure 2.5. Representation of Heat Exchange Network (El-Halwagi, 2006)

Various heat network methods have been developed, and the key responsibility is to solve these problems:

How should the heat be exchanged between hot and cold streams?

How much is the optimal heat load from external utility?

Where and how should the heat utility placed or added?

How is the thermal system arranged?

One of the techniques used here to answer these questions is by graphically generating a heat exchange pinch diagram (shown in Figure 2.6) to target for the optimal design. The first step is to list all the hot streams/cold streams by drawing the starting and ending temperatures versus enthalpy exchange. The temperatures for cold and hot streams are plotted in the coordinate one-to-one correspondingly. All hot streams are super positioned by the heat load scale using diagonal rule. And the same is applied to all the cold streams to construct the cold composite curve. Different heat exchange strategy will imply different position of cold composite curve by moving it up and down. The point where the two curve touch is the thermal pinch point, where the minimum heating utility and minimum cooling utility are obtained. The design rule to achieve the optimal heat decision follows: 1, there are no cooling utilities above the point. 2, there is no heating utilities below the point. 3, there is no heat flow passed the point (El-Halwagi, 2006). In this way, the maximum heat exchange could be integrated within the existing process streams and optimal energy design system is achieved according to this target.

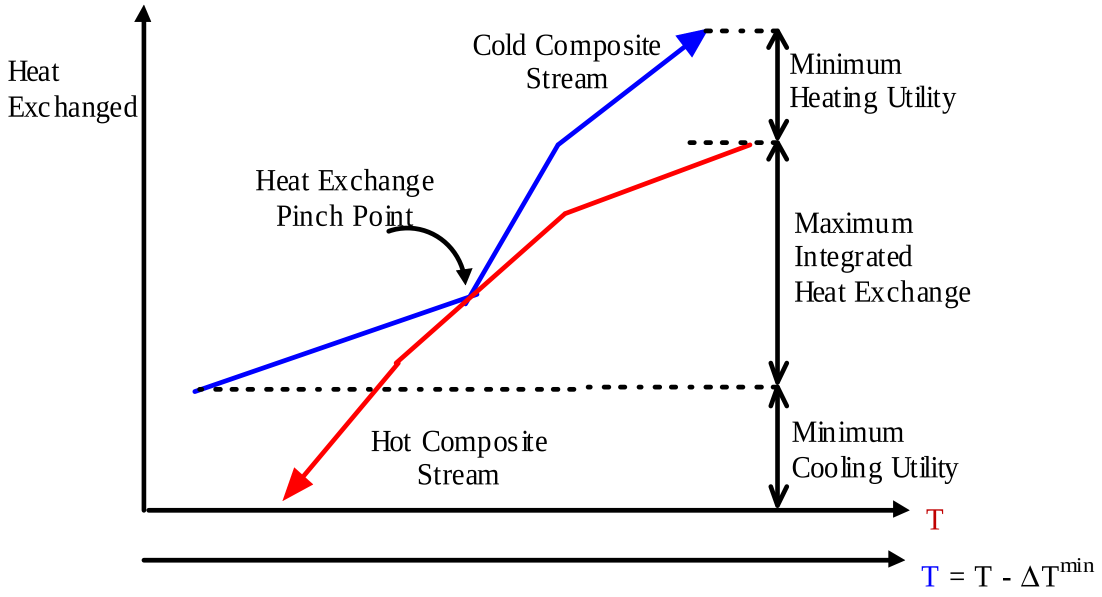
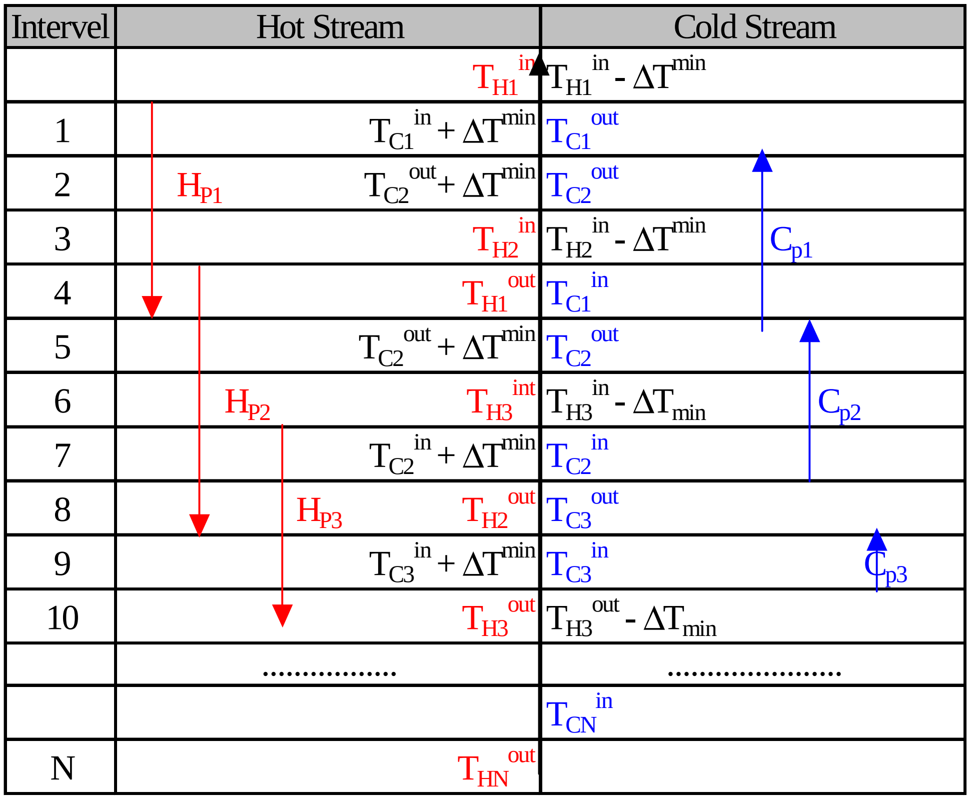


Figure 2.6. Heat Integration Diagram with Pinch Point (El-Halwagi, 2006)



Intervel	Hot Stream	Cold Stream
	T_{H1}^{in}	$T_{H1}^{in} - \Delta T^{min}$
1	$T_{C1}^{in} + \Delta T^{min}$	T_{C1}^{out}
2	H_{P1} $T_{C2}^{out} + \Delta T^{min}$	T_{C2}^{out}
3	T_{H2}^{in}	$T_{H2}^{in} - \Delta T^{min}$ C_{p1}
4	T_{H1}^{out}	T_{C1}^{in}
5	$T_{C2}^{out} + \Delta T^{min}$	T_{C2}^{out}
6	H_{P2} T_{H3}^{int}	$T_{H3}^{in} - \Delta T_{min}$ C_{p2}
7	$T_{C2}^{in} + \Delta T^{min}$	T_{C2}^{in}
8	H_{P3} T_{H2}^{out}	T_{C3}^{out}
9	$T_{C3}^{in} + \Delta T^{min}$	T_{C3}^{in} C_{p3}
10	T_{H3}^{out}	$T_{H3}^{out} - \Delta T_{min}$
	....	....
		T_{CN}^{in}
N	T_{HN}^{out}	

Figure 2.7. The Temperature Interval Diagram for Heat Loads of Hot and Cold Streams (El-Halwagi, 2006)

After that, heat intervals diagrams 2.7 will be constructed for a table of exchangeable heat loads to express the temperature and heat load relationship. From the table, the heat loads of process hot and cold streams could be calculated. It's a useful tool to represent the thermodynamic heat exchange, with the horizontal lines indicating the temperatures and vertical arrows indicating heat of each stream, where the tail defines the supply temperatures and head defines the target temperatures. The heat loads could be represented by algebraic expressions (El-Halwagi, 2006).

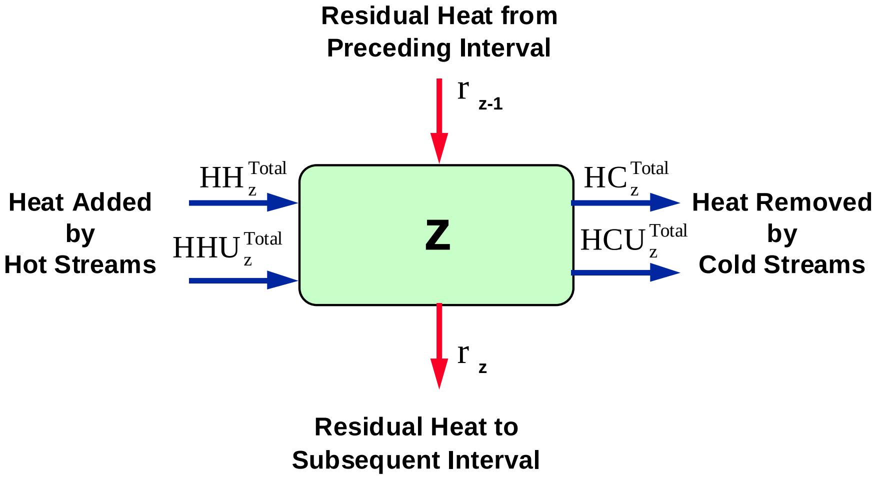


Figure 2.8. The Heat Balance for Each Heat Interval (El-Halwagi, 2006)

A schematic representation is shown in Figure 2.8 to illustrate the heat balance around each temperature interval. The heat balance around each interval is calculated by the residual heat, heat of process streams, and heat from heat utilities. With the rule of thermodynamic, it's practical to pass heat from heat intervals with higher temperatures to lower temperatures, but not the reverse direction. And it's feasible to transfer heat from heat streams to cold streams within the process (El-Halwagi, 2006).

$$r_z = HH_Z^{Total} + HHU_z^{Total} - HC_Z^{Total} - HCU_z^{Total} + r_{z-1}$$

The heat supplied from the u th hot stream is

$$HH_u = F_u C_{p,u}(T_u^s - T_u^t) \qquad u = 1, 2, \ldots, N_H$$

The heat supplied to the v th cold stream is

$$HC_v = f_v C_{p,v}(t_v^s - t_v^t) \qquad v = 1, 2, \ldots, N_C$$

Using the table of exchangeable heat loads, the heat load for each hot stream within t each temperature interval can be determined by

$$HH_{u,z} = F_u C_{p,u}(T_{z-1} - T_z)$$

And the heat load for each vth cold stream within each zth temperature interval can be determined by

$$HC_{v,z} = f_v C_{p,v}(t_{z-1} - t_Z)$$

Therefore, the total heat load entering and leaving the zth interval can be calculated by the summation of all the cold and heat streams.

$$HH_z^{Total} = \sum_{\substack{u \text{ passes through interval } z \\ \text{where } \mathrm{u}=1,2,\ldots\ldots,\mathrm{N_H}}} HH_{u,z}$$

$$HC_z^{Total} = \sum_{\substack{v \text{ passes through interval } z \\ \text{and } v=1,2,\ldots,N_C}} HC_{v,z}$$

Where

$F_u C_{p,u}$ is heat capacity of hot stream u

$f_v C_{p,v}$ is heat capacity of cold stream v

HC_v is heat supplied to the v th cold stream

HH_u is heat discharged from the u th hot stream

r_{z-1}, r_z is the residual heat entering and leaving the z th heat interval

T_{z-1}, T_z is the top and the bottom temperature defining the z th interval for the hot streams

T_u^s, T_u^t is inlet and outlet temperature for hot stream u

t_{z-1}, t_z is the top and the bottom temperature defining the z th interval for the cold streams

t_v^s, t_v^t is inlet and outlet temperature for cold stream v

After this, the heat intervals for all the temperature levels throughout the process could be interconnected and heat integration could be performed (shown in Figure 2.9). The point with the lowest heat residual which is negative will is called pocket. Since heat residual should not be negative, a heat surplus will be added from the top of the heat cascade sequence to make it be zero. This zero point will be the pinch point, where the minimum heat consumption is achieved. The heat added from the top will be the minimum heating utility and heat in the bottom will be the minimum cooling utility.

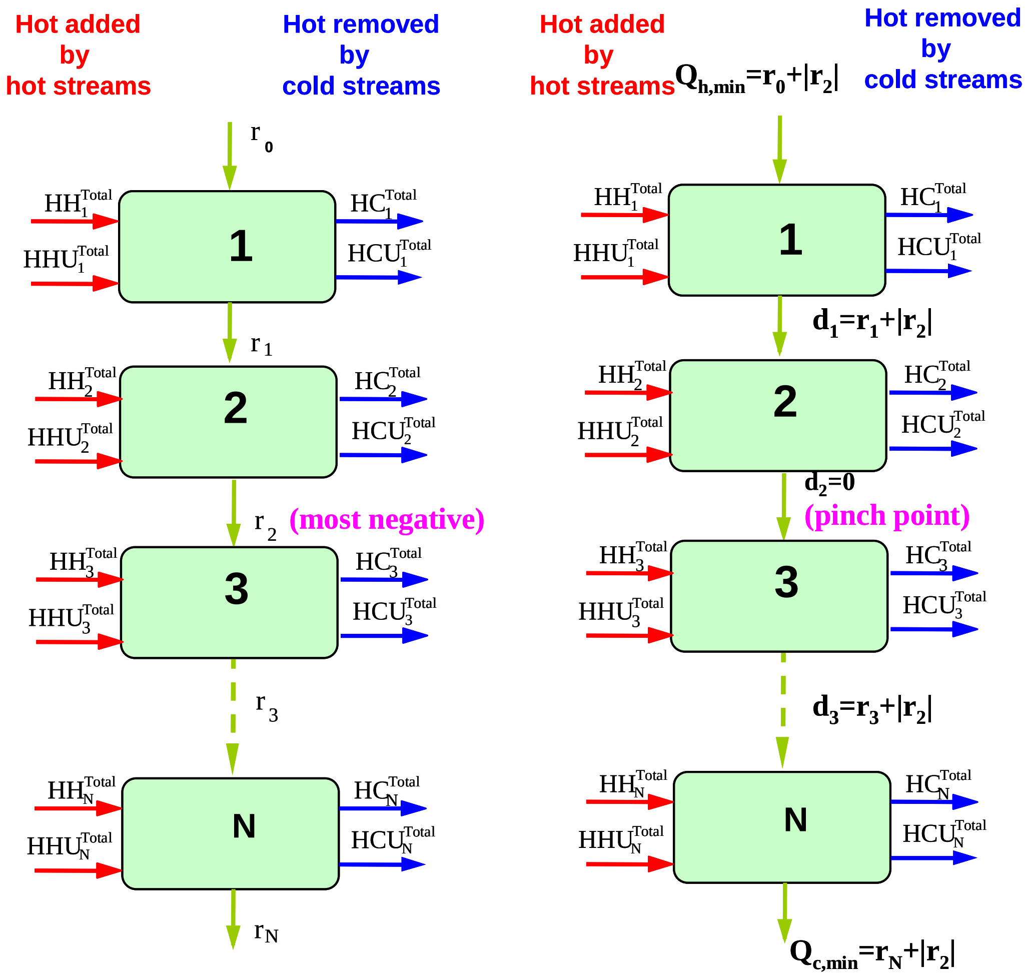


Figure 2.9. Thermal Passing Cascade Diagram and Integrated Heat Interval Representation (El-Halwagi, 2006)

3. A SHORTCUT METHOD FOR THE PRELIMINARY SYNTHESIS OF PROCESS-TECHNOLOGY PATHWAYS: AN OPTIMIZATION APPROACH AND APPLICATION FOR THE CONCEPTUAL DESIGN OF INTEGRATED BIOREFINERIES*

3.1 Introduction

Fossil fuels have been essential in meeting a substantial portion of the global energy demand. With the continuous growth of population and industrial activities, the World's energy consumption is projected to increase by 44% from 2006 to 2030 (EIA, 2009). In addition, liquid fuels are expected to remain as the world main energy source with consumption of approximately 90 million barrels per day currently (EIA, 2009). The dwindling fossil-energy resources coupled with the increasing energy demand will ultimately lead to the exhaustion of fossil fuels (Shafiee and Topal, 2008). This underlines the need to develop alternative energy sources including biofuels.

Biofuels are renewable energy forms derived from any organic material such as plants and animals. They can provide a variety of environmental advantages over petroleum-based fuels including sustainability and the reduction in greenhouse gas (GHG) emissions. For example, in a full fuel cycle, corn ethanol has the potential to reduce

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GHG by as much as 52% compared to conventional fossil fuels (EIA, 2009). Such reduction is attributed to carbon dioxide being sequestrated during photosynthesis and growth of crops. The processes that convert biomass into biofuels produce inherently low GHG emissions and are more environmental friendly as compared with processes for fossil fuels. The amount of investment and funding for biofuels research and production totaled at more than $4 billion worldwide in year 2007 and is expected to increase over the years (Bringezu et al., 2009). Biorefineries are processing facilities that convert biomass into value-added products such as biofuels, specialty chemicals, and pharmaceuticals (Ng et al., 2009). There are multiple established conversion technologies (e.g., thermochemical, biochemical, etc.) in a biorefinery. The U.S. Department of Energy suggested five primary platforms (i.e. sugar, thermochemical, biogas, carbon rich chains and plant products platforms) to describe the expanded conversion technologies for a biorefinery (NREL, 2005). Given the tremendous number of potential alternatives and combinations of technologies in a biorefinery, there is a strong need to quickly and methodically generate and screen alternatives. It is also necessary to explore different levels of integration in a biorefinery to reduce waste and conserve resources (e.g., Azapagic, 2002). In this paper, we use the term an “integrated refinery” to refer to a biorefinery that integrates multiple technologies and platforms (compared to a biorefinery that uses a single technology or a platform).

In order to synthesize a cost-effective integrated biorefinery, various technologies should be examined and analyzed. Ng et al. (2009) proposed a hierarchical procedure for the synthesis of potential pathways and developed a systematic approach to screen and identify promising pathways for integrated biorefineries. The approach uses a sequential method to screen competing technologies based on thermodynamic feasibility and gross revenue (sales minus cost of raw materials). Recently, Ng (2010) presented a pinch based automated targeting approach to locate the maximum biofuel production and revenue targets for an integrated biorefinery prior to the detail design. Simple conversion models were used in a cascade analysis to target the yield of a biorefinery based on the flows of mass from sources to sinks. While this approach is useful in getting targeting estimates, it is limited to simple technological models and does not account for capital investment. Tay et al. (2011) extended the used of a carbon-hydrogen-oxygen (C-H-O) ternary diagram to synthesize and analyze an integrated biorefinery. Using graphical insights, the overall performance target of the synthesized integrated biorefinery can be determined. Additionally, detailed techno-economic analyses have also been conducted for several biomass-to-energy pathways such as thermal processes (e.g., Goyal et al., 2008) and biodiesel production (e.g., Mohan and El-Halwagi, 2007; Myint and El-Halwagi, 2009; Pokoo-Aikins et al., 2010a; Qin et al., 2006). Research efforts have also been directed towards establishing processing routes prior to establishing the optimal product for optimal energy savings in the process (e.g., Alvarado-Morales et al., 2009; Fernando et al., 2006; Gosling, 2005). Sammons et al. (2008) incorporated economic perspective to analyze an integrated biorefinery and develop a systematic framework that evaluates environmental and economic measures for product allocation problems. Tan et al. (2009) developed an extended input-output model using fuzzy linear programming to determine the optimal capacities of distinct process units given a predefined product mix and environmental (carbon, land and water footprint) goals. Elms and El-Halwagi (2009) introduced an optimization routine for feedstock selection and scheduling for biorefineries and included the impact of greenhouse gas policies on the biorefinery design. Pokoo-Aikins et al. (2010b) included safety metrics along with process and economic metrics to guide the design and screening of biorefineries.

Since there is a very large number of available process configurations, feedstocks, and products in an integrated biorefinery, it is necessary to develop a systematic methodology that handles such complex process synthesis problem which is the subject of this work. A systematic approach is developed in this work, to quickly screen the potential technology pathways and to synthesize an integrated biorefinery based on various objective functions (e.g., maximum production, revenues, etc.). The use of limited data on the performance of technology is incorporated in a structural representation that embeds potential pathways of interest. An optimization formulation is developed to screen the potential pathways and to develop a preliminary and conceptual flowsheet of the biorefinery. Integration of multiple conversion technologies and the produced species is systematically achieved via the optimization framework to quickly screen and synthesize a technological pathway.

3.2 Problem Statement

The problem addressed in this paper can be simply stated as follows: Given a set of feedstocks and a set of desired primary products, synthesize a process that meets a certain objective (e.g., maximum yield, maximum gross revenue, etc.). Available for service are a number of processing (conversion) technologies with known characteristics of performance (e.g., yield, cost). The conceptual design procedure is intended to quickly screen the numerous alternatives, to produce a conceptual design of the major components of the biorefinery, to integrate technologies and to set the stage for more detailed techno-economic analysis. While the problem statement and the approach to be presented apply to the synthesis of general chemical processes, focus in this paper will be given to biorefineries starting with a number of biomass feedstocks. This focus is chosen because of the significant opportunities in the area of biorefineries where there are numerous evolving alternatives that should be screened and integrated.

3.3 Approach And Mathematical Formulation

Instead of tracking the biomass and product mixtures, the network is categorized into chemical species and conversion technologies (operators). The analysis is started with the following steps:

1. List the available conversion technologies along with their performance characteristics (e.g., yield, cost) based on literature survey, simulation, reaction pathways synthesis, etc.

2. Based on the characteristics of the biomass feedstock, the desired products, and the conversion technologies, develop a list of the candidate chemical species that may be involved in the biorefinery. Let *c* and NC be the index and the total number of the chemical species, respectively.
3. Break the biomass feedstock into key chemical species (quantified based on chemical analysis)

Next, a chemical species/conversion operator (CSCO) diagram is introduced (Figure 3.1). The CSCO diagram has alternating layers of chemical species followed by conversion operators (processing technologies). There are NP layers of chemical species and NP – 1 layers of conversion operators, each designated by the index *i*. The first chemical-species layer ($i = 1$) is the biomass feedstock (broken into chemical species) while the last ($i =$ NP) represents the desired product. The other chemical-species layers represent the candidate intermediates involved in the biorefinery. A certain chemical species, *c*, produced from various conversion operators in layer *i* is collected from the different conversion operators and fed to the corresponding chemical-species node, *c*, in layer $i + 1$. Recycle is allowed by allocating a species *c* to an earlier layer. Furthermore, a certain chemical species, *c*, in the chemical-species layer *i*, is allowed to split to the different conversion operators in layer *i*. In addition to available technologies in each conversion layer, blank operators are also added to allow a species to go through the layer unchanged.

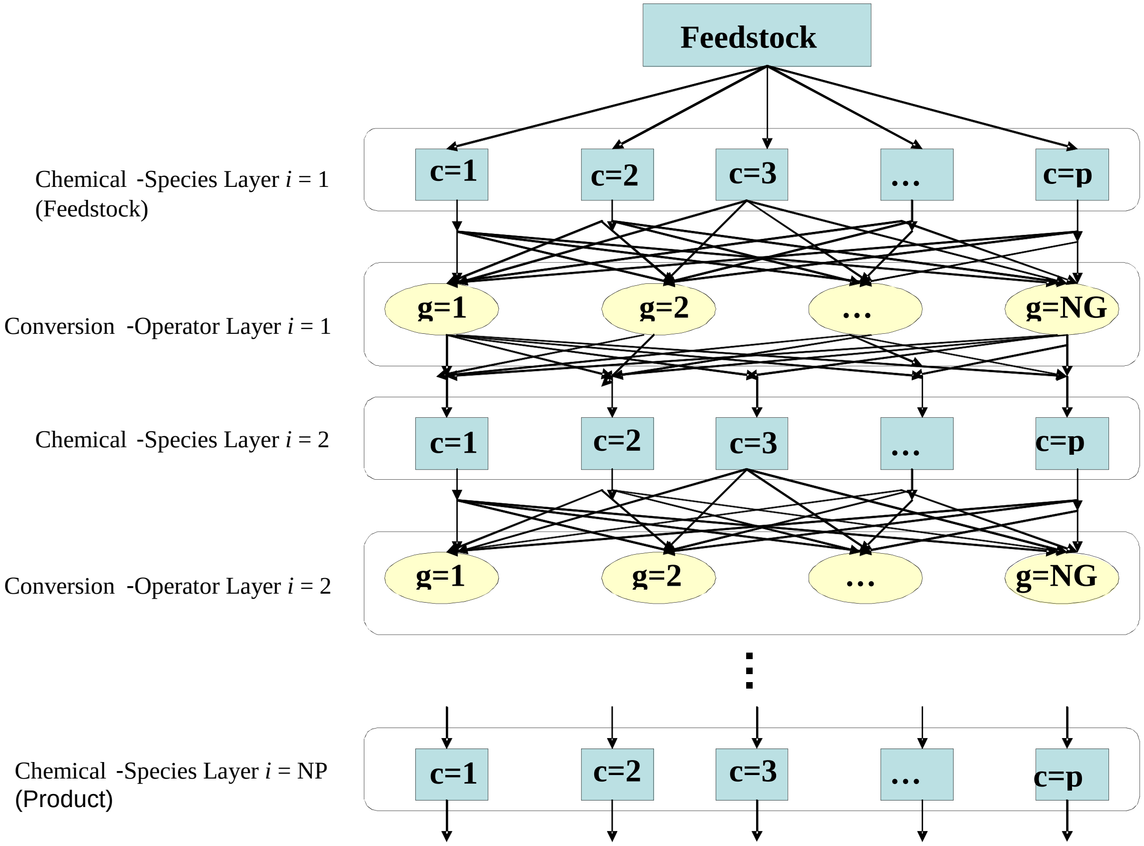

Figure 3.1 Chemical Species/Conversion Operator (CSCO) Mapping for the Structural Representation of the Biorefinery-Pathway Integration

The foregoing concepts can be included in an optimization formulation that involves the following constraints:

The performance model for conversion operator g_i in layer i (referred as $\psi_{g_i,i}$) relates the flowrates of the different chemical species entering and leaving the conversion operator, i.e.

$$(F^{out}_{g_i,i,1},\ldots,F^{out}_{g_i,i,c},\ldots,F^{out}_{g_i,i.NC}) = \psi_{g_i,i}\ (F^{in}_{g_i,i,1},\ldots,F^{in}_{g_i,i,c},\ldots,F^{in}_{g_i,i.NC},d_{g_i},O_{g_i}) \qquad \forall g_i\ ,\ \forall i$$

where $F^{out}_{g_i,i,c}$ and $F^{in}_{g_i,i,c}$ are the flowrates of chemical species c leaving and entering conversion operator g_i in layer i. The design and operating variables of g_i are denoted by d_{g_i} and O_{g_i}, respectively.

The total annualized cost of conversion operator g_i in layer i, $TAC_{g_i,i}$, is given through the function $\Omega_{g_i,i}$ as follows:

$$TAC_{g_i,i} = \Omega_{g_i,i}\ (F^{in}_{g_i,i,1},\ldots,F^{in}_{g_i,i,c},\ldots,F^{in}_{g_i,i.NC},d_{g_i},O_{g_i}) \qquad \forall g_i\ ,\ \forall i$$

The flowrates of the chemical species c in chemical-species layers i + 1 and i (designated respectively by $F_{c,i+1}$ and $F_{c,i}$) are related by the rates of formation or depletion via chemical reaction over all the conversion operators in that layer, i.e.

$$F_{c,i+1} = F_{c,i} + \sum_{g_i} r_{g_i,c,i} \qquad \forall g_i\,,\ \forall i$$

where $r_{g_i,c,i}$ is the rate of formation/depletion of chemical species c in conversion operator g_i and is given a positive sign for formation and a negative sign for depletion.

Material balance for the splitting of the flowrate of species c from chemical-species layer i to the conversion operators in layer i (Figure 3.2):

$$F_{c,i} = \sum_{g_i} F^{in}_{g_i,c,i} \qquad \forall c\,,\ \forall i$$

Material balance for the mixing of the flowrate of species c from the conversion operators in layer i to the chemical-species layer i + 1 (Figure 3. 2):

$$F_{c,i+1} = \sum_{g_i} F^{out}_{g_i,c,i} \qquad \forall c\,,\ \forall i$$

The objective of the optimization program may be aimed at maximizing the yield of the desired product, i.e.

$$\textit{Maximize}\ F_{p,NP}$$

where $F_{p,NP}$ is the flowrate of the desired product (index $c = p$) leaving the last chemical-species layer (index i = NP).

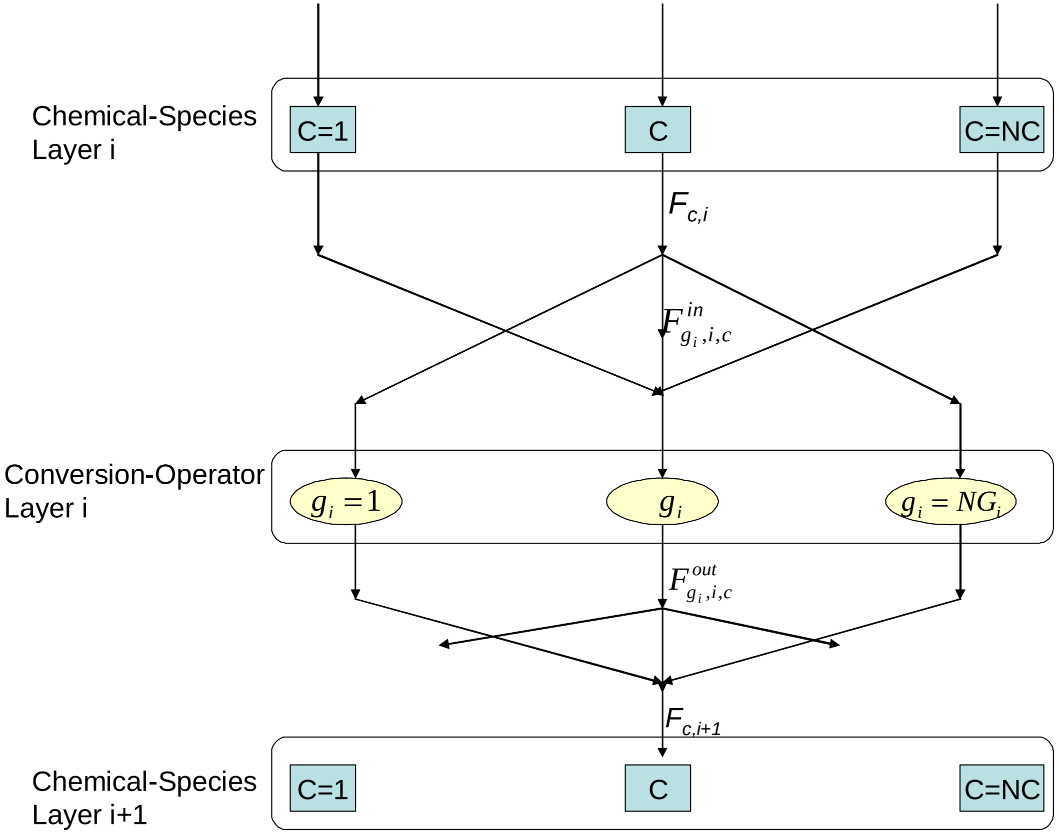

Figure 3.2 Mixing and Splitting on the CSCO Superstructure with Symbols

Another option for the objective function is to maximize the economic potential which is defined as the value of the product less the cost of feedstock and processing steps, i.e.,

$$\text{Maximize } C^{\text{Product}}F_{p,NP} - C^{\text{Feedstock}}F^{\text{Feedstock}} - \sum_{i}\sum_{g_i} TAC_{g_i}$$

where C^{Product} is the selling price of the product (e.g., \$/kg), $C^{\text{Feedstock}}$ is the cost of the feedstock (e.g., \$/kg) and $F^{\text{Feedstock}}$ is flowrate of the feedstock.

The foregoing optimization formulation is a nonlinear program (NLP) which can be solved to select the different conversion operators, interconnect them, and identify the flows throughout the biorefinery.

A particularly useful special case is when the following three conditions apply:

a. The flowrate of each component leaving conversion operator g_i is calculated through a given yield ($y_{g_i,i,c}$) times the flowrate of a limiting component (the index of the limiting component is c=$c_{g_i}^{\lim}$ and its inlet flowrate is $F_{g_i,c_{g_i}^{\lim},i}^{in}$), i.e.,

$$F_{g_i,c,i}^{out} = y_{g_i,c,i}F_{g_i,c_{g_i}^{\lim},i}^{in} \qquad \forall g_i\,,\ \forall c\,,\ \forall i$$

b. The flowrates of the different chemical species entering the conversion operator g_i are related to the flowrate of the limiting component via a stoichiometric or another form of required ratio (denoted by $\upsilon_{g_i,c,i}$). Hence,

$$F^{in}_{g_i,c,i} = \upsilon_{g_i,c,i} F^{in}_{g_i,c^{\lim}_{g_i},i} \qquad \forall g_i, \forall c, \forall i$$

c. The total annualized cost $\left(TAC_{g_i,i}\right)$ of conversion operator g_i in layer i is given by a cost factor ($\alpha_{g_i,i}$) times the flowrate of the limiting component entering the conversion operator, i.e.

$$TAC_{g_i,i} = \alpha_{g_i,i} F^{in}_{g_i,c^{\lim}_{g_i},i} \qquad \forall g_i, \forall i$$

d. To synthesize a cost-effective integrated biorefinery, the optimization objective can be an economic function. For instance, one may minimize the payback period (*PP*) of the process as follows:

Minimize *PP*

where PP is calculated as:

$$PP = \frac{\text{Fixed Capital Investment}}{(\text{Annual Sales} - \text{Total Annualized Cost}) \times (1 - \text{Tax Rate}) + \text{Annual Depreciation}}$$

The total annualized cost (TAC) is the summation of total annualized fixed (*TAFC*) and operating (*TAOC*) costs, as shown in Equation

$$TAC = TAFC + TAOC$$

Meanwhile, *TAFC* is summation of annualized fixed cost ($AFC_{g,i}$) in each technology *g* in each layer *i*; *TAOC* is summation of annualized operating cost ($AOC_{g,i}$) in each technology *g* in each layer *i* .

The optimization formulation is a nonlinear program (NLP). In some special cases, when Equations in a,b,c are used, the optimization formulation becomes a linear program (LP) which can be solved globally to determine the biorefinery configuration and the flows interconnecting the various conversion operators. To illustrate the proposed approach, three case studies are solved.

3.4 Case Studies

3.4.1 Case Study 1: Maximum Yield for Production of Gasoline from a Cellulosic Biomass

In this case study, it is desired to convert 162 tonne/day of a cellulosic biomass into gasoline. The objective of the case study is to select a technological pathway that will maximize the gasoline yield based on the idealistic case of assuming maximum theoretical yield for each technology block. This is an important scenario when little data are available about the technologies and there is a need to select the promising set of technologies for further analysis and techno-economic assessment. Cellulose was assumed to be $C_6H_{10}O_5$ and gasoline was taken as C_8H_{18}. Hydrogen and oxygen were allowed to be added as needed. Table 3.1 lists the key reactions involved in the conversion technologies. To limit the complexity of the developed biorefinery, the number of conversion-operator layers in this case study is limited to four ($i \leq 4$). Based on various technologies that are found in open literature, the CSCO pathway map is developed as shown in Figure 3.3. The ‘Blank’ operators (as shown in Figure 3.3) are employed in the CSCO representation to allow a chemical species to go unchanged through a layer.

The synthesis problem is formulated as a linear program and solved using the optimization software LINGO (version 10). Once a solution is obtained, an integer cut is added to exclude the solution and to generate another one. The procedure is continued until the value of the objective function drops below the maximum yield obtained in the first solution.

Table 3.1 Key Reactions for Case Study 1

From	Pathway	To	Reaction
$C_6H_{10}O_5$	Hydrolysis	$C_6H_{12}O_6$	$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6$
	Anaerobic digestion	CH_4 CO_2	$C_6H_{10}O_5 + H_2O \rightarrow 3CO_2 + 3CH_4$
	Gasification	CO H_2	$C_6H_{10}O_5 + O_2 \rightarrow 6CO + 4H_2 + H_2O$
	Fermentation	Carboxylate CO_2	$1.5CaCO_3 + C_6H_{10}O_5 + H_2O \rightarrow$ $1.5(CH_3COO)_2Ca + 1.5CO_2 + 0.5H_2O$
$C_6H_{12}O_6$	Anaerobic digestion	CH_4 CO_2	$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$
	Gasification	CO H_2	$C_6H_{12}O_6 + O_2 \rightarrow 6CO + 4H_2 + 2H_2O$
	Fermentation	Carboxylate CO_2	$1.5CaCO_3 + C_6H_{12}O_6 \rightarrow$ $1.5(CH_3COO)_2Ca + 1.5CO_2 + 1.5H_2O$
CH_4	Cracking	C_2H_4	$CH_4 + 0.5O_2 \rightarrow 0.5 C_2H_4 + H_2O$
CO_2	Water gas shift	CO	$CO_2 + H_2 \rightarrow H_2O + CO$
Carboxylate	Thermal conversion	Alcohol	$CH_3COOCaCOOCH_3 \rightarrow CaCO_3 + CH_3COCH_3$ $CH_3COCH_3 + H_2 \rightarrow CH_3CHOHCH_3$
CO	Synthesis	Alcohol	$CO + 2H_2 \rightarrow CH_3OH$
C_2H_4	Oligomerization	Gasoline	$4C_2H_4 + H2 \rightarrow C_8H_{18}$
Alcohol	Dehydration + oligermerization	Gasoline	$8CH_3OH + H_2 \rightarrow C_8H_{18} + 8H_2O$
Alcohol	Methanol to olefins process	Olefin	$CH_3OH \rightarrow CH_3OCH_3 + H_2O$ $CH_3OCH_3 \rightarrow C_2H_4 + H_2O$
CO_2	Methanation	Methane	$CO_2 + 4H_4 \rightarrow CH_4 + 2H_2O$
CH_4	Steam reforming	CO H_2	$CH_4 + H_2O \rightarrow CO + 3H_2$
CH_4	Dry reforming	CO H_2	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$

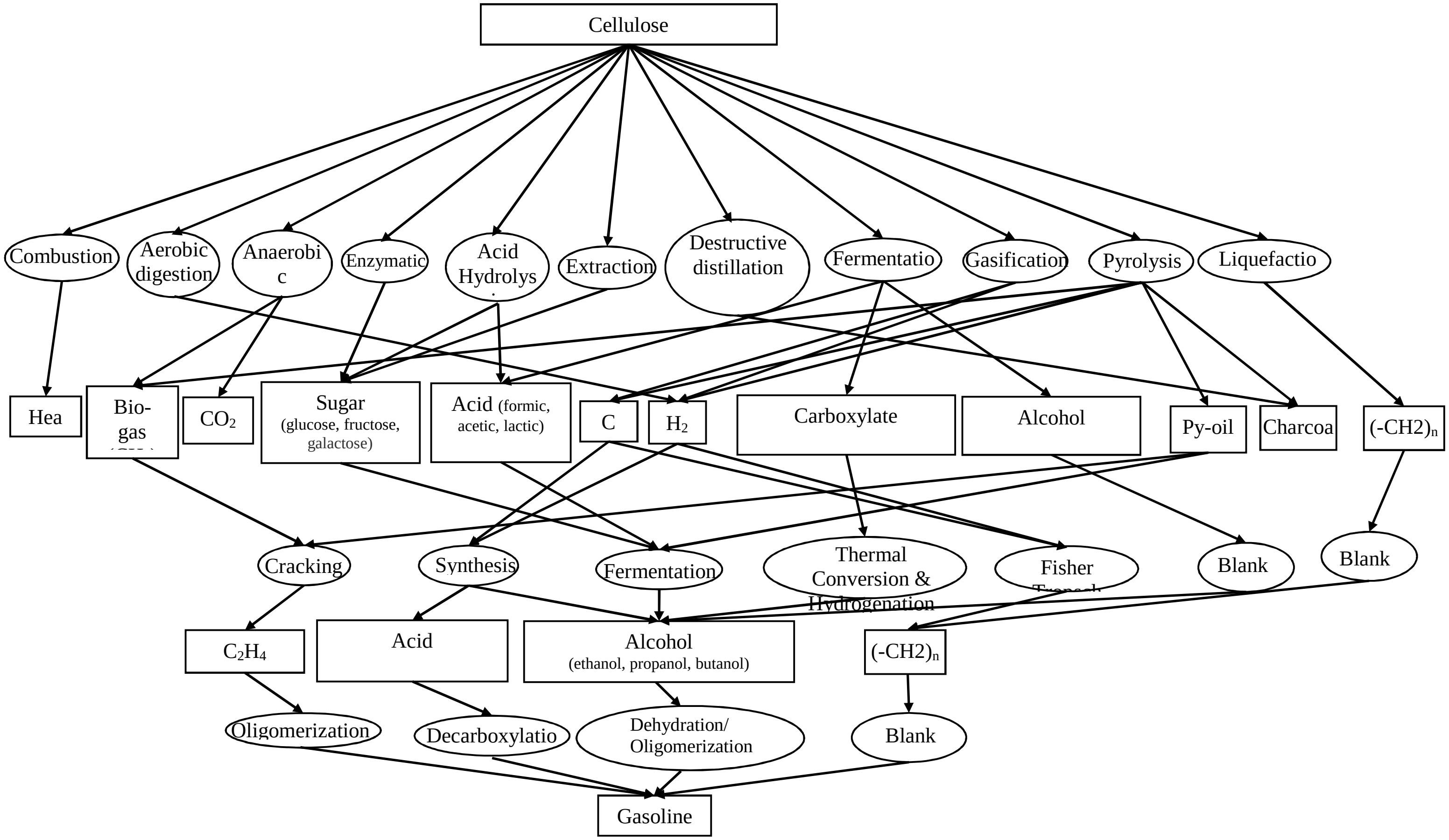

Figure 3.3 CSCO Pathway Map for Case Study 1.

Five optimal pathways were generated as shown by Fig. 3.4(a-e). All of them provide a maximum gasoline yield of 85.5 tonne/day. The first pathway (Fig. 3.4a) uses gasification to produce syngas which is converted to methanol then dehydrated and oligomerized to gasoline. The second pathway employs anaerobic digestion to produce CH_4 and CO_2. Next, CH_4 is dry reformed to syngas with the input of the co-produced CO_2. Syngas is synthesized into methanol and finally converted through dehydration and oligomerization to gasoline. More water is produced in the process than the required amount in the digestion. Therefore, the produced water is recycled to replace the fresh water used in digestion. The third pathways starts with fermentation in the presence of calcium carbonate to produce calcium acetate, $(CH_3COO)_2Ca$ which is then treated in thermal conversion to produce acetone (CH_3COCH_3) and regenerate the calcium carbonate (see Figure 3.4c). After that, it is hydrogenated to isopropyl alcohol ($CH_3CHOHCH_3$). Finally, the alcohol is dehydrated and oligomerized to gasoline. Meanwhile, the CO_2 from fermentation is hydrogenated to CO and water and the CO is synthesized to methanol (CH_3OH). Methanol then goes through the same process as isopropyl alcohol to produce gasoline. In the fourth configuration (Fig. 3.4d), cellulose is hydrolyzed and fermented to ethanol (C_2H_5OH) and CO_2. Ethanol is oligoermized to gasoline while CO2 undergoes shift reaction followed by methanol synthesis and oligomerization. Finally, in the fifth configuration, CO_2 produced from anerobic digestion is converted to methane through a methanation process with the input of additional hydrogen. Methane from digestion and methanation is converted to syngas through steam reforming then synthesized to methanol. Finally methanol goes through dehydration and oligomerization to gasoline. Hydrogen produced in the process is recycled to the methanation step.

It is interesting to note that these five configuration vary widely in their building blocks and arrangements, yet they provide the same yield. This underscores the value of the proposed approach in generating promising alternatives without the need to perform detailed design. Once these potential candidates are generated, effort is focused to these alternatives and a detailed analysis is properly carried out.

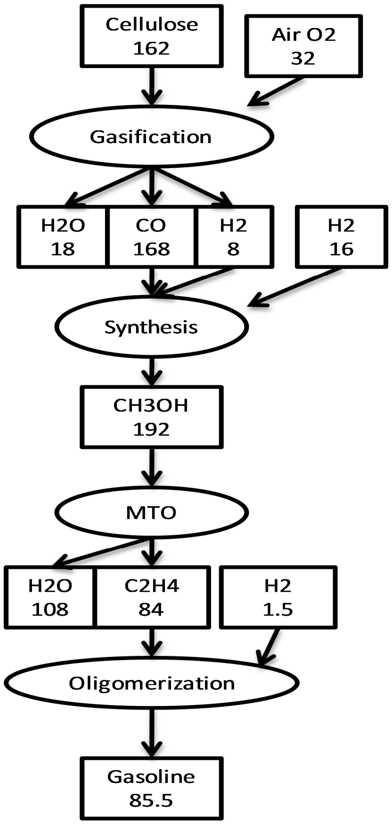

Figure. 3.4(a)

Figure 3.4. Five Optimal Pathways for Maximum Yield of Gasoline (Case Study 2) (all numbers are in tonne/day)

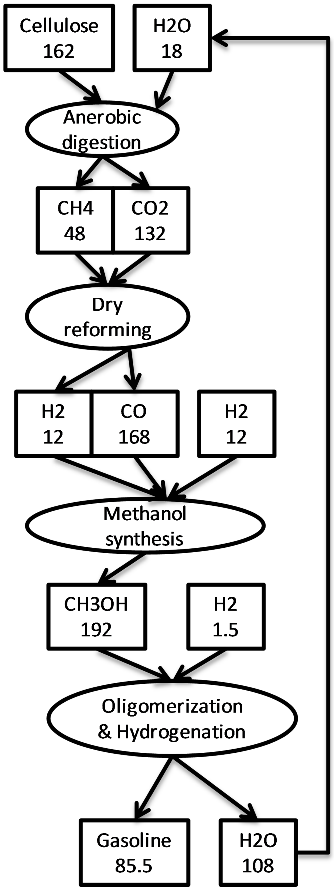

Figure. 3.4(b) continued

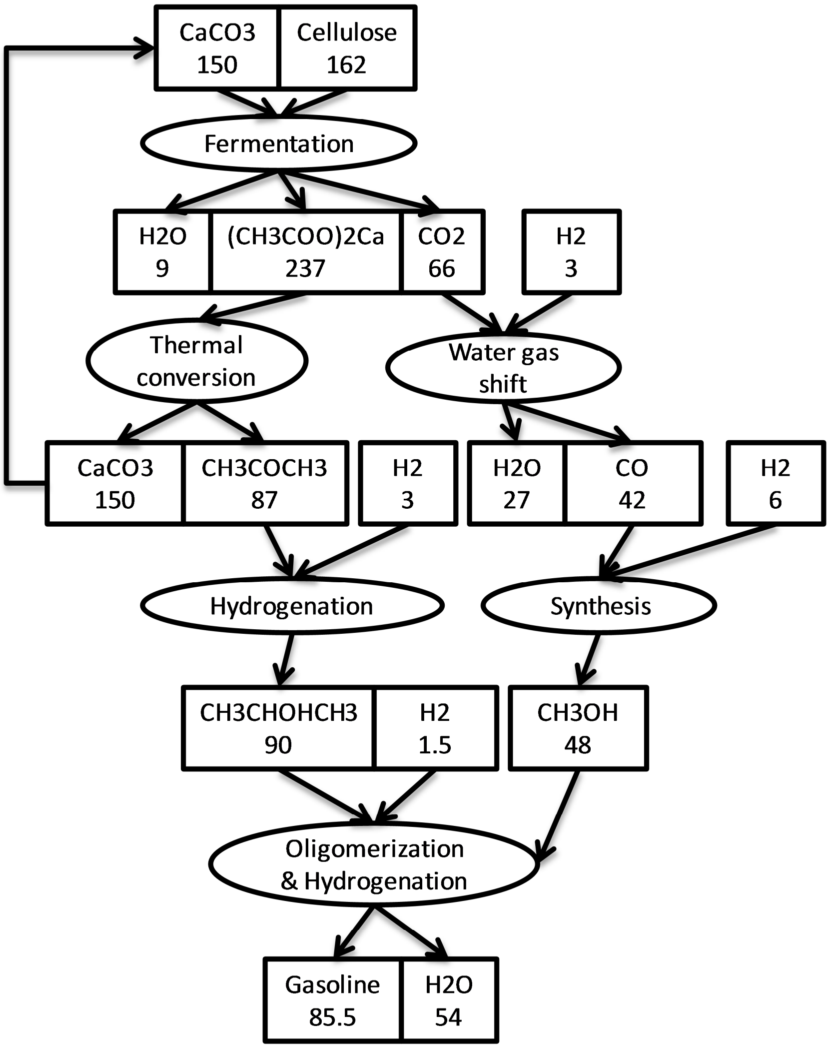

Figure. 3.4(c) continued

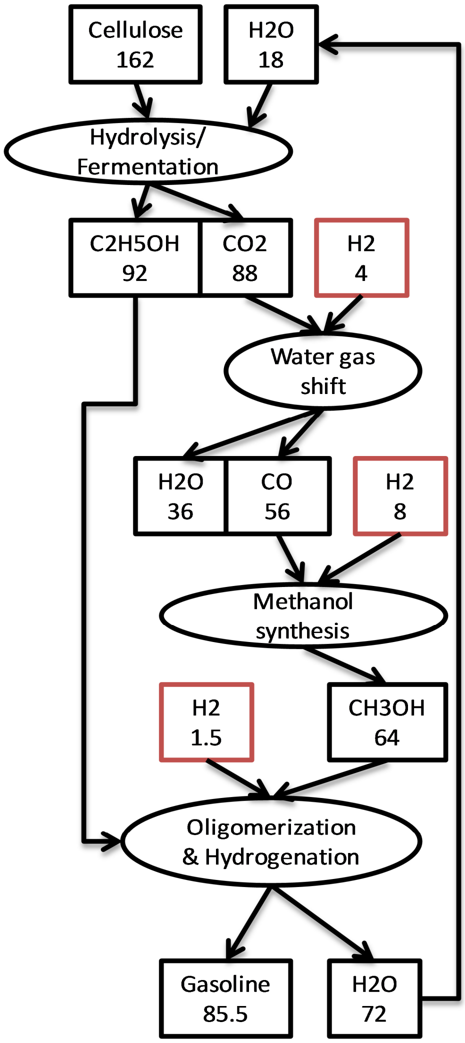

Figure. 3.4(d) continued

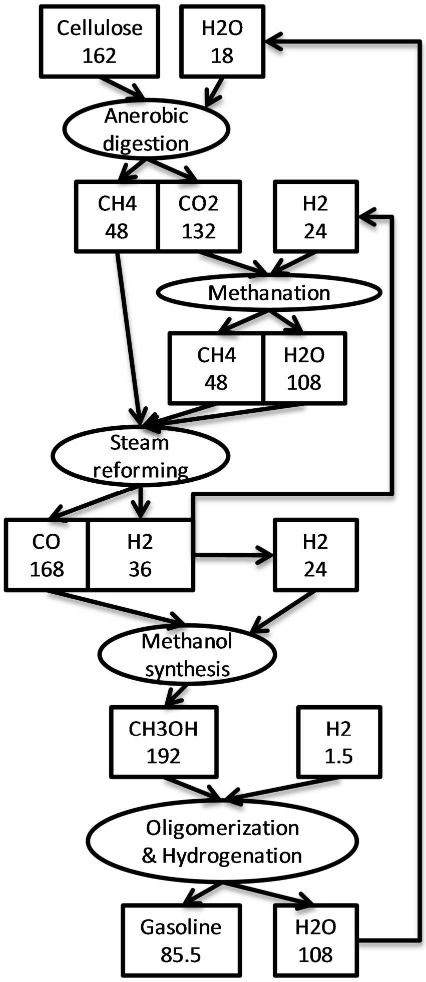

Figure. 3.4(e) continued

3.4.2 Case Study 2: Maximum Yield for the Production of Gasoline from Two Feedstocks with Actual Conversion and Yields

In this case, we increase the level of complexity of the case study by allowing two biomass feedstocks and by including reported data for conversion and yield. These data are compiled in Table 3.2. Two types of biomass are considered: 30 tonne/day of sorghum and 70 tonne/day of municipal solid waste (MSW). Table 3.3 shows the composition of both feedstocks. Note that the main components in the given feedstocks are cellulose, hemicellulose and lignin. Furthermore, the external supply of hydrogen was limited to an upper bound of 0.25 tonne/day. The optimization formulation is developed with the objective of maximizing the gasoline yield. The solution was found to be a maximum gasoline yield of 26.6 tonne/day and the identified pathway is shown by Fig. 3.5. It includes fermentation of cellulose and hemicelluloses and pyrolysis of lignin. The produced alcohol from fermentation is dehydrated and oligomerized to gasoline. The pyrolysis products are subjected to cracking, oligomerization, and Fischer-Tropsch synthesis to produce gasoline.

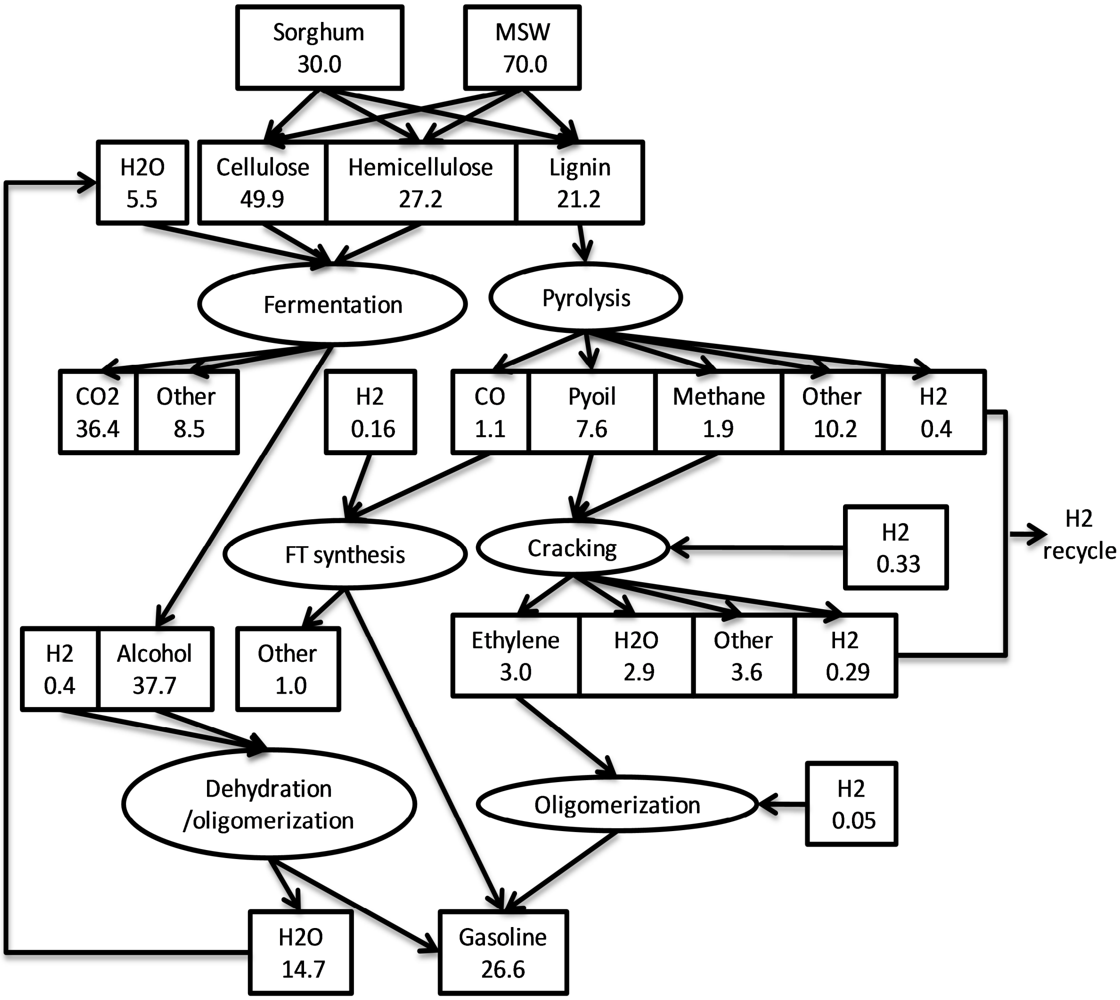

Figure 3.5. Pathway for Gasoline Production from MSW and Sorghum (Case Study 2) (all numbers are in tonne/day)

Table 3.2 Compilation of Conversion and Yield Data for Case Study 2

From	Pathway	To	Conversion %	Yield (Mass Ratio of Desired Product to Key Feed)	Reference
Cellulosic Municipal Solid Waste	Anaerobic digestion	Bio-gas	80.0	0.210	
		CO_2	80.0	0.473	Rivard (1993)
	Extraction	Sugar			
	Hydrolysis/Fermentation	Carboxylate	30.2	0.180	Aiello-Mazzarri et al. (2005)
		Acid	90.0	0.800	Schmidt and Padukone (1997)
		Alcohol	90.0	0.511	Krishnan et al.(1999)
	Gasification	CO	99.0	0.500	
		H_2	99.0	0.071	Filippis et al. (2004)
	Pyrolysis	Py-oil	99.0	0.522	Ojolo and Bamgboye (2005)
		Charcoal	99.0	0.242	
		H_2	99.0	0.040	
		CO	99.0	0.186	
	Liquefaction	Gasoline	95.0	0.260	Minowa et al. (1995)
Bio-gas	Cracking	C_2H_4	92.9	0.580	Fincke et al. (2000)

Table 3.2 Continued

Sugar	Fermentation	Alcohol	83.0	0.360	Reid and George (1945)
Acid	Fermentation	Alcohol		0.900	
CO	Synthesis	Acid	90.0	0.770	Knifton, (1985)
		Alcohol	37.5	0.208	Zhang et al. (2001)
	F-T	Gasoline	90.0	0.203	Dry (1996)
H_2	Synthesis	Acid	90.0	0.108	Knifton (1985)
		Alcohol	37.5	0.015	Zhang et al. (2001)
	F-T	Gasoline	90.0	0.014	Dry (1996)
Carboxylate	Thermal conversion	Ketone	99.5	0.365	Holtzapple, et al. (1999)
Bio-oil	Cracking (Hydroprocessing)	C_2H_4	99.0	0.250	Bridgwater (2008)
	Gasification	Syngas	99.0	0.530	
C_2H_4	Oligomerization	Gasoline	99.0	1.017	Khanmetov et al (2006)
Acid	Decarboxylation	Gasoline	60.0	0.252	Sharma and Olson (1994)
Alcohol	Dehydration/Oligomerization	Gasoline	99.0	0.619	Costa et al. (1985)
Lignin	Pyrolysis	Bio-gas	100.0	0.089	
		Bio-oil		0.360	
		CO		0.050	
		H_2		0.020	
	Gasification	H2	100.0	0.075	Jangsawan et al. (2005)
		CO		0.018	

Table 3.2 Continued

Hemicellulose	Pyrolysis	Bio-gas	100.0	0.089	
		Bio-oil		.360	
		CO		0.050	
		H_2		0.020	
	Gasification	H2	90.0	0.072	
		CO		0.170	
	Fermentation	Alcohol	90.0	0.450	Murphy and McCarth (2005)
		Acid	80.0	0.760	Jin et al. (2005)
	Anerobic digestion	CH4	80.0	0.180	
	Enzymic hydrolysis	Sugar	90.0	0.830	Adsul et al. (2007)

Table 3.3 Composition of Sorghum and MSW (NREL, 2007)

Wt %	Sorghum	MSW
Cellulose	45	52
Hemicellulose	30	26
Lignin	24	20

3.4.3 Case Study 3: Minimum Payback Period

Other than targeting the maximum biofuel yield as shown in case studies 1 and 2, including economic objectives may be desired early enough in the development activities. In this case study, minimum payback period is selected as the optimization objective. The intent is to include key economic indicators without getting trapped in an in-depth economic analysis that will require tremendous time and effort for all the potential candidates. Tables 3.4 and 3.5 show the cost data for the processing technologies and the cost/selling price of the targeted species. A feed flowrate of 1,620 tonne/day of cellulose is used. A ten-year linear depreciation scheme is used with no salvage value. The synthesis task is formulated as a nonlinear programming problem whose objective is to minimize the payback period and the constraints include the developed optimization formulation coupled with the data from Tables 3.2, 3.4, and 3.5. The solution obtained using the optimization software LINGO (version 10) is shown by Fig. 3.6. As shown, the pathway involves hydrolysis and fermentation of cellulose followed by dehydration and oligomerization. The produced gasoline is 511 tonne/day. The solution has an objective function for a minimum payback period of 8.8 years. It is worth noting that upon further techno-economic analysis, the payback period will be longer because of the addition of equipment that have not been accounted for in the program. Nonetheless, the intent of this approach is to quickly provide preliminary synthesis alternatives that warrant additional analysis. It is also worth noting that once the cost criterion has been included in this case study, the complexity of the synthesized solution has significantly decreased compared to the previous two case studies which only focused on yield without cost. This is attributed to the ability of this approach to exclude pathways or portions of the pathways that will not be cost effective even if they enhance the yield.

Table 3.4. Cost Data for Case Study 3

Technology	AOC per daily tonne ($/yr/daily tonne)	α AOF* ($/yr/daily tonne$^{0.7}$)
Combustion	1.00×10^{6}	1.00×10^{6}
Aerobic Digestion	1.15×10^{5}	3.62×10^{5}
Anaerobic Digestion	1.34×10^{5}	1.97×10^{5}
Enzymatic	1.00×10^{6}	1.00×10^{6}
Acid Hydrolysis	1.00×10^{6}	1.00×10^{6}
Extraction	1.00×10^{6}	1.00×10^{6}
Destructive Distillation	1.00×10^{6}	1.00×10^{6}
Fermentation (to acid)	8.90×10^{4}	1.19×10^{5}
Fermentation (to carboxylate)	2.06×10^{5}	2.14×10^{5}
Fermentation (to alcohol)	5.72×10^{4}	1.35×10^{5}
Gasification	1.43×10^{5}	2.28×10^{5}
Pyrolysis	1.04×10^{5}	1.88×10^{5}
Liquefaction	3.33×10^{5}	4.47×10^{5}
Methane Cracking	2.43×10^{4}	7.27×10^{5}
Acid Synthesis	6.73×10^{4}	8.64×10^{4}
Alcohol Synthesis	6.73×10^{4}	8.64×10^{4}
Sugar Fermentation	2.86×10^{5}	2.69×10^{5}
Thermal Conversion	1.17×10^{4}	1.92×10^{5}
Fisher Tropsch	3.01×10^{5}	4.70×10^{5}
Pyoil Gasification	8.91×10^{4}	4.46×10^{5}
Pyoil Cracking	5.98×10^{4}	4.55×10^{5}
Oligomerization	2.16×10^{4}	3.89×10^{5}
Decarboxylation	2.85×10^{5}	1.65×10^{5}
Dehydration	3.57×10^{4}	4.37×10^{4}

*The AFC is modeled using the following formula: AFC = α*Flowrate$^{0.7}$

Table 3.5. Costs and Selling Prices for the Species of Case Study 3

Species	Price
Cellulose	60 $/tonne
Gasoline	3.1$/gal
Biogas	6.86$/1000SCF
Sugar	$765/tonne
Acid	$1,496/tonne
H_2	4,000$/tonne
Carboxylate	$1,100/tonne
Alcohol	3.2$/gal
Pyoil	2$/gal
Charcoal	77$/tonne
C_2H_4	$1,386/tonne
H_2O	$1.5/1000gal
$CaCO_3$	65$/tonne
O_2	$210/tonne

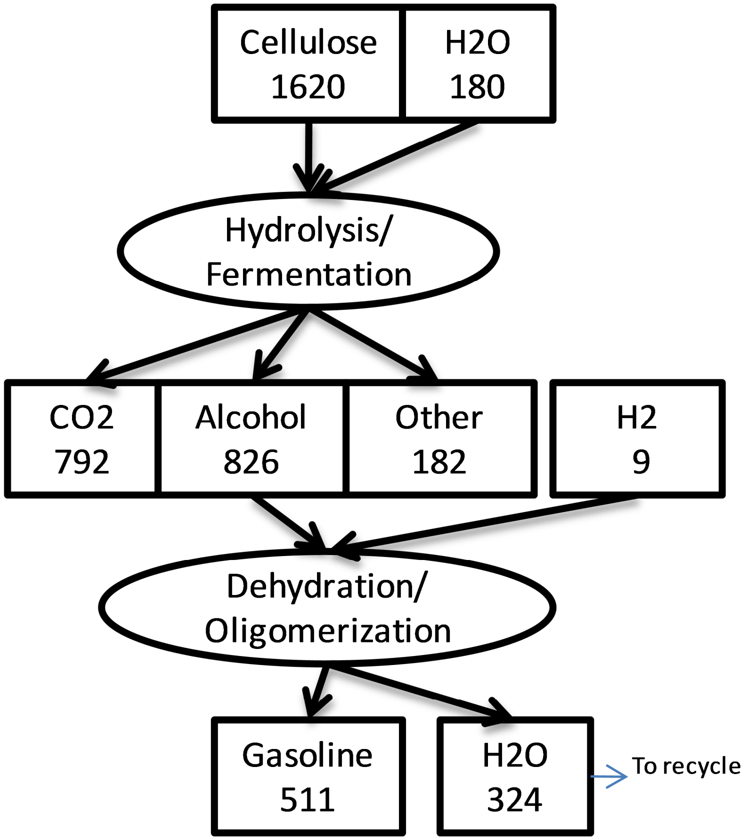

Figure 3.6 Solution to the Problem of Minimum Payback Period (Case Study 3)
(all numbers are in tonne/day)

3.5 Conclusions

In this paper, a shortcut method has been introduced for the conceptual design and preliminary synthesis of alternative pathways of the process industries with focus on the applications for biorefineries. The chemical species/conversion operator structural representation has been introduced. It tracks chemical species, connects various streams with processing technologies, and embeds potential configurations of interest. An optimization formulation has been developed to maximize the yield or the economic potential subject to constraints that include process models, distribution of streams and species over the conversion technologies, interconnection of the candidate technologies, and techno-economic data. Three case studies have been solved to demonstrate the effectiveness and applicability of the developed approach. The case studies covered the scenarios of maximum theoretical yield, accounting for actual process yield, including more than one feedstock, and incorporating an economic objective (payback period), The solutions of the case study illustrate the ability of the proposed approach to generate a wide variety of pathways that achieve the same target but vary significantly in their building blocks and interconnections. The solution of the case studies also demonstrate that by including an economic objective function that the complexity of the devised pathways is greatly reduced.

4. AN INTEGRATED APPROACH FOR THE BIOREFINERY PATHWAY OPTIMIZATION INCLUDING SIMULTANEOUSLY CONVERSION, RECYCLE AND SEPARATION PROCESSES

4.1 Abstract

Biorefinery is an industrial facility that produces a lot of products from biomass, and nowadays it has gained a lot of attention because the increasing depletion of fossil fuels and the environmental problems caused by the use of fossil fuels. In this regard, biomass can be considered as a sustainable resource and it provides significant environmental benefits because the reduction of the greenhouse gas emissions. While there are tremendous technologies and pathways concerning the selection for a biorefinery, this work presents a systematic approach to determine the optimum pathway of technologies to convert biomass into biofuels, combining the necessary steps to recover and recycle intermediate products during the synthesis. A system of mass treatment network and technology conversion network is presented to model the problem. Mathematic formulations are constructed to analyze the optimization network. A case study has been presented to illustrate the problem for producing gasoline from cellulose, and results show that the optimal pathway corresponds to alcohol fermentation and oligomerized to gasoline with a minimum payback period of 11.7 years with 1620 tonne/day of feedstock; whereas, when the capacity is increased to 120,000 BPD of gasoline production, the payback period is reduced to 3.4 years.

4.2 Introduction and Literature Review

Fossil fuels have been supplying a large share of global energy demand. With the continuous growth of population and industrial activities, the world's energy consumption is projected to increase by 49% from 495 quadrillion Btu in 2007 to 739 quadrillion Btu in 2035 (EIA, 2010), while the world crude oil and natural gas reserve can only last for 50 years (IEA, 2010). The pressure of fossil energy supply for meeting the increasing demand situation prompts the need to develop alternative energy resources including hydro, wind, solar, geothermal, marine energy, and biomass. Biofuels provide a variety of advantages over petroleum-based fuels including: (a) the biomass feedstock are sustainable and environmentally friendly, (b) biofuels are neutral in greenhouse gas (GHG) emissions if efficient processes are applied, which can help to satisfy the Kyoto regulations (Bioenergy, 1998), (c) a wide variety of versatile biomass can serve as the feedstock and they are easy and cheap to be accessed, and as a result a large production of fuels or chemicals could be derived, (d) with the increasing price and depletion of fossil fuels, the biofuels will show promising economical potential and supplement the energy supply. There have been an increase of public awareness towards biofuels production, and global government investment to biofuels is projected to rise to 45-65$ billion per year from 2010-2035 (IEA, 2010). In addition, conventional chemical companies like Shell, Conoco-Phillips, Dupont, Dow and BP between others have been stepping into the area of developing technologies and processes for producing biofuels and bio-chemicals (Huber et al., 2006).

A biorefinery is a processing facility that can transform biomass to fuels, power, and value added chemicals by integrating conversion technologies and processes (NREL, 2005; Ng, 2009). A variety of forms of biomass including energy crops, agricultural wastes, forestry residues and municipal solid wastes can serve as the main resources of feedstock (Bridgwater, 2003). Biomass components include lignin, cellulose, proteins, acids, and various other chemicals (Askew, 2005), and the target of a biorefinery is to obtain the maximum value from the biomass components through optimal processes. Although biomass has been taken as an input to derive products in extensive applications, the application of converting it through a complex petroleum like refinery to produce multiple products is relatively new (Fernando et al., 2006). There are various routes in biorefineries, among which biological conversion, physical conversion and thermal conversion are the three main paths for producing bio-energy. Given the intensive capital cost in a biorefinery, there is a need to explore different levels of integration to enhance the performance of a biorefinery, which includes increasing the energy efficiency, maximizing overall value of products derived from feedstock, adding flexibility of products conversion, and reducing the overall cost.

Much research efforts have been involved in chemical process synthesis (Douglas, 1988). Rudd (1968) pioneered the process synthesis work in the 1960s,whereas Westerberg (1980) and Nishida et al. (1981) later defined the process synthesis as an approach to determine the optimal structure of the process system and the optimal process design to satisfy the specified performance. Extensive works have been conducted in the synthesis area, including separation sequences, reaction pathways, heat integration, etc. In this regard, El-Halwagi (1997; 2006) introduced the concept of mass-exchange networks (MEN) in the area of mass integration and Bagajewicz (2000) presented a review on various methods for the wastewater treatment and material allocation problem.

There are a few challenges facing the designing and synthesis of multi levels of integrated biorefineries, these include the complex chemical structures and compositions of biomass (which increases the difficulty of feedstock analysis and treatment as well as regional dependent, and lack of established information for the thermodynamic properties and reaction kinetics (Ng et al., 2010)). This makes many synthesis and design approaches of conventional chemical processes not compatible for the synthesis of integrated biorefineries. In this regard, Kokossis et al. (2009) discussed the status and the challenges for the synthesis and integration of a biorefinery, and they proposed a systematic approach to identify optimal opportunities for biomass-chemical production and combining with other technologies. Mansoornejad et al. (2009) presented a biorefinery framework in marketing decision aspects, through integrating supply chain design with process design. Bridgwater (2003) presented multiple products and multi-scale processes in a biorefinery. Sammons et al. (2007) then presented a framework to evaluate multiple production routes and product portfolios based on profitability optimization. Later, Sammons et al. (2008) extended the work by including economic perspective with other process insights to facilitate evaluating an integrated biorefinery through a mathematic framework to optimize product allocation problems based on environmental and economic measures. Later, Tan et al. (2009) developed a fuzzy linear programming integrated with an input-output mass-energy balance system to target the optimum of process units capacities based on product metrics and environmental goals. At the same time, Elms and El-Halwagi (2009) presented a systematic procedure for scheduling of biorefineries and biomass resources selection, the optimization was performed to design and integrate the biorefinery along with the consideration of GHG emissions reduction. In addition, Ng et al. (2009) proposed a hierarchical approach for the synthesis and integration of biorefineries to determine promising pathways, where a sequential screening method was utilized for targeting potential technologies by analyzing thermodynamic feasibility and gross revenue. Ng et al. (2010) then introduced an automated optimization method to target the maximum biofuel production and revenue for an integrated biorefinery, this approach used simple conversion models to calculate the yield of a biorefinery through a source to sink mass flow structure. Although the approach by Ng et al. (2010) is convenient in targeting yield estimates, it does not consider capital investment and only simple technological models could be applied. Pokoo-Aikins et al. (2010) also presented a method to design and guide the screening of alternative biorefineries based on safety, process and economic metrics. In addition, Tay et al. (2011) used graphical techniques of a carbon–hydrogen–oxygen (CHO) ternary diagram to synthesize and optimize for the performance target of an integrated biorefinery. Bao et al. (2011) then proposed a structural representation and optimization approach for synthesis and screening of integrated biorefineries. Research efforts have also covered optimal biofuel production and optimal energy reduction in designing alternative biorefinery routes (see Gosling, 2005; Alvarado-Morales et al., 2009). Additionally, detailed techno-economic analyses have been carried out for biorefineries with thermal cogeneration considerations (Qin et al. 2006; Mohan et al., 2007; Goyal et al., 2008). Furthermore, design and optimization alternatives have been conducted for biodiesel production from a variety of feedstock like soybean oil and algal oil (Myint and El-Halwagi, 2009; Pokoo-Aikins et al., 2010).

On the other hand, mass integration techniques have been effectively used in process optimization by dealing with the material separation, allocation and conversion of species and processes. There are mass integration strategies to recycle and reuse process sources using the pinch analysis method and mathematical programming models (El-Halwagi, 2006; Pillai and Bandyopadhyay, 2007). Interception systems can be utilized in the mass synthesis to separate target species from process streams as a strategy for material recovery and waste minimization. El-Halwagi and Manousiouthakis (1989) developed an approach for synthesizing mass exchange networks (MENs) to transfer species between a set of rich streams and a set of lean streams. Later a graphical strategy for minimizing wastewater was introduced by Wang and Smith (1995). Garrard and Fraga (1998) and Xue et al. (2000) used generic algorithms techniques to synthesize MENs. Quesada and Grossmann (1995) presented a mass exchange networks model and dealt with the bilinear terms. Dhole et al. (1996) presented a graphical supply and demand composite that relates flow rate versus concentration to locate the water pinch point. El-Halwagi and Spriggs (1998) presented a source sink system to analyze the recycling problem. Later, Polley and Polley (2000) proposed an approach to optimize the recycling conditions coupled with material recovery. Multicomponent systems of material recovering and recycling have also been addressed by Benko et al. (2000), Dunn et al. (2001a; 2001b), Teles et al. (2008), and Alvarado-Morales et al. (2009) by using mathematical programming techniques. Manan et al. (2004) developed strategies to target minimum fresh water using a surplus diagram and design mass recovery using a non iterative approach in a wastewater treatment problem. Gomes et al. (2007) proposed a heuristic approach when dealing with synthesizing mass exchange networks, and Ng et al. (2007a; 2007b) also addressed the problem to get maximum water recycle by coupling with regeneration system to meet environmental regulations. In addition, different approaches for mass integration based on different properties have been recently reported (see Ponce-Ortega et al., 2009; 2010; Napoles-Rivera et al., 2010; Grooms, et al., 2005).

Therefore, even that the previous improvements identified in the design of integrated biorefineries, previous methodologies have the following drawbacks: 1) In the previous methodologies only a few of the existing technology alternatives from experiences could be suggested, and the real optimum process solutions maybe neglected. 2) They are time and cost consuming for evaluating each alternative. 3) Since they are derived from experiences and existing knowledge, the application will be limited. 4) The simultaneously optimization for the technology and mass recovery selection was not considered. 5) The optimal interconnecting products and flow rates can not be considered. And therefore, 6) No systematic approach for the optimal cost-effective design of an integrated biorefinery that considers the optimal selection of conversion, separation and recycle has been reported.

Therefore, to overcome the drawbacks of the previously reported methodologies, this paper proposes an approach to synthesize an optimum biorefinery pathway by coupling conversion techniques with material recycle and reuse to provide a generic biorefinery synthesis approach. To consider the diverse potential of conversion technologies/feedstocks and alternative combinations of the pathways in a biorefinery, there is a strong need to effectively and systematically generate optimal alternatives that meet specified objective of cost effective, pollution preventive and resources conservative design (e.g., Azapagic, 2002; Chouinard-Dussault et al., 2011). The target of the model is to find an optimal alternative of biorefinery pathway that also considers the process specifications, design and selection of process separation and recover/recycle besides the conversion technologies. As a result, a systematic approach is developed to select the optimal biorefinery pathway. The optimal allocation of conversion technologies, recycle design and interconnecting flow rates are determined for the selected feedstock and products.

4.3 Problem Statement

The problem addressed in this paper is defined as follows.

Given a process with:

1. A set of biomass feedstock: $FEEDSTOCK = \{r|\ r = 1, 2, \ldots, N_{FEEDSTOCK}\}$. Each feedstock has a given flow rate H_r and a given composition $C^{FRESH}{}_{c,r}$.

2. A set of desired primary products: $PRODUCTS = \{pr|\ pr = 1, 2, \ldots, N_{PRODUCT}\}$. Each product requires a flow rate W_{pr} and composition $C^{PROD}{}_{c,pr}$ that satisfy the following constraint:

$$C_{c,pr}^{PROD\ min} \leq C_{c,pr}^{PROD} \leq C_{c,pr}^{PROD\ max}, \qquad c \in NCOMP, pr \in NPRODUCT$$

$$W_{pr} \geq W_{pr}^{min},\ \ pr \in NPRODUCT$$

where $C_{c,pr}^{PROD\ min}$ and $C_{c,pr}^{PROD\ max}$ are given lower and upper bounds on acceptable component composition c for products pr, and W_{pr}^{min} is given lower bounds on acceptable flow rate for products pr.

3. A set of interception units: $INTERCEPTORS = \{u|\ u = 1, 2, \ldots, N_{UNITS}\}$ that can be used to treat each component composition c.

4. Available for service is a set of processing (conversion) technologies: $TECH = \{g|\ g = 1, 2, \ldots, N_{TECH}\}$ with known characteristics of performance (e.g., yield, unit cost, composition).

The objective is to synthesize a biorefinery and develop an optimization method to determine the following:

1. Minimum cost of the biorefinery pathway including the cost of conversion technologies, separation and recycling that satisfy the process requirements.

2. Optimum selection of conversion technologies and feedstock.

3. Optimum pathway of conversion technologies and process flow rate allocation.
4. Optimum selection and allocation of interception units.

The conceptual design procedure proposed in this paper is intended to screen the numerous alternatives, to produce an optimal technology pathway of the major process components of the biorefinery, and to perform a detailed techno-economic analysis.

4.4 Approach and Mathematical Formulation

The methodology presented in this paper consists in a systematic approach and mathematical formulations (as it shown in **Figure 4.1**). First the systematic approach is presented and then the mathematical programming formulation is shown.

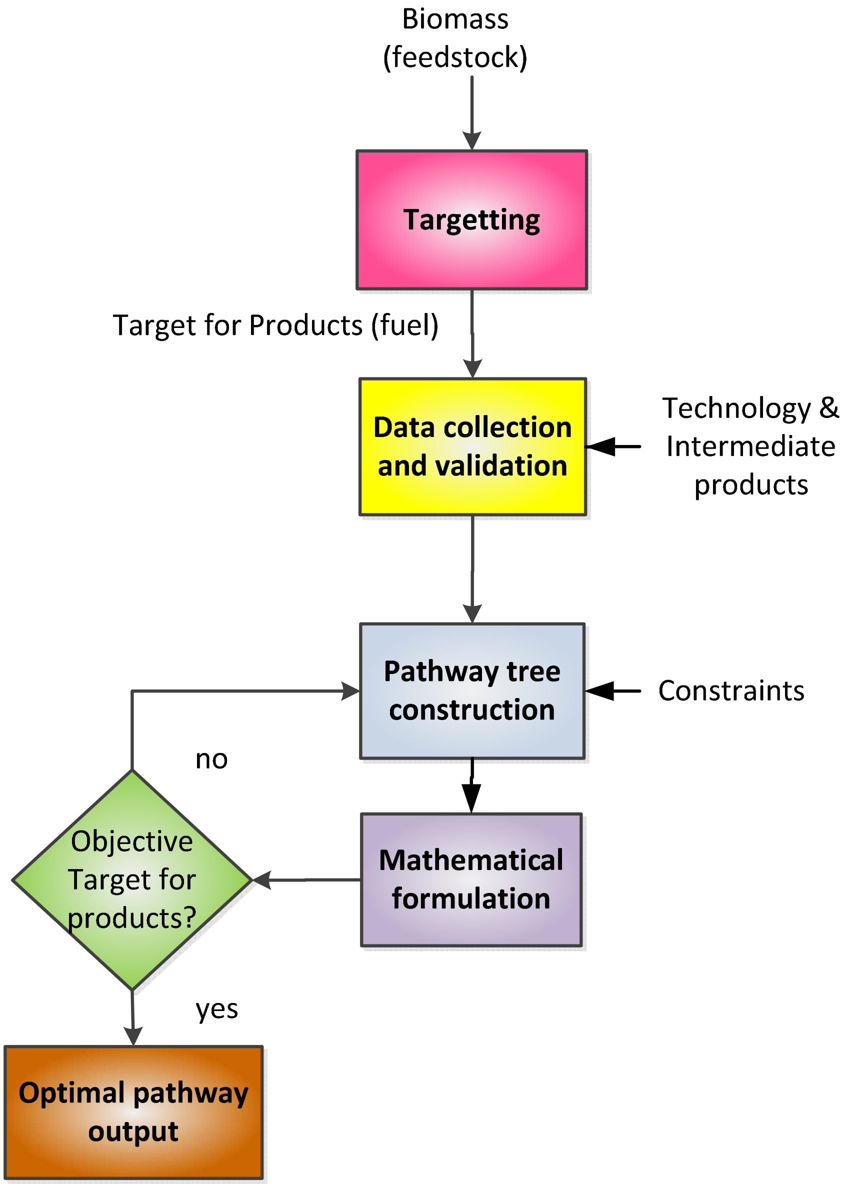

Figure 4.1 Proposed Solution Approach.

First, based on the available biomass and desired fuel products, targetting is performed before the optimization steps to evaluate the best feasible solution. Then, the information of all the available technologies and intermediate products is collected for a pathway tree construction. After that, the mathematic model is formulated to select the optimal pathway based on certain objectives with necessary constraints. If the objective is met, then the solution will be output as the optimal pathway with the intermediate products and technologies selected. If the objective is not met, the pathway tree is revised and the constraints are changed for the mathematical optimization again until the objective is met.

4.4.1 Systematic Approach

The problem is formulated as a network representation, and this network is categorized into conversion (technologies) operator block and material separation block. The analysis is started with the following steps:

1. List the available conversion technologies along with their performance characteristics (e.g., yield, unit cost) based on literature survey, simulation, reaction pathways synthesis, etc. The constraints (inlet components concentration, operation conditions, properties, etc) for each technology are listed as well.
2. Based on the characteristics of the biomass feedstock, the desired products, and the conversion technologies, develop a list of the candidate chemical species that may be involved in the biorefinery. Let *c* and *NSPECIES* be the index and the total number of the chemical species, respectively. Also, use a list of candidate compositions that are used to track the process streams and break the biomass feedstock into key chemical species (quantified based on chemical analysis).

3. Based on the available chemical species and the performance characteristics of products from the available technologies, list the possible units that can be used to treat each component. Simulation or preliminary calculations of separation scheme with some heuristic rule are carried out first. Let N_{UNIT} be the total number of available units. The performance and inlet conditions of the units are also included to select the optimum treatment units. Environmental requirements are considered wherever necessary.

4. After the previous steps are performed, the two blocks of conversion operator and material separation system are interconnected with the process streams mixing and splitting. Then, a network of the synthesized pathway is constructed and the mathematical model is finally formulated to optimize the system.

The outline for the mathematical model is given in the next section.

4.4.2 Outline for the Mathematical Model

The conversion operator-interception-conversion operator representation proposed in this paper is shown in **Figure 4.2**. The diagram is comprised of alternating layers of conversion technologies followed by the interception network. There are *NP* layers of conversion operators and each layer is designated by the index i. The conversion operators in the first layer ($i=1$) accept flow rates from feedstock. There are $N_{FEEDSTOCK}$ of feedstock and each feedstock is designated by the index r. Each feedstock is allowed to split to different process convertors. The convertors in the last layer ($i=NP$) are used to store process streams unchanged into product acceptors. There are $N_{PRODUCT}$ products and each product is designated by the index pr. Streams fed into conversion operator g_{NP} go unchanged into product acceptor pr with the relation of $g_{NP} = pr$. Each process convertor g_i can accept multiple streams from the mass treatment system, and the streams produced from each conversion operator g_{NP} is segregated into unknown flow rates and are allocated to the mass treatment system to be treated and recycled. Within each conversion operator, the streams with specific component characteristics can be converted to streams with new or intermediate species, and those intermediate species can be treated and further converted through other technologies to finally produce the desired products. Within the interception network, the composition of each stream is altered if an interception device is used. After the separation and purification steps are carried out, the streams leaving the interception network are allowed to mix and fed to process convertors in the next layer or recycled to previous layers.

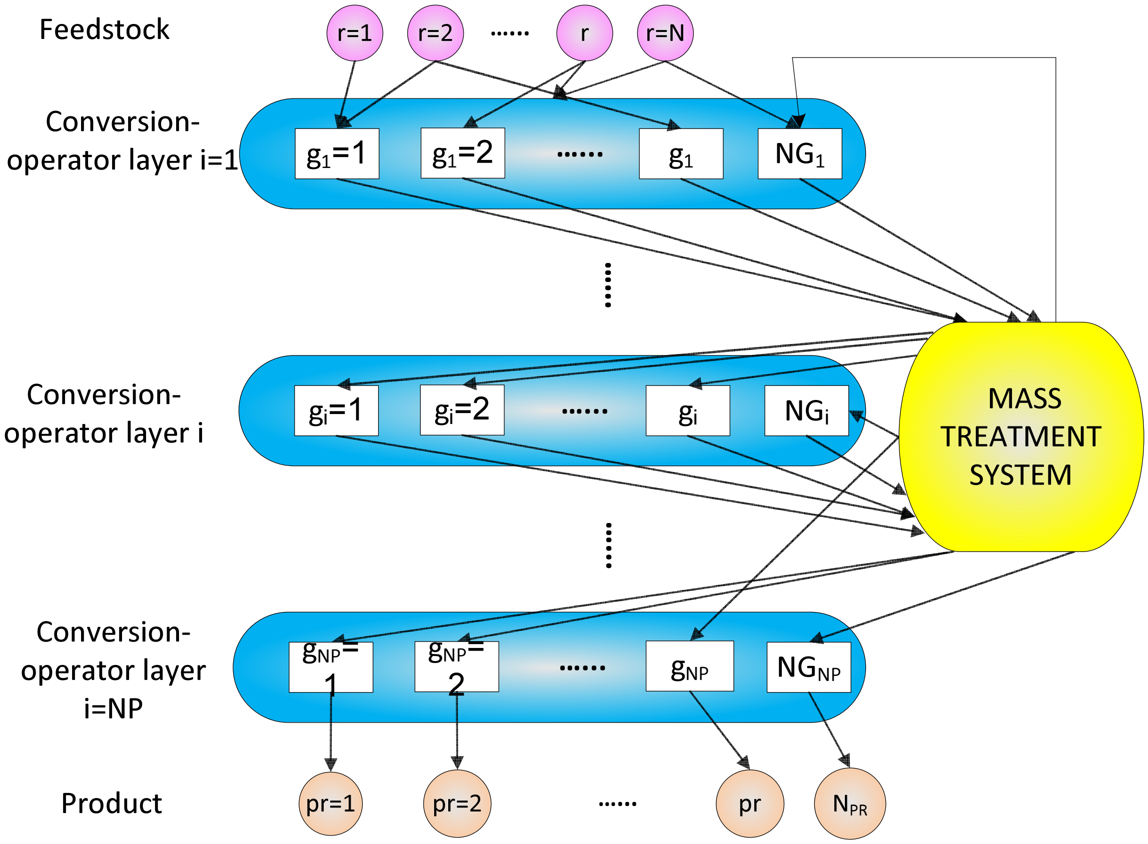

Figure 4.2 Conversion Operator-Interception-Conversion Operator Representation for Biorefinery Pathway Synthesis.

The more detailed structure of the mass and property treatment system is shown in **Figure 4.3**. The mathematical model is based on the configuration shown in **Figure 4.3**, and it includes mass and material balances at mixing points of each process streams, mass balances at splitting points, and process and performance constraints. It is a source-sink network integrated with a technology convertor system. All the process streams coming from the conversion operators with flow rate $F_{i,g}^{OUT}$ represent the process sources for the interception network, and all the process streams entering the operators with flow rate $F_{i,g}^{IN}$ represent the sinks for the interception network. An optimum allocation of operation convertors g_i is determined and an optimum flow rate connecting these convertors is determined. Each source is segregated into fractions and allocated to the interception network. Streams leaving the separation network are mixed before entering each sink. The splitting fractions and mixing ratios are optimized. In the mass treatment network, there are *NUNITS* treatment units with index *u* to refer to each unit, and NK_i discretized interceptors to treat each stream. Each unit has a certain interception extent, efficiency and cost performance. The optimum interception for the streams and selection of treatment units are determined.

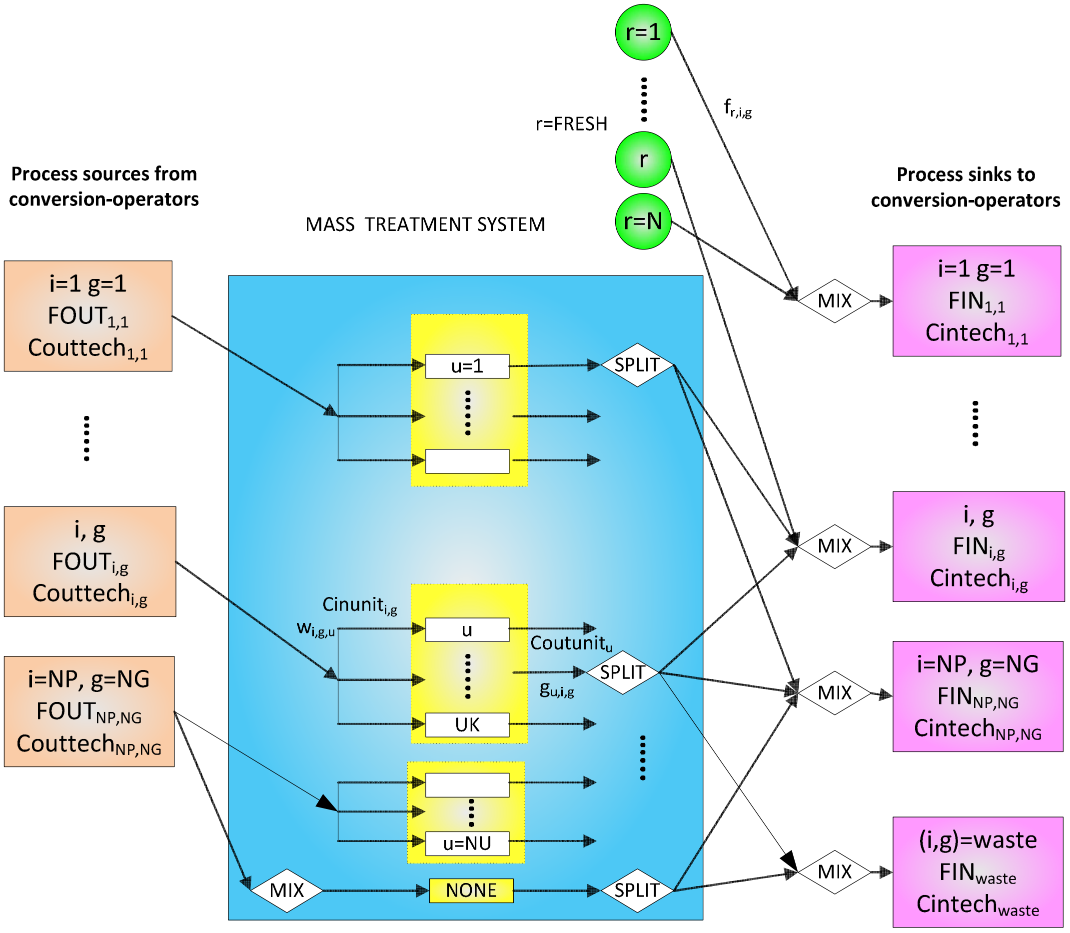

Figure 4.3. Structural Representation of the Mass Treatment Network Integration with Conversion Operator.

A blank unit is put in the interception system to allow a stream that need pass through the system unchanged. An additional sink is placed to represent the waste material. Also, some external fresh resources can be purchased to supplement the use of existing process streams.

4.4.3 Mathematical Formulation

The foregoing concepts can be conducted in an optimization formulation that involves the following model.

The performance model (shown in **Figure 4.4**) for conversion operator g_i in layer i (referred to as $\pi_{i,g,p}$) relates the flow rates of the different streams entering and leaving the conversion operator:

$$(F_{i,g}^{OUT},\ C_{c,i,g}^{out\ tech}) = \pi_{i,g,c}\left(F_{i,g}^{IN}, C_{c,i,g}^{in\ tech}, D_{i,g}, O_{i,g}\right),\ \forall i \in NLAYERS, g \in NTECH, c \in NCOMP \qquad (4.1)$$

where $F_{i,g}^{OUT}$ and $F_{i,g}^{IN}$ are the flow rates of process streams leaving and entering the conversion operator g_i in layer i. And $C_{c,i,g}^{out\ tech}$ and $C_{c,i,g}^{in\ tech}$ are the composition for component c of process streams leaving and entering the conversion operator g_i. The design and operating variables of g_i are denoted by $D_{i,g}$ and O_{g_i}, respectively.

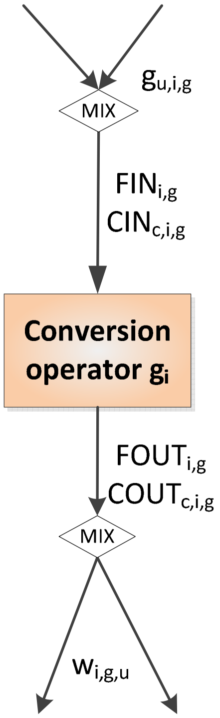

Figure 4.4 Mixing and Splitting Representation Around the Conversion Operator.

The mass balance around the conversion operator indicates that the total flow rates coming out of the operator g_i in layer i should not exceed the flow rates fed into the operator g_i:

$$F_{i,g}^{OUT} \leq F_{i,g}^{IN}, \ \forall i \in NLAYERS, g \in NTECH \tag{4.2}$$

Splitting of fresh sources: Fresh sources can be split and sent to any sink but not to the waste to satisfy the treatment capabilities. Feedstock can be among those fresh sources.

$$H_r = \sum_{\substack{i \in NLAYERS \\ (i,g) \neq waste}} \sum_{g \in NTECH} h_{r,i,g}\,, \ \forall r \in FRESH, FEEDSTOCK \subset FRESH \tag{4.3}$$

Splitting of process sources: Process sources are split and sent to each treatment unit:

$$F_{i,g}^{OUT} = \sum_{u \in Ui,g} w_u\,,\ \ \forall i \in NLAYERS, g \in NTECH \tag{4.4}$$

Mass balance in the splitting point at the exit of the interceptors: The flow rate of streams leaving the interceptor is equal to the summation of streams sent to the available sinks and the waste.

$$\sum_{i \in NLAYERS} \sum_{g \in NTECH} g_{u,i,g} = w_u,\ \ \forall u \in NUNITS \tag{4.5}$$

Mixing of streams entering the sinks: The flow rate entering each sink is equal to the summation of the streams from the interceptors plus the fresh sources.

$$F_{i,g}^{IN} = \sum_{u \in NUNITS} g_{u,i,g} + \sum_{r \in FRESH} h_{r,i,g}\,,\ \ \forall i \in NLAYERS, g \in NTECH \tag{4.6}$$

The component balance around the mixing point before the sinks is given by the following equation:

$$F_{i,g}^{IN} C_{c,i,g}^{in\ tech} = \sum_{u \in NUNITS} g_{u,i,g}\, C_{c,u}^{out\ unit} + \sum_{r \in FRESH} h_{r,i,g}\, C_{c,r}^{fresh},\ \ \forall i \in NLAYERS, g \in NTECH, c \in NCOMP \tag{4.7}$$

Mixing of waste: Streams leaving the network are allowed to mix into the waste block.

$$waste = \sum_{u \in NUNITS} g_{u,(i,g)=waste} \tag{4.8}$$

The performance function for the *u*th interceptor is given by the following relationship:

$$C_{c,u}^{out\ unit} = f_u\big(\, C_{c,u}^{in\ unit}, D_u, O_u\big),\ \ \forall u \in NUNITS, c \in NCOMP \tag{4.9}$$

Previous relationships state that the composition of each component c in the output stream from interceptor u is the function of the design D_u and operating O_u factors (these could be the temperature, pressure, solvent selection, catalyst, etc.) and the composition of the stream fed to the unit. Notice that each unit has specific constraints.

Constraints: A set of constraints for the process convertors is needed for the process limits and environmental regulations. These include the constraints for the quality of the products, given in terms of upper ($\leq C_{c,i,g}^{in\ tech\ max}$) and lower bounds ($C_{c,i,g}^{in\ tech\ min}$) for the composition of the product.

$$C_{c,i,g}^{in\ tech\ min} \leq C_{c,i,g}^{in\ tech} \leq C_{c,i,g}^{in\ tech\ max}, \quad \forall i \in NLAYERS, g \in NTECH, c \in NCOMP \tag{4.10}$$

The environmental constraints for the waste generated are stated in terms of upper ($C_{c,waste}^{ENV\ max}$) and lower ($C_{c,waste}^{ENV\ min}$) bounds for the composition as follows:

$$C_{c,waste}^{ENV\ min} \leq C_{c,waste}^{waste} \leq C_{c,waste}^{ENV\ max}, \quad \forall C \in NCOMP \tag{4.11}$$

The feedstocks are fed to the technologies in the first layer:

$$\sum_{g \in NTECH} h_{r,1,g} = H_r, \quad \forall r \in FEEDSTOCK, FEEDSTOCK \subset FRESH \tag{4.12}$$

Notice that the index *r* refers to the feedstock, which is among the total fresh sources.

No streams can enter to the technologies in the first layer other than the feedstock:

$$g_{u,1,g} = 0, \ \forall u \in NUNITS\ , g \in NTECH \tag{4.13}$$

Bounds for the product flow rate: The flow rates of products require lower bounds. The streams entering to the convertors in the last layer *NP* are equal to the streams of the desired products; therefore, the flow rates of the streams entering to the convertors in the last layer require the following lower bounds:

$$F_{NP,g_{NP}}^{IN} \geq W_{g_{NP}}^{min}, \quad \forall g \in NTECH \tag{4.14}$$

A particularly useful special case is when the concentration of each component *c* leaving the conversion operator g_i is calculated through a given yield ($y_{c.i.g}$) times the concentration of a limiting component ($c_{g_i}^{\mathrm{lim}}$):

$$C_{c,i,g}^{out\ tech} = y_{c.i.g} \times C_{c_g^{lim},i,g}^{in\ tech}, \quad \forall i \in NLAYERS, g \in NTECH, c \in NCOMP \tag{4.15}$$

Note that the concentration of all the components *c* should be less than or equal to 1.

$$\sum_{c \in NSPECIES} C_{c,i,g}^{in\ tech} \leq 1, \forall i \in NLAYERS, g \in NTECH, c \in NCOMP \tag{4.16}$$

The flow rates of the different chemical species entering to the conversion operator g_i are related to the flow rate of the limiting component via a stoichiometric or another form of required ratio (denoted by $\nu_{c.i.g}$). Hence, the following relationship is included in the model:

$$C_{c,i,g}^{in\ tech} = \nu_{c.i.g} \times C_{c_g^{lim},i,g}^{in\ tech}, \ \forall\ i \in NLAYERS, g \in NTECH, c \in NCOMP \tag{4.17}$$

The total annualized cost of the conversion operator g_i in layer *i* is given by a cost factor ($\beta_{i,g}$) times the flowrate of the limiting component entering to the conversion operator:

$$TACTECH_{i,g} = F_{i,g}^{IN} \times \beta_{i,g}, \quad \forall i \in NLAYERS, g \in NTECH \tag{4.18}$$

The total annualized cost for the interceptor *u* is given by a cost factor (α_u) times the flowrate of the stream entering to the interceptor:

$$TACUNIT_u = w_u \times \alpha_u, \quad \forall u \in NUNITS \tag{4.19}$$

The pollutant removal for the *u*th interceptor is given by the following relationship:

$$C_{c,u}^{out\,unit} = (1 - \gamma_u) \times \, C_{c,u}^{in\,unit}, \quad \forall u \in NUNITS \; c \in NCOMP \tag{4.20}$$

Where γ_u is the efficiency for unit *u* to remove the pollutants.

Objective function: The objective function consists in to maximize the net annual profit ($PROFIT$), constituted by the annual sales of products minus the cost of fresh sources, minus the cost of the pathway technologies used to convert the feedstock to products ($TACTECH_{i,g}$), minus the cost of selected interceptors to treat the process streams ($TACUNIT_u$).

$$\begin{aligned} \max PROFIT = & \sum_{product} F_{NP,product}^{IN} \times COST_{product} - \sum_{r \in FRESH} H_r \times COST_r \\ & - \sum_{i \in NLAYERS} \sum_{g \in NTECH} TACTECH_{i,g} - \sum_{u \in NUNITS} TACUNIT_u \end{aligned} \tag{4.21}$$

Where, $COST_{product}$ and $COST_r$ are the unit cost for the products and fresh sources respectively.

The cost of technologies g_i is related to the flow rates entering to the convertor and the type of convertor selected ($\Omega_{i,g}$). In addition the cost for the technology selected depends on the design and operating parameters as follows:

$$TACTECH_{i,g} = \Omega_{i,g}\left(F_{i,g}^{IN}, D_{i,g}, O_{i,g}\right), \quad \forall i \in NLAYERS, g \in NTECH \qquad (4.22)$$

The total cost for technology *g* in the i*th* layer is a function of the design and operating factors and the flow rate fed into the conversion technology ***g*.**

Previous relationships constitute a mathematical programming problem that could be linear and the problem can be solved globally to determine the biorefinery configuration including the flows interconnecting the various conversion operators and the optimum interceptors for treatment of required properties. If the relationships are not linear and non convex, appropriate non linear programming solutions methods must be use to get the optimal solution.

4.4.4 Remarks for the Methodology Presented

- The proposed methodology considers simultaneously the optimal selection of conversion technology, separation and recycle for the synthesis of a biorefinery.

- The problem could be formulated as a linear programming problem to guarantee the optimal solution.
- To reduce the cost burden and process complexity, layers of technologies are limited to 3.
- Fresh streams include feedstock and necessary external species for the technologies conversion.
- The input stream output from the conversion operator are taken as input stream for the mass treatment system, and output stream from the mass treatment system are taken as input for the conversion operator.

4.5 Case Study

The following case study is used to illustrate application of the proposed approach. There are 3 layers of conversion technologies, and the feedstock is selected as cellulose. There are 11 technologies to convert biomass into intermediates (see **Table 4.1**), and these 11 intermediates can be further processed to other products until producing bio-gasoline. After each technology, there are the separation units to recover the necessary products. The separation cost of each unit for different sources is listed in **Table 4.1** (information taken from Perry and Green, 1984; Peters, 1991; Sinnott, 2005; Vatavuk, 1990; Watson, 1999). The unit cost for treating the waste is 0.22$/tonne. The data for yield, conversion, unit costs for each considered technology were taken from Bao et al. (2011). The pathway tree is constructed and the problem is solved using the mathematical model shown in the previous section using the Lingo software to get the global optimum solution, where a variety of selections could be chosen. The solution for the minimum payback period of the optimal pathway with separation unit is shown in **Figure 4.5,** which corresponds to the pathway with cellulose fermented to alcohol and alcohol dehydrated to gasoline with a payback period of 11.7 year with 1620 tonne/day of feedstock. In addition, the second best solution is shown in **Figure 4.6** and it corresponds to the pathway with cellulose fermented to carboxylate and carboxylate thermal converted to ketone and hydrogenated and oligomerized to gasoline with a payback period of 12 years. It is noteworthy to mention that when the capacity is increased to 120,000 BPD of gasoline production, the payback period for both previous solutions are 3.4 years and 4.2 years, respectively. This information is very important, because the proposed approach allows to indentify the production required for a desired payback period.

Table 4.1. Separation Cost for Various Streams from Different Sources.

Source stream	**Technology**	**Separation**	**Removal efficiency (%)**	**Cost ($/kg recovered)**
Cellulose	Anaerobic digestion	Methane separation	10	0.01
			60	0.02
			95	0.03
	Fermentation to alcohol	Filter and Liquid separation	95	0.03
	Gasification	Syngas separation	10	0.003
			50	0.006
			70	0.012
			95	0.023
	Fermentation to carboxylate	Filter & Liquid separation	95	0.03
	Fermentation to acid	Filter& Liquid separation	95	0.03
	Pyrolysis	Syngas separation	10	0.004
			50	0.008
			70	0.015
			95	0.025
	Liquefaction	Filter	95	0.02
Lignin	Pyrolysis	Syngas separation	10	0.008
			50	0.015
			70	0.02
			95	0.03
	Gasification	Syngas separation	10	0.004
			50	0.008
			70	0.015
			95	0.025
Hemicellulose	Pyrolysis	Syngas separation	10	0.008
			50	0.015
			70	0.02
			95	0.03
	Gasification	Syngas separation	10	0.005
			50	0.01
			70	0.016
			95	0.026
	Fermentation to alcohol	Filter and Liquid separation	95	0.02
	Fermentation to acid	Filter and Liquid separation	95	0.015
	Anaerobic digestion	Methane separation	10	0.01
			60	0.02
			95	0.03
	Enzymatic hydrolysis	Filter and Liquid separation	95	0.01

Table 4.1. Continued

CH4	Cracking	Ethylene separation	95	0.02
Sugar	Fermentation to alcohol	Liquid separation	95	0.02
CO	Synthesis to acid	Liquid separation	95	0.01
	Synthesis to alcohol	Liquid separation	95	0.012
	FT	Liquid separation	95	0.01
Pyroil	Cracking	Ethylene separation	95	0.02
	gasification	Syngas separation	10	0.002
			50	0.005
			70	0.01
			95	0.02
Acid	Decarboxylation	Liquid separation	95	0.01
Alcohol	Dehydration	Liquid separation	95	0.01

In **Figure 4.5** (optimal solution), the pathway starts with hydrolysis of cellulose to alcohol. After separation of alcohol from CO_2 and other byproducts, alcohol and external H_2 input is converted by dehydration and oligomerization into gasoline. Gasoline is separated from water byproducts to get the final products of 511 tonne/day. On the other hand, in **Figure 4.6** for the second best solution, the pathway starts with the fermentation of cellulose into carboxylates. After separating carboxylates from water and lignin residues, the carboxylates are further converted by thermal conversion into ketones. After separation and recovery, $CaCO_3$ is recovered and recycled back to supply the fresh feed, and the recovered ketones are hydrogenated with external H_2 and through oligomerization and hydrogenation converted into gasoline products. Separation steps are applied to remove the excess water to get the final product (i.e., gasoline) with flow rate of 234 tonne/day.

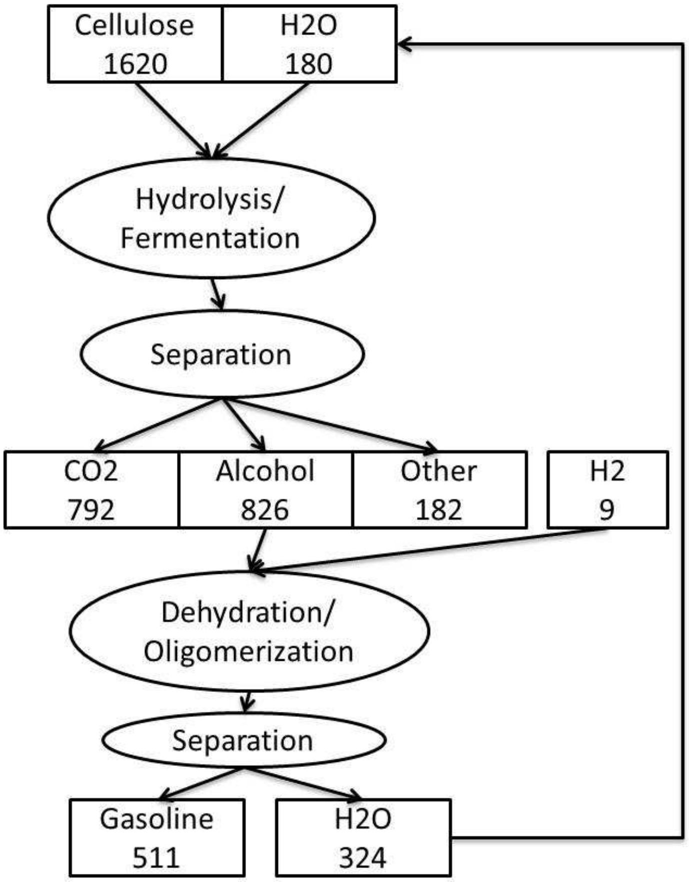

Figure 4.5 Optimal Pathway for the Case Study (Alcohol Fermentation).

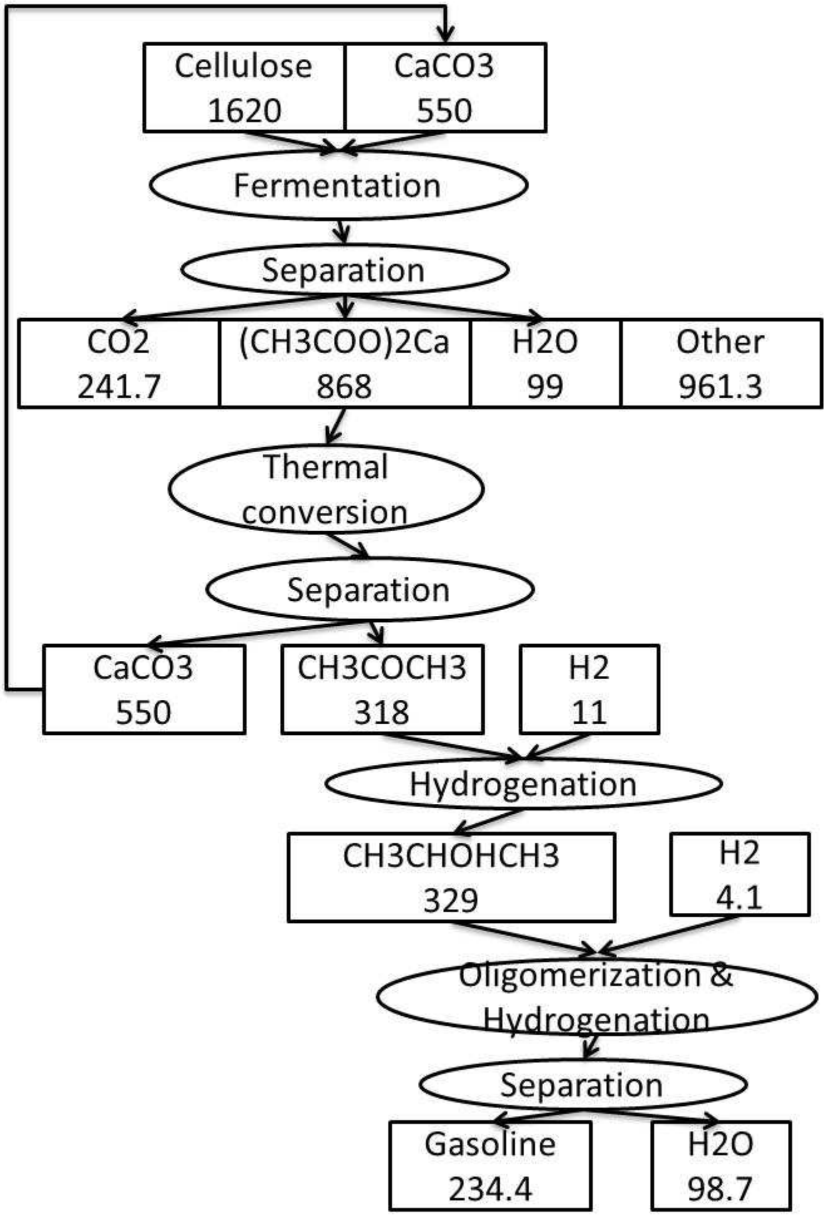

Figure 4.6 Second Best Solution Identified for the Case Study (Carboxylate Thermal Conversion).

4.6 Conclusions

This work presents a new methodology to effectively optimize a biorefinery technology pathway integrated with species separation and recycle networks. The proposed methodology allows to determine the optimal allocation of the conversion technologies and the recycle. In addition, the proposed methodology is able to identify the cost effective process of conversion technologies combinations and the optimal interconnecting flow rates for the selected feedstock and desired products.

A case study has been conducted to illustrate the proposed approach, and results show that the optimal pathway for the gasoline production from cellulosic materials corresponds to the alcohol fermentation through oligomerization with a minimum payback period of 11.7 years; whereas the pathway of cellulose fermented to carboxylate and carboxylate thermal converted to ketone and hydrogenated and oligomerized to gasoline has a payback period of 12 years for 1620 tonne/day of cellulose feedstock. When the capacity is increased to 120,000 BPD of gasoline production, the payback period for each case is 3.4 years and 4.2 years, respectively. These results allow to identify optimal pathways and to analyze different scenarios for the implementation of a biorefinery. Finally, the proposed methodology is applicable to different cases, and the systematic approach allows to solve easily a problem that originally is complicated.

5. A SYSTEMATIC TECHNO-ECONOMICAL ANALYSIS FOR THE SUPERCRITICAL SOLVENT FISCHER TROPSCH SYNTHESIS

5.1 Abstract

Supercritical solvents offer significant economic benefits in the synthesis of biofuels using the Fischer-Tropsch synthesis technology. The current study is focused on the methods to efficiently recycle the supercritical solvent from the Fischer-Tropsch synthesis products (referred to as light hydrocarbons, syncrude and water) while taking advantage of the high pressure operation in the reactor bed of the supercritical solvent Fischer-Tropsch synthesis. In addition, the study is aimed at ensuring the recovery of middle distillates product as well (jet fuel and fuel fractions of the syncrude). Several parameters were investigated and optimized in this process, including the separation sequence and the heat duty (energy consumption) of the separation units. Results show that from the proposed separation configuration, the solvent is recovered 99% from the FT products, while not affecting the heavier components recovered and light gas recovery, and 99% of wastewater is recycled. The case that uses super critical fluids in the Fischer-Tropsch process is competitive with the traditional FT case with a similar ROI of 0.26 year. The proposed process has comparable major parts cost with typical gas to liquid process and the capital investment per BPD is within the range of existing gas to liquid plant. In addition, several scenarios have been analyzed to show potential configurations comparable with the optimal one for the FT process.

5.2 Introduction

Fischer-Tropsch (FT) reaction has been studied and investigated for nearly a century, and it is basically described as converting synthesis gas into value added chemicals and fuel products. The rapid increasing interest on this technology comes from the notice that natural gas (GTL: gas to liquid), coals (CTL: coal to liquid), biomass (BTL: biomass to liquid) and other types of wide available resources can be utilized to produce high value fuels (Alden, 1946; Schulz, 1999). The products are of large range from methane to wax, and types from branched compounds to oxygenates. The diesel produced from FT has quality of high cetane number and no sulfur, less CO, NO_x and particles resulting in an environmental friendly fuel.

The application of supercritical fluids in the Fischer-Tropsch synthesis (SCF-FTS) is aimed mainly at low temperature (LTFT) reactor (Eilers et al., 1990; Fox and Tam, 1995). LTFT bases the main target to produce long chains wax and diesel, by utilizing the catalyst type of either precipitated iron or supported cobalt (Anderson,1956), and reactor choice between fixed bed or slurry reactor (Caldwell and van Vuuren, 1986). In high temperature Fischer-Tropsch (HTFT) there is no liquid phase outside the catalyst particles, which is the major difference from the LTFT (Steynberg and Dry, 2004). HTFT usually utilizes a fused iron catalyst with fluidized bed reactor to produce syncrude including light olefins and gasoline (Steynberg et al., 1999).

The first type of LTFT reactor is the fixed bed reactor. It is worth noting that the FT reaction is highly exothermic; therefore, a large number of tubes is required to remove the heat released from the reactor and this brings in the problem of poor economies for scaling up. In addition, the non uniformity in the temperature profile resulting from the tubes needs increases the catalyst loading rate. This design also results in high pressure drop, and thus high compression costs (El-Bashir et al., 2010). To avoid previous problems, Sasol developed a slurry bed FT reactor that uses a fluid media (i.e., wax produced from the reaction) to operate the reactor as a continuous stirred tank reactor (CSTR) to keep a uniform temperature profile throughout the reactor (Jager and Espinoza, 1995). Therefore, the catalyst activity is kept high under uniform temperature and a good products selectivity is achieved. In addition, this design brings low compression cost. However, the difficulty in separation of the solid catalyst from the liquid products remains as a problem in this type of reactors (El-Bashir et al., 2010).

Therefore, there is urgent desire to combine the simplicity of fixed bed reactor and take advantage of slurry reactor to improve the FT reaction performance. SCF-FTS provides the platform for this concern, as supercritical fluid has the advantage of gas like diffusivity and liquid like solubility. Operating FTS under supercritical fluid (SCF) conditions improves the catalyst selectivity and activity. In addition, SCF can provide benefits as provide high solubility in extracting heavy hydrocarbons from the catalyst and excellent heat transfer performance for the reactor. Furthermore, the superior diffusivity feature eliminates the molecule transport limitations and enhances high α-olefin selectivity for products (Jacobs et al., 2003; Yokota et al., 1990; Bochniak and Subramaniam, 1998; Durham et al., 2008).

One of the first works in SCF-FTS was undertaken by Yokota and Fujimoto (1989), where they evaluated the products, solvent and reaction performances of the FTS reaction under supercritical phase, under gas and under liquid phases, and compared the results among these conditions in fixed bed reactor and suggested encouraging future for SCF-FT. Yokota et al. (1990) and Fan et al. (1992) also conducted research on the catalyst characteristics, hydrocarbon selectivity and reaction performance under the effect of solvent in SCF-FT analysis. Bochniak and Subramaniam (1998) took a study for SCF-FTS process and investigated different pressure conditions for the reaction performance and compared their influence on the catalyst. Huang and Roberts (2003) carried out a series of experiments using different catalysts and identified several benefits for the SCF-FTS reaction with cobalt catalyst. El-Bashir and Roberts (2005) conducted SCF-FTS reaction research using cobalt catalyst and found out that the standard Anderson-Shutlz-Flory (ASF) model does not apply in near-critical and supercritical conditions. Recently, El-Bashir et al. (2009) reported a solvent recovery model under SCF conditions and proposed a design for the optimization of SCF separation processes as part of FT reactor design.

Previous researches provide a good perspective for the FT reactor. However, previous researches did not consider the large cost and energy associated with using supercritical fluid operation, and did not notice the design of separation solvent from liquid products from process optimization view. Proper selection of separation conditions plays a vital role in obtaining desirable performance. Therefore, this paper proposes a new design for the separation process of supercritical solvent from reaction mixture optimizing the pressure drop and the temperature to separate the light hydrocarbons fractions as well as the permanent gases (syngas and CO_2) from reaction mixture coupled with Radfrac distillation to improve the separation efficiency. Success in utilizing pressure drop in the separation processes for supercritical phase FTS could represent a major advantage for this process over conventional FTS technologies since it has always been challenged by the high price needed for the compression process in addition to other costs associated for high pressure equipments. Therefore, this paper is focused on the design of separation sequences of the supercritical solvent as well as the rest of the process by utilizing the energy from the potential of manipulating the high pressure and temperature profile from the FTS reaction, in order to evaluate the potential of SCF-FT to beat traditional FT design.

5.3 Problem Statement

The focus of this paper is to investigate the cost and energy analysis of the gas to liquid (GTL) process with supercritical fluids in FTS, and to evaluate the potential to compete with the non supercritical FT process. The main process differences between the two types are the products distribution range, the reactor operation, and the SCF incorporation and recovery. Therefore, the paper focus on the step to recover supercritical solvent to reduce cost and obtain sustainable operations. To recover the solvent from the SCF-FT products, there are several elements to consider: products purity, products yield, solvent purity, solvent recoverability, energy cost, and operation feasibility.

The objective of this work is to minimize the process cost and energy consumption, while maintaining no less than 95% of solvent recoverability, with consideration for constraints of hydrocarbon products recoverability and purity, and ease of operation. Also, the work is aimed at taking advantage of the high pressure operation in the reactor and comparing the process cost of the SCF-FT and non SCF-FT.

5.4 Proposed Approach

This paper proposed a systematic approach to deal with the addressed problem. The approach is conducted in two main steps and the details are shown in Figure 5.1.

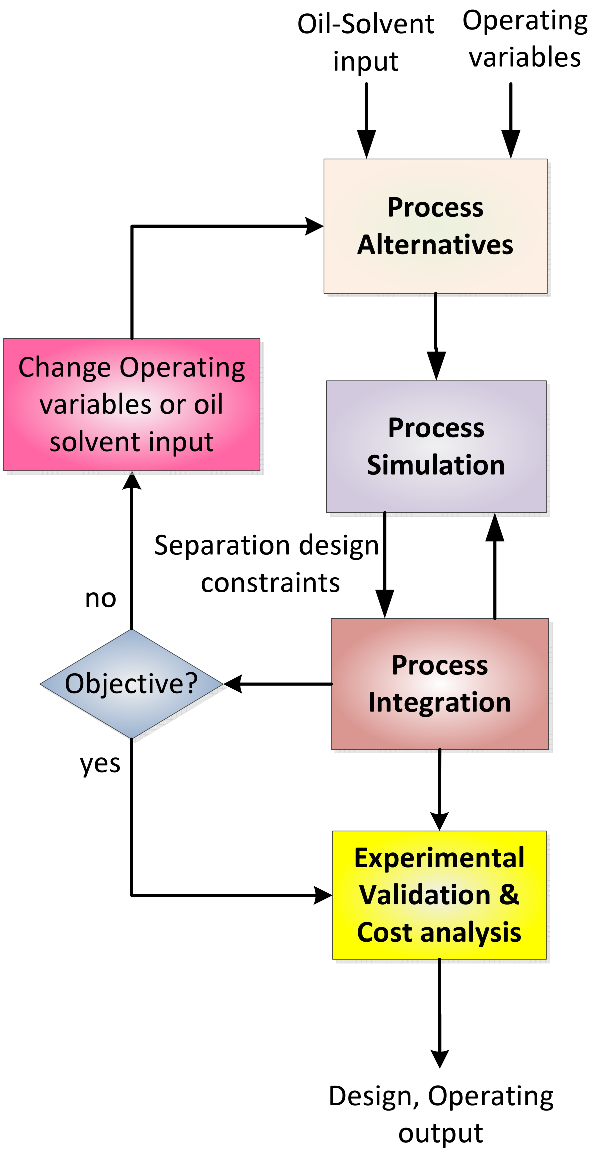

Figure 5.1. Proposed Approach for the SCF-FT Solvent Recovery Technology.

In the first step, the approach starts with formulating design and operating variables prior to selection of the optimum separation design. Firstly, a preliminary flowsheet is established, and separation design specifications are analyzed and searched from the literature with the basis of the input oil-solvent mixture characteristics. They are then synthesized and sent to simulation software to generate the mass and heat balance for later steps. Alternative scenarios are generated based on the performance condition of the process (arrangement of the sequence of separation units, selection of the units and the operating conditions of the units). Then, energy integration is performed to target the minimum energy cost for each scenario and an economic analysis is conducted for each synthesized process. A certain objective metric is generated based on either cost optimization, material conservation or environmental efficiency, and it is used to compare the process performance of each scenario. Certain constraints are also given including recoverability, composition requirement, etc to assist the optimization step. After that, if the objective is met, the data are used for experimental validation and economic evaluation; otherwise, the input data is adjusted and refined, and the previous steps are went through again until qualified optimum design alternatives are generated.

The second step is to compare the potential of the generated process with the process without SCF utilization. The comparison is based on certain metric of cost, energy efficiency or products yield. The first step of SCF separation process design could be embed in this step.

5.5 Generic Mathematic Formulation for the Separation Design Selection

This section presents the generic mathematic formulation for the selection of the optimal separation design. **Figure 5.2** shows the schematic representation of the addressed problem. Given a series of scenarios k of different separation design processes, it is desired to select the optimum case *k* that has the maximum return of investment (*ROI*). In each case *k* there is a sequence of units *j* to choose from, and there are feedstocks and external input streams *RawFlow(i)*, and output and products streams *ProdFlow(i)*. Some output streams including solvents and water could be recycled back as input streams.

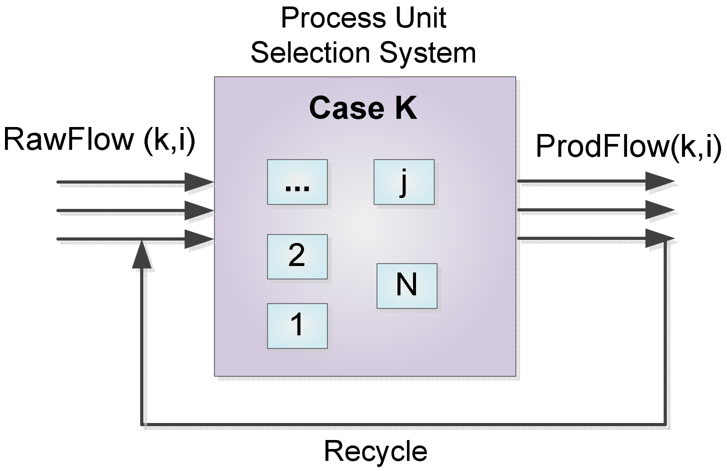

Figure 5.2. Mathematic Formulation for the Optimum Separation Designing.

The objective is to maximize the return of investment (*ROI*):

$$\text{Objective Function} = \text{MAX}\ ROI\ (return\ of\ investment) \tag{5.1}$$

And the return of investment is the annual net profit divided by the total capital investment (*TCI*):

$$ROI = \frac{Annual\ net\ profit}{TCI(Total\ capital\ investment)} \tag{5.2}$$

The total capital investment is the summation of the working capital investment and the fixed capital investment (*FCI*):

$$TCI = working\ capital\ investment + FCI\ (Fixed\ capital\ investment) \tag{5.3}$$

The annual net profit is equal to the annual sale minus the annual operating cost, the annualized fixed cost and the tax:

$$Annual\ net\ profit = (Annual\ sale - Annual\ operating\ cost - Annualized\ fixed\ cost) \times (1 - tax) + Annualized\ fixed\ cost \tag{5.4}$$

The annualized fixed cost is equal to the fixed capital investment minus the salvage value over the life period:

$$Annualized\ fixed\ cost = \frac{FCI - salvage\ value}{life\ period} \tag{5.5}$$

Because only one case k could be selected as the optimal one, the following disjunction is used to account for the economic aspects.

$$\bigvee_{k \in NCASE} \begin{bmatrix} E_k \\ Annual\ sale = \sum_i \sum_{c_i} Price_c \times ProdFlow_{k,i} \times Frac_{k,i,c_i} \\ AOC = \sum_i \sum_{c_i} Price_c \times RawFlow_{k,i} \times Frac_{k,i,c_i} + OperCost_k \\ FCI = \sum_j FixCost_{k,j} \times \beta_{k,j} \end{bmatrix}$$

Therefore, if the case k is selected, then the binary variable E_k is 1 and the associated economic parameters for that technology k apply; otherwise, when the technology k is not selected, E_k is 0 and the associated economic parameters do not apply.

The annual sale is the summation of all the products flow rate ($ProdFlow_{k,i}$) multiplied by the products fraction ($Frac_{k,i,c_i}$) multiplied by the price of that component *c* (*Price*$_c$). FCI is the summation of all fixed costs of each unit *j* multiplied by the size coefficient β. The annual operating cost ($OperCost$) is the summation of the feedstock cost and other operating costs (utility, labor, maintenance, etc.). The feedstock cost is the summation of the entire feedstock flow rate ($RawFlow_{k,i}$) multiplied by the fraction $Frac_{k,i,c_i}$ and multiplied by the price of the component *c* (*Price*$_c$).

To model previous disjunction, the following set of algebraic relationships are used. Only one case *k* is selected as optimum:

$$\sum_k E_k = 1 \tag{5.6}$$

To find the best possible solution, the above formulation could be solved as follows:

$$Annual\ sale \leq \sum_i \sum_{c_i} Price_c \times ProdFlow_{k,i} \times Frac_{k,i,c_i} + M \times \left(1 - E_k\ \right),\ \forall k \tag{5.7}$$

$$Annual\ sale \geq \sum_i \sum_{c_i} Price_c \times ProdFlow_{k,i} \times Frac_{k,i,c_i} - M \times \left(1 - E_k\ \right),\ \forall k \tag{5.8}$$

$$Annual\ operating\ cost \leq \sum_i \sum_{c_i} Price_c \times RawFlow_{k,i} \times Frac_{k,i,c_i} + OperCost_k + M \times \left(1 - E_k\ \right), \forall k \tag{5.9}$$

$$Annual\ operating\ cost \geq \sum_i \sum_{c_i} Price_c \times RawFlow_{k,i} \times Frac_{k,i,c_i} + OperCost_k - M \times \left(1 - E_k\right), \forall k \tag{5.10}$$

$$FCI \leq \sum_j FixCost_{k,j} \times \beta_{k,j} + M \times \left(1 - E_k\right),\ \forall k \tag{5.11}$$

$$FCI \geq \sum_j FixCost_{k,j} \times \beta_{k,j} - M \times \left(1 - E_k\right),\ \forall k \tag{5.12}$$

In previous relationships, when the binary variable E_k is equal to one, the relationships apply properly; on the other hand, when the binary variable E_k is equal to zero, the relationships are relaxed because of the big M parameter.

In the same way, when the technology is selected, the appropriate relationships for the mass, component and feasibility constraints apply. This is modeled through the following disjunction:

$$\bigvee_{k \in NCASE} \left[\begin{array}{c} E_k \\ \sum_i RawFlow_{k,i} = \sum_i ProdFlow_{k,i} \\ \sum_i RawFlow_{k,i} \times Frac_{k,i,c} = \sum_i ProdFlow_{k,i} \times Frac_{k,i,c},\ \ \forall c \\ Frac_{k,i,c_i} \geq MinFrac_{k,i},\ \ \forall i, \forall c_i \\ ProdFlow_{k,i} \geq MinProdFlow_{k,i},\ \ \forall i \end{array} \right]$$

The overall mass balance of the process for each case k should be equal.

$$\sum_i RawFlow_{k,i} \leq \sum_i ProdFlow_{k,i} + M \times \left(1 - E_k\right),\ \forall k \tag{5.13}$$

$$\sum_i RawFlow_{k,i} \geq \sum_i ProdFlow_{k,i} - M \times \left(1 - E_k\right),\ \forall k \tag{5.14}$$

The component balance *c* of the process for each case *k* should be equal.

$$\sum_i RawFlow_{k,i} \times Frac_{k,i,c} \leq \sum_i ProdFlow_{k,i} \times Frac_{k,i,c} + M \times \left(1 - E_k\right), \ \forall k, \forall c \tag{5.15}$$

$$\sum_i RawFlow_{k,i} \times Frac_{k,i,c} \geq \sum_i ProdFlow_{k,i} \times Frac_{k,i,c} - M \times \left(1 - E_k\right), \ \forall k, \forall c \tag{5.16}$$

Some of the output streams should satisfy that the component purity be greater than a constraint.

$$Frac_{k,i,c_i} \geq MinFrac_{k,i} - M \times \left(1 - E_k\right), \ \forall k, \forall i, \forall c_i \tag{5.17}$$

Some of the output streams must satisfy that the flow rate must be greater than a certain constraint.

$$ProdFlow_{k,i} \geq MinProdFlow_{k,i} - M \times \left(1 - E_k\right), \ \forall k, \forall i \tag{5.18}$$

The model presented is general, and it must be adjusted to the specific case analyzed.

5.6 Case Study and Results

This section presents a case study for analyzing the implementation of SCT-FTS process considering the systematic approach proposed in this paper. Several scenarios are considered and these are discussed in detail and compared each other in the following sections.

5.6.1 Preliminary Flowsheet Result

Pentane and hexane's critical properties could qualify as candidate for SCF, since LTFT typically operates at ranges of 220 to 250 ºC, in addition, they are inert with cobalt and iron catalyst and show high solubility for other hydrocarbons; hence, in this work solvent of C_5-C_7 is selected. As indicated previously, the FTS products are composed of a variety of hydrocarbon products, gases (CO_2 and unreacted CO and H_2), and liquids (water) whereby the hydrocarbons consist of components from light gases of cetane number approximately 1 up to heavy hydrocarbons with cetane number larger than 30. In a conventional separation setup, these products are normally separated in three fraction: (i) permanent gases with light key CO, H_2, H_2O, C_1-C_4, (ii) Light hydrocarbons (e.g. C_5-C_8), and (iii) Middle and heavy distillates of C_{9+} components.

The FTS products distribution is calculated according to the Anderson-Shutlz-Flory (ASF) equation (Steynberg and Dry, 2004) following the procedure explained in Bartholomew and Farrauto (2006) for Shell’s Middle Distillate Synthesis (SMDS) reactor technology. The chain growth or propagation probability (α-value) is set as 0.96, and the H_2 conversion is set as 73% with syngas feed mole ratio at $H_2/CO = 2.15$. To reduce the complexity, hydrocarbons with cetane number bigger than 30 are all represented as C_{30+} components. The simulated process capacity is assumed to be 120,000 BPD, compared to Sasol setup of approximately 34,000 BPD (Espinoza et al, 1999). The solvent for the SCF- FTS is simulated as C_5-C_7 and this is co-fed with the syngas into the FTS reactor at molar ratio of 3:1. The products from the FTS reactor are obtained from a reaction conditions of 45 bar and 240 °C over cobalt-based catalyst. Feedstock and products representation at a typical and the aforementioned conditions for a GTL process are listed in **Tables 5.1a** and 5.**1b**.

Table 5.1a. Mass Balance for a Typical GTL Process.

Mass Flow (kg/hr)	**NG**	**Makeup water**	**O_2**	**Condense water**	**Syngas output**	**Syngas ratio adjust input**	**CO_2 sequestration**	**H_2 stream production**	**FT output cobalt 230**
H_2O	-	712,800	-	657,763	657,763	-	-	-	780,855
METHANE	1,199,785	-	-	-	7,212	7,212	-	-	8,184
NITROGEN	1,764	-	6,360	-	8,123	8,123	-	-	8,123
OXYGEN	-	-	1,445,640	-	-	-	-	-	-
ETHANE	92,024	-	-	-	92,024	92,024	-	-	93,890
PROPANE	1,039	-	-	-	1,039	1,039	-	-	3,725
CO	-	-	-	-	1,547,828	1,547,828	-	-	333,171
CO_2	20,020	-	-	-	859,581	-	859,581	-	-
H_2	-	-	-	-	305,859	237,702	-	68,157	64,180
c_4	-	-	-	-	-	-	-	-	3,439
c_5	-	-	-	-	-	-	-	-	4,127
c_6	-	-	-	-	-	-	-	-	4,754
c_7	-	-	-	-	-	-	-	-	5,324
c_8	-	-	-	-	-	-	-	-	5,842
c_9	-	-	-	-	-	-	-	-	6,309
c_{10}	-	-	-	-	-	-	-	-	6,730
c_{11}	-	-	-	-	-	-	-	-	7,106
c_{12}	-	-	-	-	-	-	-	-	7,442
c_{13}	-	-	-	-	-	-	-	-	7,740
c_{14}	-	-	-	-	-	-	-	-	8,002

Table 5.1a. Continued

c_{15}	-	-	-	-	-	-	-	-	8,231
c_{16}	-	-	-	-	-	-	-	-	8,428
c_{17}	-	-	-	-	-	-	-	-	8,597
c_{18}	-	-	-	-	-	-	-	-	8,738
c_{19}	-	-	-	-	-	-	-	-	8,855
c_{20}	-	-	-	-	-	-	-	-	8,948
c_{21}	-	-	-	-	-	-	-	-	9,020
c_{22}	-	-	-	-	-	-	-	-	9,071
c_{23}	-	-	-	-	-	-	-	-	9,104
c_{24}	-	-	-	-	-	-	-	-	9,120
c_{25}	-	-	-	-	-	-	-	-	9,120
c_{26}	-	-	-	-	-	-	-	-	9,105
c_{27}	-	-	-	-	-	-	-	-	9,077
c_{28}	-	-	-	-	-	-	-	-	9,037
c_{29}	-	-	-	-	-	-	-	-	8,985
c_{30+}	-	-	-	-	-	-	-	-	401,555
	-	-	-	-	-	-	-	-	-
Total	1,314,631	712,800	1,452,000	657,763	3,479,431	1,893,929	859,581	68,157	1,893,936

Table 5.1b. Mass Balance for a GTL Process with Supercritical Conditions.

Mass Flow (kg/hr)	**NG**	**Makeup water**	**O_2**	**condense water**	**syngas output**	**syngas ratio adjust input**	**CO_2 sequestration**	**H_2 stream production**	**SCFT**
H_2O	-	712,800	-	657,763	657,763	-	-	-	855,728
METHANE	1,199,785	-	-	-	7,212	7,212	-	-	7,212
NITROGEN	1,764	-	6,360	-	8,123	8,123	-	-	8,123
OXYGEN	-	-	1,445,640	-	-	-	-	-	-
ETHANE	92,024	-	-	-	92,024	92,024	-	-	92,024
PROPANE	1,039	-	-	-	1,039	1,039	-	-	1,039
CO	-	-	-	-	1,547,828	1,547,828	-	-	216,696
CO_2	20,020	-	-	-	859,581	-	859,581	-	-
H_2	-	-	-	-	305,859	237,702	-	68,157	47,541
c_4	-	-	-	-	-	-	-	-	-
c_5	-	-	-	-	-	-	-	-	-
c_6	-	-	-	-	-	-	-	-	115,194
c_7	-	-	-	-	-	-	-	-	86,124
c_8	-	-	-	-	-	-	-	-	71,164
c_9	-	-	-	-	-	-	-	-	62,330
c_{10}	-	-	-	-	-	-	-	-	53,463
c_{11}	-	-	-	-	-	-	-	-	43,606
c_{12}	-	-	-	-	-	-	-	-	36,480
c_{13}	-	-	-	-	-	-	-	-	31,426
c_{14}	-	-	-	-	-	-	-	-	25,829

Table 5.1b. Continued

c_{15}	-	-	-	-	-	-	-	-	24,893
c_{16}	-	-	-	-	-	-	-	-	22,793
c_{17}	-	-	-	-	-	-	-	-	18,071
c_{18}	-	-	-	-	-	-	-	-	15,395
c_{19}	-	-	-	-	-	-	-	-	14,470
c_{20}	-	-	-	-	-	-	-	-	11,794
c_{21}	-	-	-	-	-	-	-	-	10,368
c_{22}	-	-	-	-	-	-	-	-	7,496
c_{23}	-	-	-	-	-	-	-	-	5,810
c_{24}	-	-	-	-	-	-	-	-	4,950
c_{25}	-	-	-	-	-	-	-	-	3,971
c_{26}	-	-	-	-	-	-	-	-	-
c_{27}	-	-	-	-	-	-	-	-	-
c_{28}	-	-	-	-	-	-	-	-	-
c_{29}	-	-	-	-	-	-	-	-	-
c_{30+}	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-
Total	1,314,631	712,800	1,452,000	657,763	3,479,431	1,893,929	859,581	68,157	1,893,988

The flowsheet and mass balance of the two processes to be compared are shown in **Figures 5.3a** (typical) and 5.**3b** (SCF). The process is composed mainly of autothermal reactor (ATR) to convert natural gas (NG) into synthesis gas, FT reactor to produce syncrude from synthesis gas, and the upgrading units. There are units of air separation (ASU) to generate O_2 from air, units to separate CO_2, water and other components from the output gas from ATR, and units to produce H_2 from synthesis gas to adjust the syngas ratio before feed in the FT reactor. In the supercritical solvent FT process, there are additional separation units to feed fresh solvent to supercritical condition, separate solvent from liquid products, and separate other products components for further upgrading. This step is to ensure that: the fresh and recycled solvent are properly mixed, the temperature and pressure are controlled for syngas and solvent mixture before feed to the reactor bed, the separation columns are efficient in separating solvent from synthesis gas, light components, and middle distillates, the pressure drop from the products is utilized for energy concern.

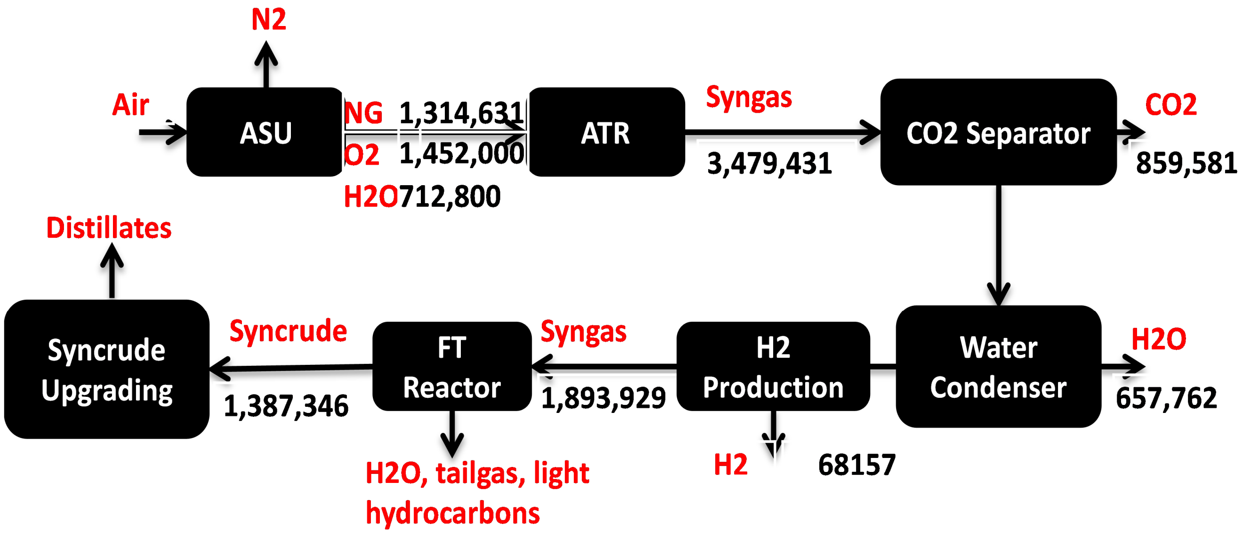

Figure 5.3a. Flowsheet of Typical GTL Process.

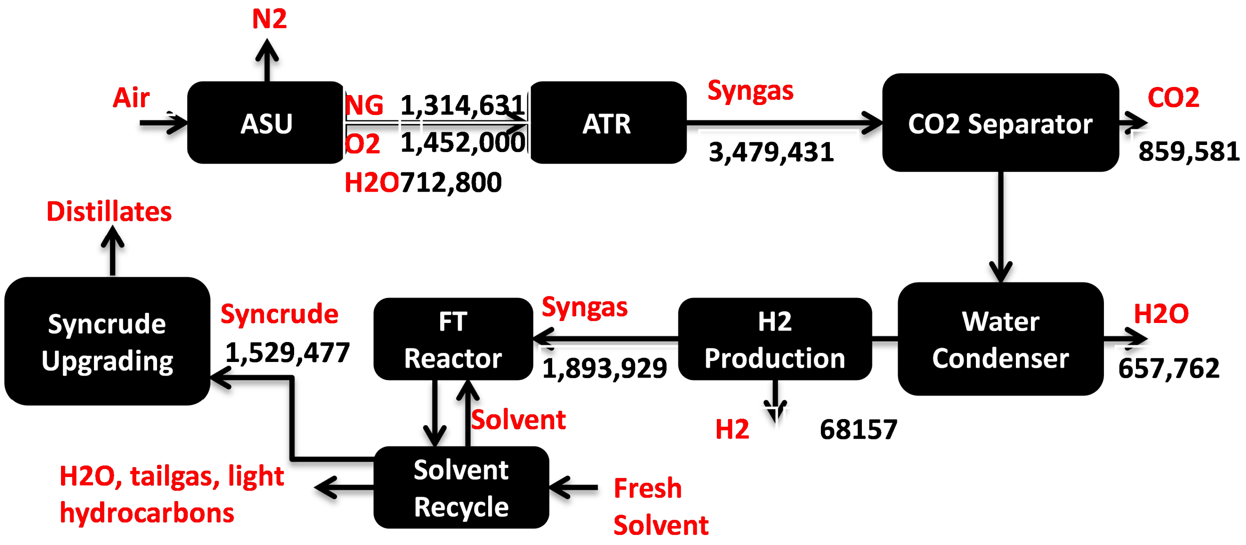

Figure 5.3b. Flowsheet of SCF-FT GTL Process.

The simulation of the solvent/product separation units (**Figures 5.4**) has been conducted in Aspen 2006 Plus utilizing the NRTL-RK property method to evaluate the separation result based on the phase behavior of the product mix. Alkanes are used to model hydrocarbons from C_1 to C_{30} in this work since they are the major products from the FTS over the cobalt-based catalyst. The separations units are distillation based, where the flash column modules play a major role in light hydrocarbons and solvent recovery. The RadFrac distillation 1 is simulated with 30 stages partial-vapor RadFrac distillate column with reflux ratio of 2, feed on the first stage and the side draw extracted from the stage 15, the condenser pressure is of 10 bar with a stage pressure drop of 0.1 bar. The flowsheet of the separation process is described in **Figure 5.4**.

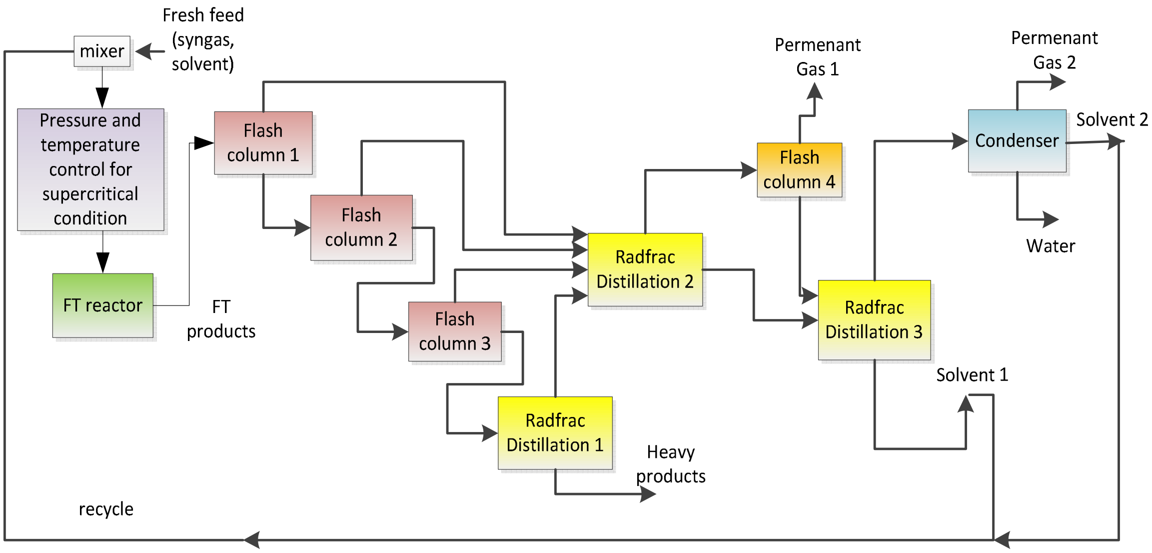

Figure 5.4. Flowsheet for Supercritical Solvent Separation Process.

The products from FTS (typical outlet products of the FTS reactor bed) (Elbashir et al., 2009) are represented in stream FT Products where the outlet tailgas recycle streams are represented in the stream Permenant Gas1 and Permenant Gas2, and the outlet solvent streams are represented by SOLVENT1 and SOLVENT2, the middle distillate and the heavy hydrocarbons (i.e. C_{8+}) are represented by HEAVY stream while the water outlet stream is represented by stream water. The separation process starts in the block flash column1, 2 and 3, where lighter components are initially separated from heavier ones to reduce large capacity for later separation. The second step in the separation process is the recovery of middle distillate hydrocarbons in Radfrac Distillation 1. The remaining lighter fractions from the former steps are sent to Radfrac Distillation 2 and 3. A portion of Permenant gas could be recovered by a Flash. The Radfrac Distillation 3 will recover most of the solvent in the bottom of the column. The remaining vapor streams are separated in the coalesce to obtain the remaining permenant gas, solvent and water. The separated water is cleaned and reused to purity of 10 ppm to 1000 ppm as indicated in the patent 7147775. The recovered solvent could be sent back to be mixed with fresh solvent and feed into the FT reactor. The flow rate of solvent (C_5-C_7) is averaged among each component.

The heat duty released or consumed by the flash distillation unit has been accounted for based on both temperature and pressure factors as shown above. The SCS-FTS is normally operated at elevated pressure to accommodate the single phase operation for the reaction mixture as required by this process. Our objective from this analysis is to take advantage of the high pressure operation and to utilize energy input (for the compression) in the separation process by utilizing phase split in pressure drop.

According to our simulation, as pressure and temperature are dropped, products are separated and energy could be utilized. Our effort in this study is focused on finding optimum separation conditions whereby maximum heat release is obtained coupled with high recoverability of the supercritical solvents and other products. The feed stream of products from the FT reactor for a solvent- oil syngas ration of 3:1is shown contains by 8% of pergas, 85 % of solvent, 1% of heavier (C8+) and 7% of water.

The condenser/separator system is used for the water/oil product separation after the FT reactor from patent search of Syntroleum, that condenser/separator is dependent upon various factors such as overall operating condition, quality and quantity of water produced by associated Fischer-Tropsch process and quantity and type of contaminants contained in the natural gas feed stream supplied to autothermal reformer (John, 2004). One VSEP unit of nano-filtration membranes can be undertaken at pressure of 250 psig to separate in industrial scale the water from syncrude with the resulting water purity of 16 ppm. Since the water/oil emulsion happen when less than 26% water present in the system (Hon et al., 2001); therefore, it is desired to separate part of the solvent first and then use a condenser and a decanter to separate the rest of the mixture of water and solvent.

5.6.2 Results and Analysis of Aeparation Acenario Optimization

There is a variety of alternatives that could be used to optimize the design of the separation supercritical solvent from the FT products. In this case, 5 alternatives are used:

the abovementioned process (**Figure 5.4**), the process with optimization of the heavy components recovery (**Figure 5.5a**), the process with the design of flash columns sequence (**Figure 5.5b**), the adding of condenser after column 4 to increase pergas purity (**Figure 5.5c**), and the replacement of Radfrac column with flash column in separating solvent (**Figure 5.5d**). These alternatives are designed and simulated in the Aspen Plus software. The mass and energy balance are produced for these alternatives. The methodologies presented in the approach section are used to analyze and select the optimum separation design. The design of each alternative process is described in the following section.

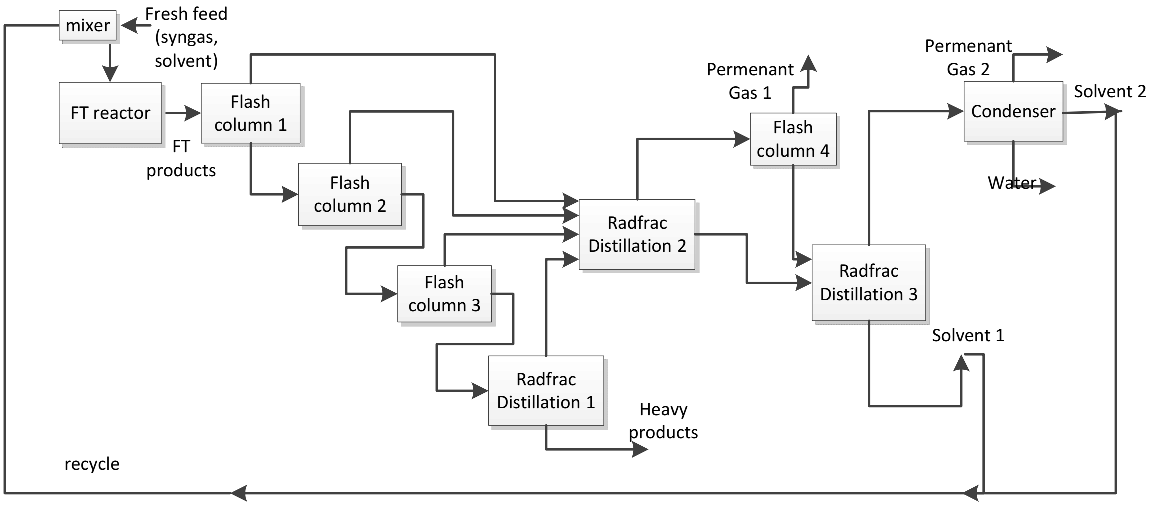

Figure 5.5a. Optimization of the Heavy Components Recovery.

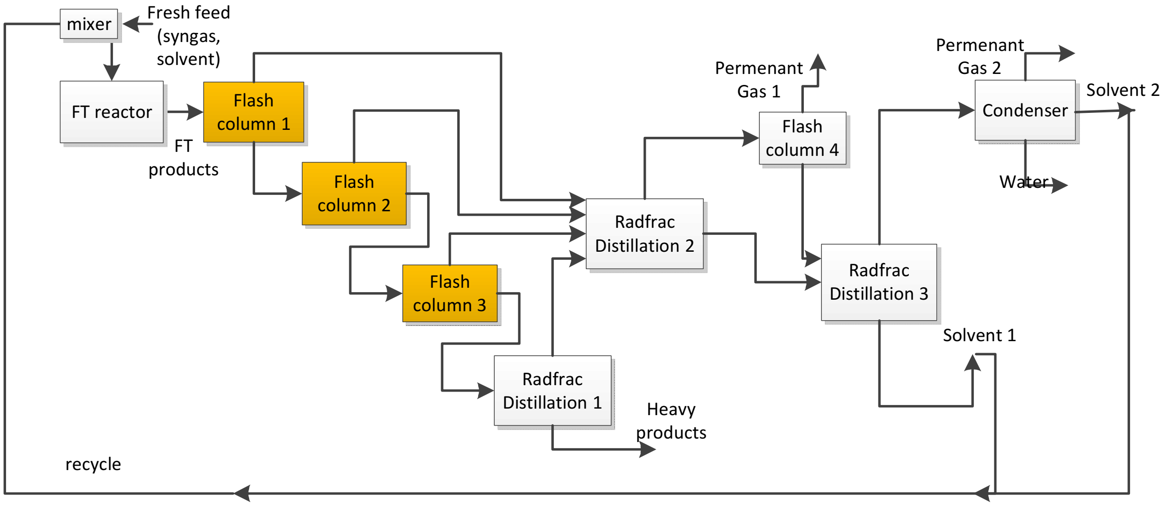

Figure 5.5b. The Design of Flash Columns Sequence.

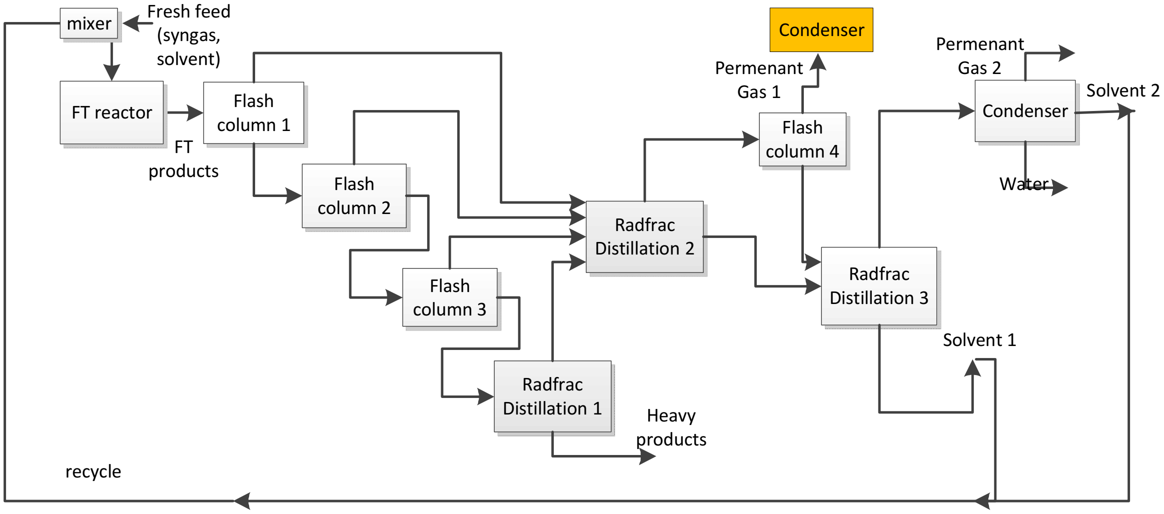

Figure 5.5c. The Adding of Condenser to Increase Pergas Purity.

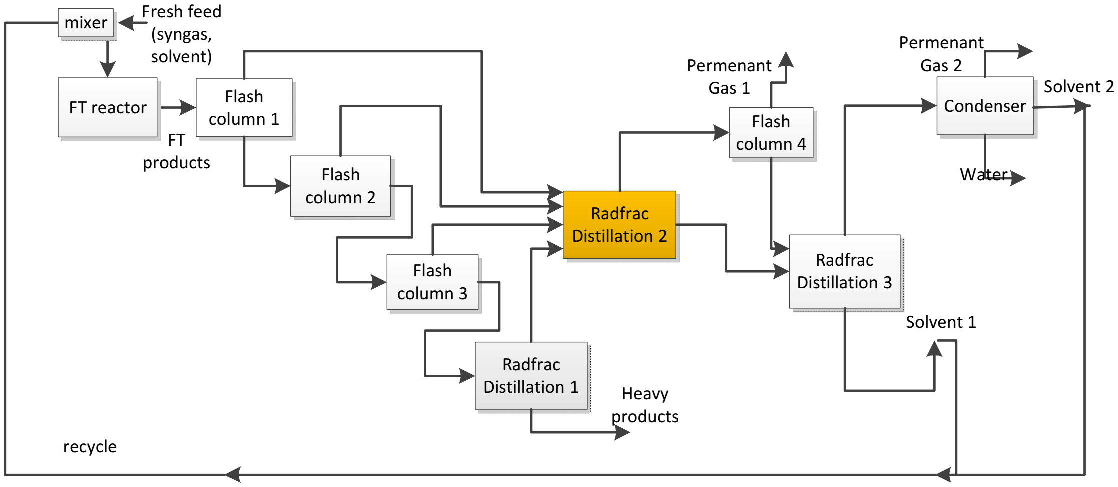

Figure 5.5d. The Replacement of the Radfrac Column with the Flash Column in Separating Solvent.

For the separation of the heavy fractions part, the Radfrac column 1 is operated at condenser pressure of 5 bar with 0.1 bar of stage pressure drop. The total number of stages is 30. The recoverability is increased as the bottom rate increases. The sensitivity of the reboiler duty and the recoverability of the heavy (C_9-C_{30+}) components versus the feed stage are analyzed (**Figures 5.6a** and 5.**6b**) to determine the optimal feed stage. It is intended to reduce the external energy cost and keep high recoverability of heavy components. In **Figure 5.6a** the reboiler duty of 2.24E+09 Btu/hr is shown as the lowest value at some feed stages. In **Figure 5.6b** the recoverability of heavy components starts to drop after the stage 25. The other component compositions are not affected. This way, the combination of the two figures gives the optimal feed in stage at 5.

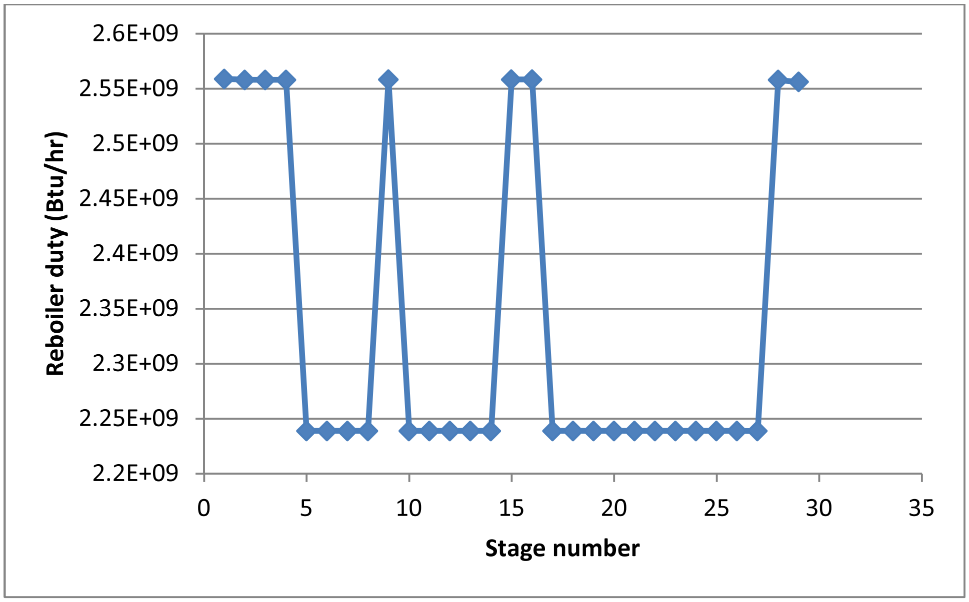

Figure 5.6a. Sensitivity Analysis of Reboiler Duty Versus Feed Stage in Radfrac Column.

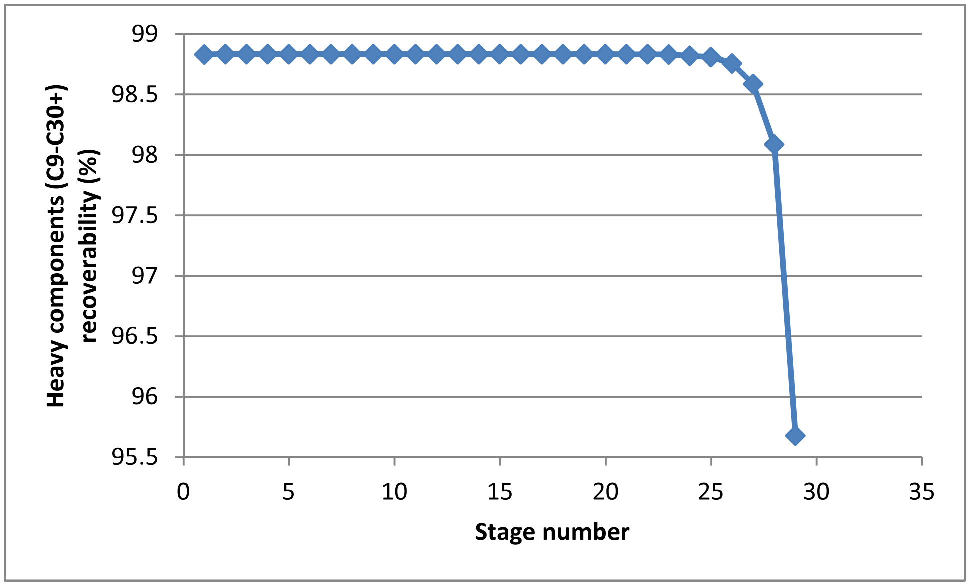

Figure 5.6b. Sensitivity Analysis of Recoverability of Heavy (C_9-C_{30+}) Components Versus Feed Stage in the Radfrac Column.

The analysis of the reboiler duty versus the condenser duty with the above condition is then conducted to determine the optimal condenser duty with the same objective in **Figures 5.7a** and 5.**7b**. In **Figure 5.7a** the reboiler duty is reduced as the condenser duty drops below 1.8E+09 Btu/hr. In **Figure 5.7b** the recoverability significantly drops below the condenser duty of 0.5E+09 Btu/hr. This way, the cross point of the two figures gives the optimal condenser duty at 0.5E+09 Btu/hr. The other components composition is not affected. Both lower condenser duty and reboiler duty reduce the energy cost.

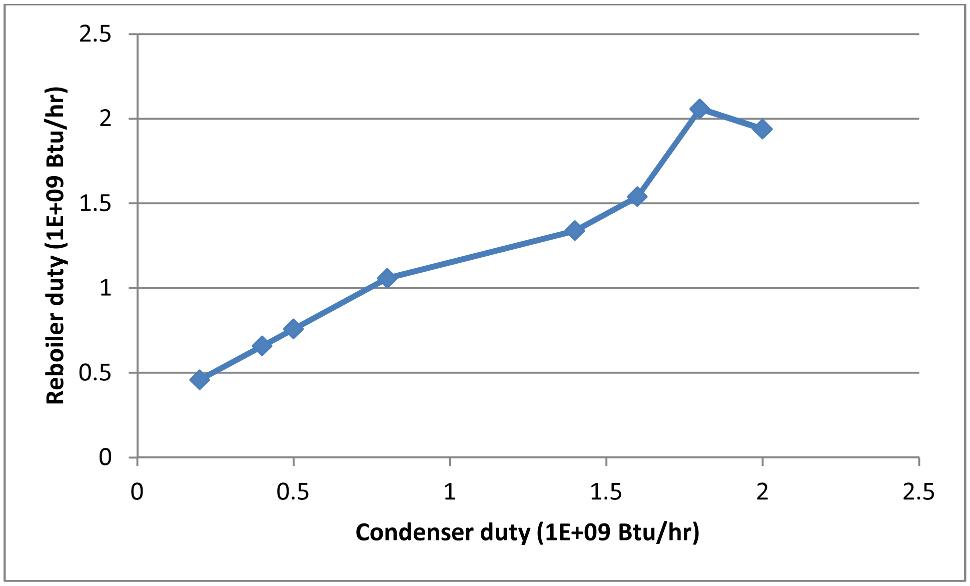

Figure 5.7a. Reboiler Duty Versus Condenser Duty.

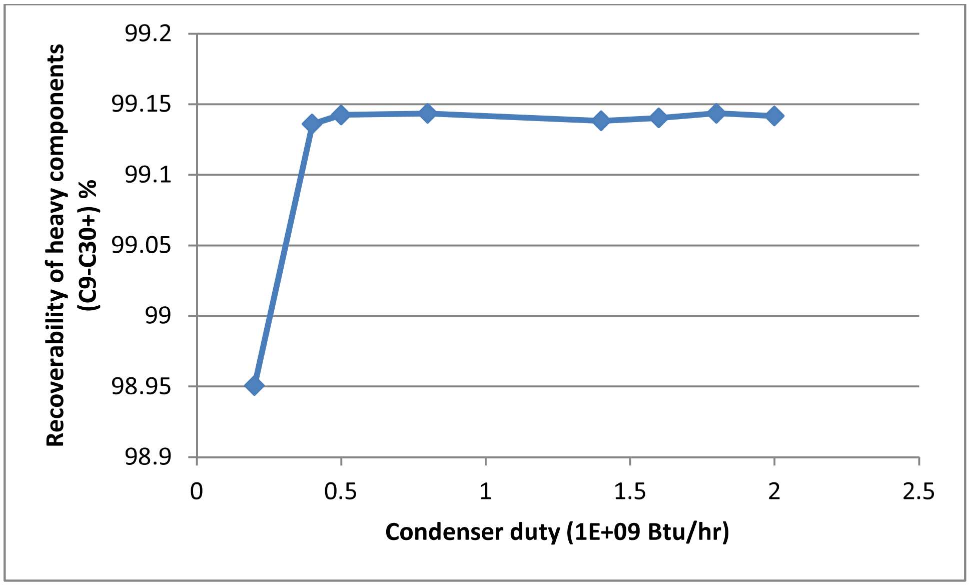

Figure 5.7b. Recoverability of Heavy (C_9-C_{30+}) Components Versus Condenser Duty.

The total number of stages is then optimized to reduce the cost of the Radfrac column with the above conditions in **Figures 5.8a** and 5.**8b**. In **Figure 5.8a**, the reboiler duty is reduced as the number of stages reduces. In **Figure 5.8b** the recoverability is greatly affected as the number of stages is below of 20. The other components composition starts to be affected below the stage number 20. Therefore, the optimal stage numbers is chosen as 20.

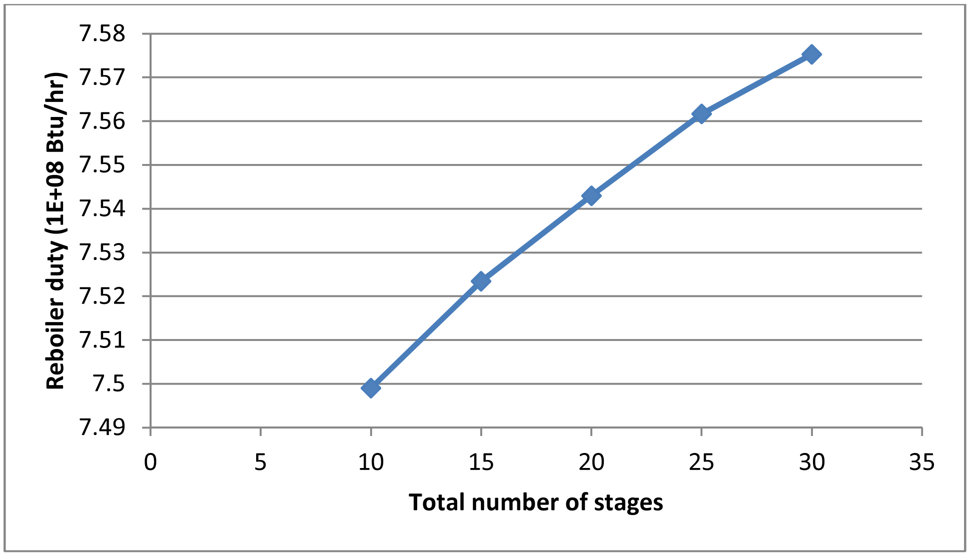

Figure 5.8a. Reboiler Duty Versus the Total Number of Stages.

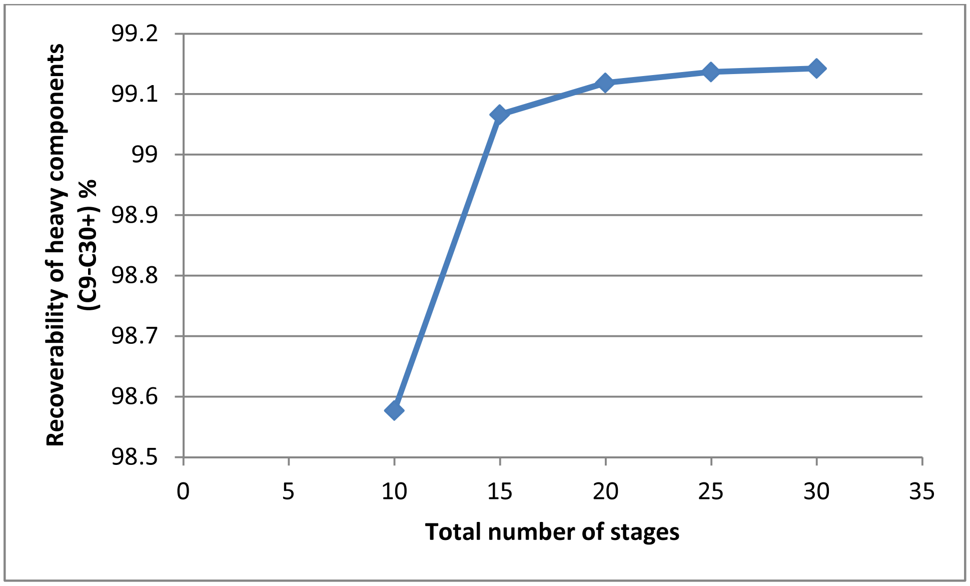

Figure 5.8b. Recoverability of Heavy (C_9-C_{30+}) Components Versus the Total Number of Stages.

The product streams from the FT reactor could be separated with flash columns first to reduce the capacity of the stream and to reduce the operation burden and cost burden of later steps. The separation could be conducted by dropping the pressure and temperatures of the columns. The sequence of the columns could be operated in two ways shown in **Figures 5.9a** and 5.9**b**. In **Figure 5.9a**, it is primarily to drop the pressures of the columns and in **Figure 5.9b** it is primarily to drop the temperatures of the columns.

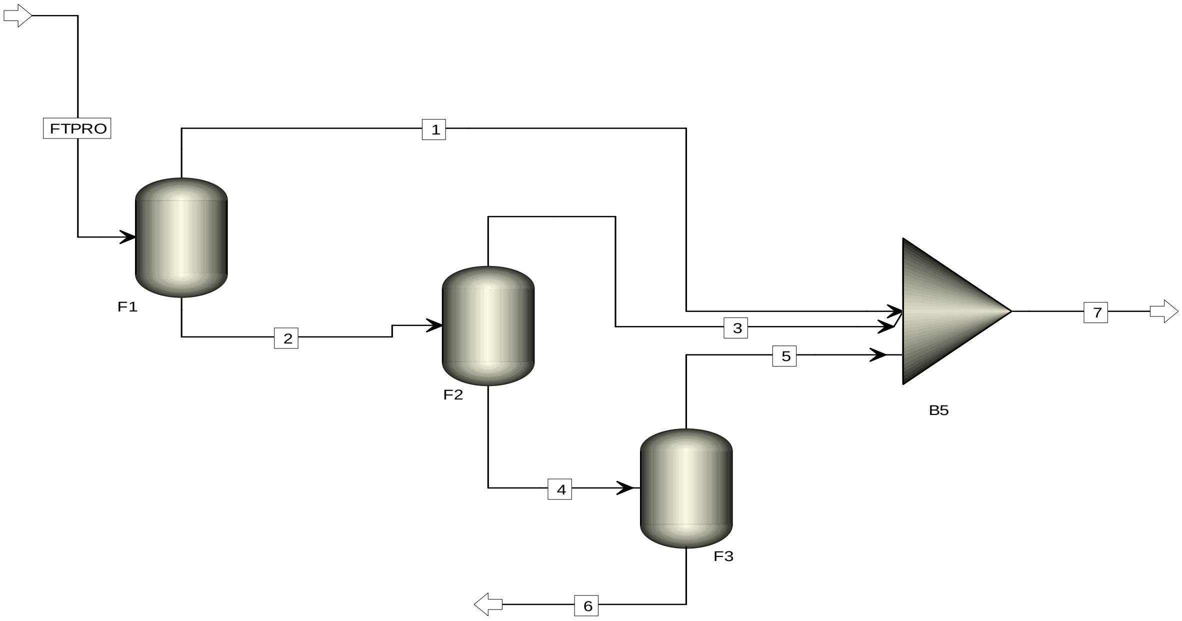

Figure 5.9a. Combination of the Flash Columns with Dropping Pressures.

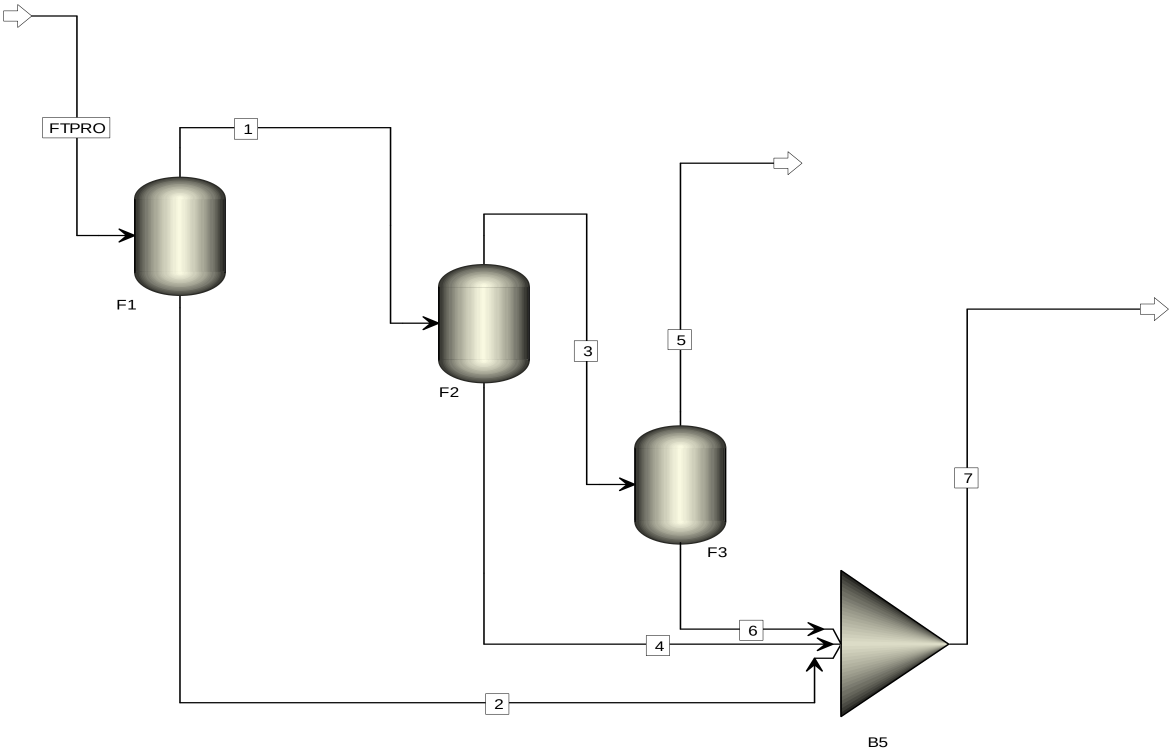

Figure 5.9b. Combination of Flash Columns with Dropping Temperatures.

The combination of the operating conditions of the three columns is shown in **Table 5.2**. Condition 1 and 2 are standing for the condition **in Figures 5.9b**, and other conditions stand for **Figure 5.9a**.

Table 5.2. The Conditions of the Three Columns.

	Column 1		Column 2		Column 3	
Condition	T (°C)	P (bar)	T (°C)	P (bar)	T (°C)	P (bar)
1	220	45	200	45	180	45
2	230	45	220	45	210	45
3	200	45	200	40	200	35
4	200	45	200	40	200	30
5	200	45	200	35	200	30
6	200	45	200	35	200	25
7	220	45	220	35	220	30
8	210	45	210	35	210	30
9	190	45	190	35	190	30
10	180	45	180	35	180	30
11	190	45	190	35	190	25
12	180	45	180	35	180	25
13	180	45	180	30	180	20
14	160	45	160	30	160	15

The analysis result is shown in **Figures 5.10a** and 5.**10b**. Condition 1 and 2 from **Figures 5.9b** are not the optimum choices because the recovered flow rate is high, which increases the later steps cost. The choices are focused on the combination in **Figure 5.9a**. The requirements should be high for heavy components recoverability and low for recovered flow rate. This way, the results in the two figures give the choices in condition 4, 5, 11, and 13; and in this work, condition 5 is used for later steps.

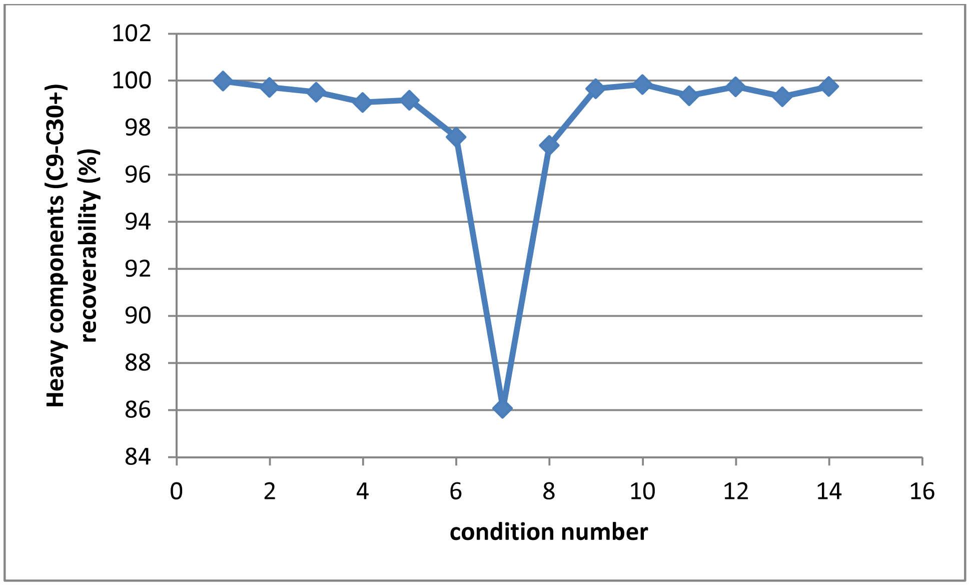

Figure 5.10a. Recoverability of Heavy (C_9-C_{30+}) Components Versus Pressure and Temperature Conditions of the Flash Columns.

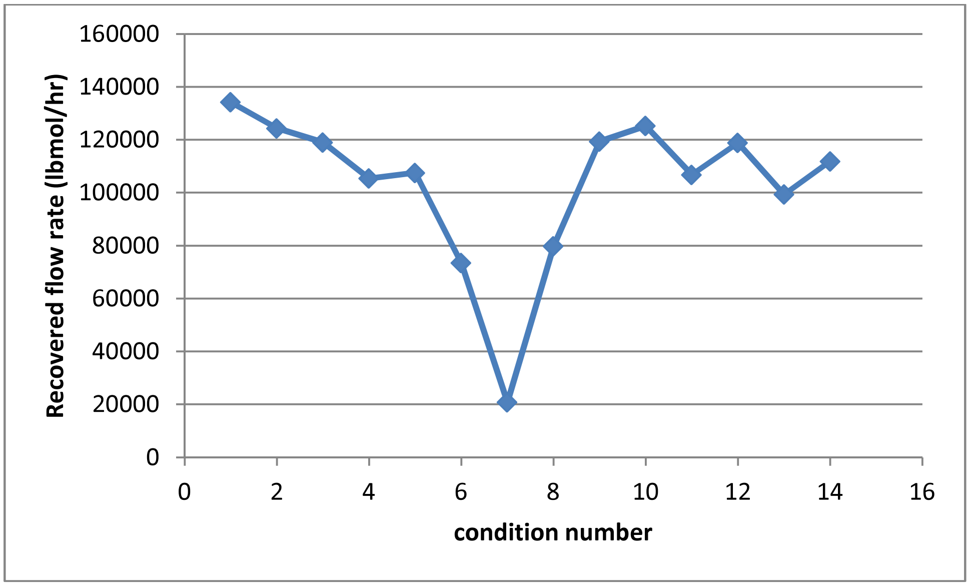

Figure 5.10b. Recovered Heavy Components Flow Rate Versus the Pressure and Temperature Conditions of the Flash Columns.

From this analysis, the molar recoverability of heavy components increases from 98.8% to 99.2% and it does not influence the recovering of other components. At the same time, external utility and column cost are reduced.

The part of recovering light fractions process is conducted in the following. The Radfrac column 2 is replaced with a flash column to analyze the effect. The result of simulation shows that the recovered pergas and solvent streams are not affected greatly, while at the same time the energy cost of the flash column reduces significantly. Then, the flash column 4 is added with a condenser after it to increase the purity and recovery of the pergas stream. The simulation result shows that the overall recovery of pergas increases from 98.9% to 99.2% and the solvent recoverability increases from 97.4% to 99.9% while the external energy consumption reduces.

An economic analysis was carried out with the software Aspen Icarus and the results are shown in **Table 5.3**, notice that the fixed cost is composed of direct and indirect cost based on all the equipment cost in the process from the simulation result. The case with Radfrac column installed has the highest cost, and the case with heavy column adjusted has the lowest fixed cost. The heat balance of each scenario is identified and heat integration is carried out and optimized using the software Lingo to yield a heating utility cost of 3$/MMBtu and cooling utility cost of 5$/MMBtu. The main results for the heat integration are shown in **Table 5.4**, notice that the case with heavy component separation optimized is the one with the minimum utility costs, whereas the case with the radfrac column is the one with the highest utility costs.

The mass balance of the separation result for each scenario is identified and then the mass integration is carried out. For the process economic analysis, the following unit costs were used, syngas \$13/GJ, hexane \$1.15/gal, diesel \$82/bbl, gasoline \$63/bbl, H_2 \$2/kg, H_2O \$1.2x10^{-3}/gal, tailgas \$50/bbl. The cost analysis is shown in **Table 5.5**. The result shows that the case with heavy column optimized has the highest return of investment. While the case with the condenser added has the highest recoverability and purity, and the case with the flash sequence optimized has the highest sale of production. The case with the Radfrac column replaced has the highest energy saved. This information is very useful, because this allows to the designer to choose the best case dependent on the objective of the design.

Table 5.3. Fixed Cost (US$) for Different Scenarios Analyzed.

Unit	**with condenser**	**with no condenser**	**replace radfrac**	**flash sequence**	**heavy column**
flash column1	30,844,719	30,844,719	30,844,719	34,732,760	30,844,719
flash column2	29,623,455	29,623,455	29,623,455	3,948,988	29,623,455
flash column3	22,368,446	22,368,446	22,368,446	1,701,861	22,368,446
flash column4	844,882	844,882	844,882	844,882	844,882
radfrac distillation 1	483,388,081	483,388,081	483,388,081	483,388,081	428,024,094
radfrac distillation 2	5,911,850	5,911,850	58,159,170	5,911,850	5,911,850
radfrac distillation 3	69,822,826	69,822,826	69,822,826	69,822,826	69,822,826
FT synthesis	680,335,917	680,335,917	680,335,917	680,335,917	680,335,917
heat exchanger1	4,195,567	4,195,567	4,195,567	4,195,567	4,195,567
heat exchanger2	9,759,880	9,759,880	9,759,880	9,759,880	9,759,880
heat exchanger3	1,068,199	1,068,199	1,068,199	1,068,199	1,068,199
heat exchanger4	3,632,622	3,632,622	3,632,622	3,632,622	3,632,622
heat exchanger5	3,632,622	3,632,622	3,632,622	3,632,622	3,632,622
pump	2,605,364	2,605,364	2,605,364	2,605,364	2,605,364

Table 5.3. Continued

condenser1	1,268,254	-	-	-	-
condenser2	754,625	754,625	754,625	754,625	754,625
total	**1,350,057,309**	**1,348,789,055**	**1,401,036,374**	**1,306,336,043**	**1,293,425,069**

Table 5.4. Results Comparison for The Energy Consumption.

Case	**Hot utility requirement (BTU/hr)**	**Cold utility requirement (BTU/hr)**	**Cost for hot utility (MM$/yr)**	**Cost for cold utility (MM$/yr)**	**Total utility cost (MM$/yr)**
With condenser added	0.1039885E+11	0.1678697E+11	288	776	1064.023
With no condensed added	0.1039885E+11	0.1678697E+11	288	776	1064.023
with heavy components separation optimized	0.8619653E+10	0.1528577E+11	239	706	945.322
with flash sequence optimized	0.1139260E+11	0.1582207E+11	316	730	1046.911
With Radfrac column	0.1084365E+11	0.1750977E+11	301	808	1109.746

Table 5.5. Cost Analysis of Five Scenarios Analyzed.

Case/concept	With condenser	With no condenser	Replace radfrac	Flash sequence	Heavy column
Annual capital cost (MM$/yr)	61	61	63	59	58
Annual operating cost (MM$/yr)	3,017	3,056	3,231	2,863	2,836
Utility cost without heat integration (MM$/yr)	1,715	1,715	1,880	1,530	1,592
Utility cost with energy integration(MM$/yr)	1,064	1,064	1,110	1,047	945
Total sales(MM$/yr)	3,619	3,619	3,619	3,621	3,611
ROI without energy integration	0.29	0.28	0.19	0.38	0.39
ROI with energy integration	0.60	0.58	0.54	0.62	0.71

Overall, for the cases analyzed, the permenant gas has been separated from solvent stream with 99% of recoverability, the solvent has been separated with 99% of recoverability, and the heavier components product has been recovered with 99% of recoverability, and the recovery of the components is shown in **Figure 5.11,** where the x axis shows the components from carbon 1 to carbon 31, water, H_2 and CO, and the y axis shows the recoverability of the component. There are 8 series showing 8 output streams, including water streams, solvent streams, permenant gas streams, and heavier components streams. The graph shows that 99% of water is recovered in the water stream, 99% of solvent (C_5-C_8) is recovered in the solvent stream, 99% of C_{9+} components is recovered in the heavier stream, and 99% of the C_1-C_4 is recovered in the pergas stream.

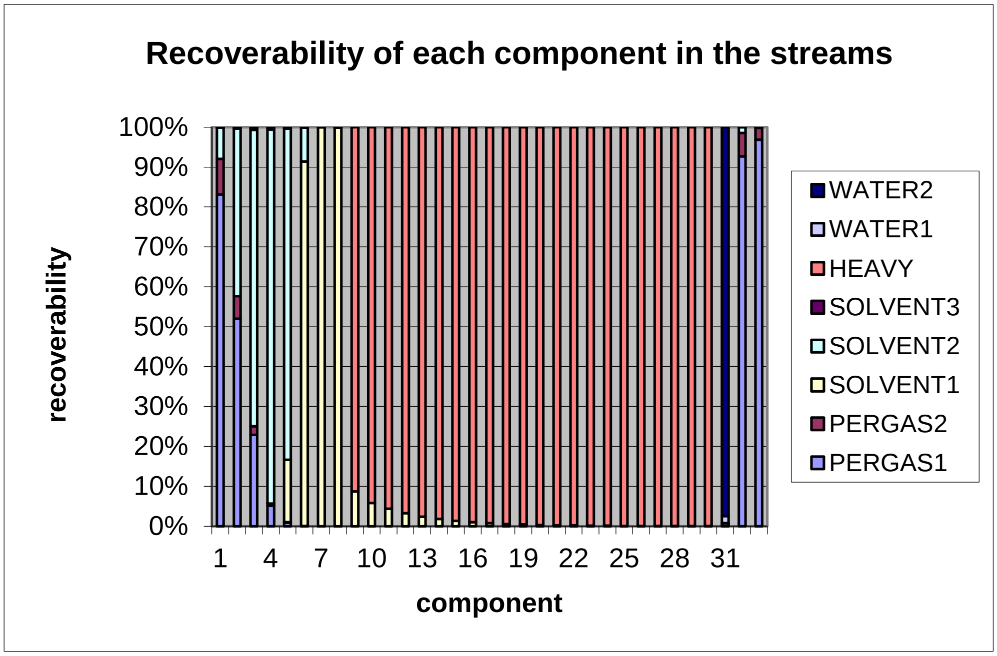

Figure 5.11. Recovery of the Components in Each Stream.

5.6.3 Economic Evaluation to Compare the SCF-FT and Conventional FT Process

The optimum scenario of the abovementioned separation design is included in the SCF-FT process to compare the cost potential with conventional FT process on the GTL basis. The major parts included in calculating the fixed cost are shown in **Figure 5.12**. Results show that although GTL with SCF-FT design has higher cost due to the installation of the pressure compression units and solvent separation units, it could be more energy efficient in utilizing the pressure and temperature when separating, and in this way the overall return of investment of GTL is higher than the conventional process. This means that the GTL process with supercritical solvent design is competitive.

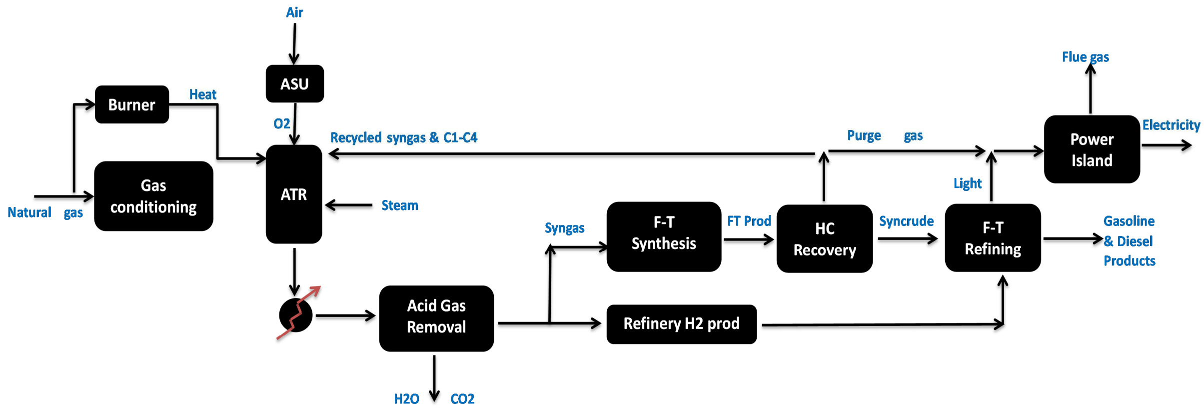

Figure 5.12. Process Units in the GTL Process.

The costs calculation for the components of the units is based on the literature reports of the NETL (Kreutz et al., 2008) using the corresponding scaling factor in addition to Aspen Icarus estimations. The equipment cost is calculated using the following scaling methods from the existing cost case. The train capacity is calculated as $S=Sr/n$, $C=C0\times(S/S0)^f$, $Cm=C\times n^m$, where Cm is the component cost, C is the train cost, Sr is the required capacity, S is the train capacity, $S0$ is the base capacity, n is the train number, $C0$ is the base cost reported, f is the scaling factor and m was assumed as 0.9. Project contingencies were added to cover project uncertainty and the cost of any additional equipment that could result from a detailed design. For typical chemical plants, the OSBL costs are only 20% of the ISBL costs. However, in a GTL plant the volumes of the side streams are very high (i.e. the oxygen and nitrogen from the ASU as well as water by-product from the FT synthesis) and handling and treatment of these streams require correspondingly more auxiliary operations (Richardson, 1993).

Table 5.6 shows a results comparison for the traditional FT process optimized in this paper respect to the SCF-FT process proposed in this paper. Notice that the capital cost for the SCF-FT respect to the traditional FT process increases 36%, the operational costs decreases 9% and the total sales increase 5%; as a results the *ROI* increase from 0.25 to 0.26 for the SCF-FT process proposed in this paper respect to the traditional FT process optimized using the strategy proposed in this paper.

Table 5.6. Economic Comparison for the Traditional and SCF FT Processes.

Process	Total capital Cost (MM$)	Total Operational cost (MM$/yr)	Total Sales (MM$/yr)	ROI
Traditional FT process	**3248**	**5203**	**7493**	0.25
SCF-FT process	**4406**	**4730**	**7826**	0.26

The comparison of $/BPD of this case is compared with current GTL processes shown in **Table 5.7,** and the unit cost of each major part is shown in **Table 5.8**. The data show that the capital investment per BPD of the proposed case is a little higher than the existing plant of GTL and it is within the range of the typical cost trend. The cost distribution of this case is compatible with the typical GTL cost distribution of each major part. In this case, the upgrading cost is a little higher than typical case, indicating the cost related with the gas recovery and additional installation of solvent recovery system.

Table 5.7. Total Capital Investment (TCI) of the Process.

Plant	BPD	TCI (MM$)	$/BPD
Bintulu (Shell)	12,500	850	68,000
Oryx (Sasol)	34,000	1,100	32,353
Nigeria (Sasol)	34,000	2,000	58,824
This case	120,000	10,718	89,320

Table 5.8. The Distribution of the Cost of the GTL Process.

UNIT	Typical case (%)	This case (%)
ASU	30	27
syngas manufacture	30	17
FT	25	20
upgrading	15	21
power	0	15

5.7 Conclusions

In this work the performance of supercritical solvent separation from Fischer-Tropsch products has been evaluated. An approach has been proposed to recover solvent from SCF-FT products. A process for recovering is developed followed by optimization and heat integration to analyze the economic potential. A flowsheet is established for separation of the products. A case study is implemented to optimize the efficiency of separating and the effect of products. Alternative scenarios for supercritical solvent separation for FT products have been investigated and selected based on the developed mathematic model. A comparison of cost efficiency between common FT process and SCF-FT process has been carried out, and the result shows that SCF-FT is competitive to conventional GTL processes when supercritical operation is coupled with proper separation designs.

6. SUMMARY, CONCLUSIONS AND FUTURE WORK

In this work, a shortcut method has been introduced for the conceptual design and preliminary synthesis of alternative pathways of the process industries with focus on the applications for biorefineries. The chemical species/conversion operator structural representation has been introduced. It tracks chemical species, connects various streams with processing technologies, and embeds potential configurations of interest. An optimization formulation has been developed to maximize the yield or the economic potential subject to constraints that include process models, distribution of streams and species over the conversion technologies, interconnection of the candidate technologies, and techno-economic data. Three case studies have been solved to demonstrate the effectiveness and applicability of the developed approach. The case studies covered the scenarios of maximum theoretical yield, accounting for actual process yield, including more than one feedstock, and incorporating an economic objective (payback period), The solutions of the case study illustrate the ability of the proposed approach to generate a wide variety of pathways that achieve the same target but vary significantly in their building blocks and interconnections. The solution of the case studies also demonstrates that by including an economic objective function that the complexity of the devised pathways is greatly reduced.

Also, in this work a system to effectively optimize a biorefinery technology pathway integrated with species separation and recycle networks has also been developed.

The synthesis and design of separation networks has also been studies for a supercritical fluid Fischer-Tropsch (SCF FT) gas-to-liquid (GTL) process. . A solvent-recovery process has been synthesized. Optimization and heat integration have been employed to improve the economic performance of the process. A case study has been solved to include and screen alternative scenarios for supercritical solvent separation. A comparison of cost efficiency between common FT process and SCF-FT process has been carried out. The results show that the SCF-FT is competitive with conventional GTL processes when the supercritical operation is coupled with proper separation designs.

The following research activities are proposed for future work:

- Inclusion of fluctuation in the feedstock quality in the synthesis procedure for biorefineries (design under uncertainty).
- Integration of process design and operation for biorefineries.
- Inclusion of process safety as an objective in the design of biorefineries.
- Assessment of different solvents for SCF FT and analysis of techno-economic factors for the various solvents.

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VITA

Name: Buping Bao

Address: Artie McFerrin Department of Chemical Engineering
Texas A&M University
College Station, TX 77843-3136

Email address: bupingbb@gmail.com

Education: B.S., Chemical Engineering, 2006
Zhejiang University, Hangzhou, P.R.China

M.S., Chemical Engineering, 2008
Texas A&M University, College Station, TX

P.h.D. Chemical Engineering, 2012
Texas A&M University, College Station, TX