DESIGN AND ANALYSIS OF FLEXIBLE BIODIESEL PROCESSES

WITH MULTIPLE FEEDSTOCKS

A Dissertation

by

GRACE AMARACHUKWU POKOO-AIKINS

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

August 2010

Major Subject: Chemical Engineering

DESIGN AND ANALYSIS OF FLEXIBLE BIODIESEL PROCESSES

WITH MULTIPLE FEEDSTOCKS

A Dissertation

by

GRACE AMARACHUKWU POKOO-AIKINS

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

Approved by:

Chair of Committee,	Mahmoud El-Halwagi
Committee Members,	Juergen Hahn
	Karen Butler-Purry
	M. Sam Mannan
Head of Department,	Michael Pishko

August 2010

Major Subject: Chemical Engineering

ABSTRACT

Design and Analysis of Flexible Biodiesel Processes with Multiple Feedstocks.

(August 2010)

Grace Amarachukwu Pokoo-Aikins, B.A., Austin College; M.S., Texas A&M

University

Chair of Advisory Committee: Dr. Mahmoud El-Halwagi

With the growing interest in converting a wide variety of biomass-based feedstocks to biofuels, there is a need to develop effective procedures for the design and optimization of multi-feedstock biorefineries. The unifying goal of this work is the development of systematic methodologies and procedures for designing flexible multi-feedstock biorefineries. This work addresses four problems that constitute building blocks towards achieving the unifying goal of the dissertation.

The first problem addresses the design and techno-economic analysis of an integrated system for the production of biodiesel from algal oil. With the sequestration of carbon dioxide from power plant flue gases, algae growth and processing has the potential to reduce greenhouse gas emissions. Algae are a non-food oil feedstock source and various pathways and technologies for obtaining algal oil were investigated. Detailed economic and sensitivity analysis reveal specific scenarios that lead to profitability of algal oil as an alternative feedstock.

In the second problem, a new safety metric is introduced and utilized in process design and selection. A case study was solved to assess the potential of producing biodiesel from sewage sludge. The entire process was evaluated based on multiple criteria including cost, technology and safety.

The third problem is concerned with incorporating flexibility in the design phase of the development of multi-feedstock biofuel production processes. A mathematical formulation is developed for determining the optimal flexible design for a biorefinery that is to accommodate the use of multiple feedstocks. Various objective functions may be utilized for the flexible plant depending on the purpose of the flexibility analysis and a case study is presented to demonstrate one such objective function.

Finally, the development of a systematic procedure for incorporating flexibility and heat integration in the design phase of a flexible feedstock production process is introduced for the fourth problem. A mathematical formulation is developed for use in determining the heat exchange network design. By incorporating the feedstock scenarios under investigation, a mixed integer linear program is generated and a flexible heat exchange network scheme can be developed. The solution provides for a network that can accommodate the heating and cooling demands of the various scenarios while meeting minimum utility targets.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my deepest gratitude to God, my creator and provider, for having a plan for my life from the beginning and guiding me through every step of the way.

Words cannot express my sincere appreciation and indebtedness to Dr. Mahmoud El-Halwagi for his guidance, kindness and support during my graduate studies at Texas A&M University. He is more than an advisor and mentor, but he is an extraordinary human being who truly cares about helping others develop into extraordinary human beings and well-rounded engineers. Dr. El-Halwagi, thanks for pouring into me and helping to shape me throughout these years as I develop as an engineer.

Sincere thanks, gratitude and appreciation go to the members of my committee, Dr. Juergen Hahn, Dr. Karen Butler-Purry, and Dr. Sam Mannan. I am grateful that they always challenge me to think more critically and for their helpful advice. Thanks to Drs. Hahn and Butler-Purry for helping me think about keeping my research goals and career focus aligned. To Dr. Mannan I am truly privileged to have had the opportunity to learn from him the importance of safety in engineering and to be challenge to keep a broad focus.

I would like to acknowledge Ahmed Nadim and Dr. Vladimir Mahalec for their knowledge of and for the opportunity to collaborate with them on research pertaining to of the upstream processing of algae. I am grateful to have had the opportunity to interact

face-to-face with Ahmed here at Texas A&M University and both at McMaster University.

Thanks to former group members Lay Myint and Brandon Shaw. I am deeply grateful to Lay, whose hard work laid the foundations for this research. Even though she's graduated and is now working, she very graciously answered all my e-mails and phone calls in regards to better understanding her thesis work. Brandon is owed much thanks for his numerous trips to College Station from his work in Houston, demonstrating his continued dedication to advancing biodiesel research.

Many thanks go to my colleagues and former group members Dr. Eva Lovelady and Dr. René Elms for their support, encouragement and advice. I would also like to thank other members of the Process Integration group for their assistance, their advice and their support through brilliant academic exchanges in the Process Integration Laboratories for the past seven years. There have truly been moments of enlightenment during those third floor interactions.

I would like to thank the departmental staff for making things smooth for me. I am so grateful to Towanna Arnold for being a listening ear, a bridge to the Office of Graduate Studies and just for her willing spirit and countless knowledge about how things work department-wise and university-wise. Thanks to the Jeff Polasek and the departmental computing staff. Without their dedication, this journey would have been a lot more difficult. I am grateful for all their help with, amongst many other things, group laptops and ASPEN troubleshooting.

my parents Dr. Bennett and Mrs. Olive Nworie, and members of my extended family for their love, support, prayers and encouragement.

Finally, I would like to thank my loving husband, Anthony Pokoo-Aikins for all the wonderful things he has done to support me in achieving my educational and life goals. He always encouraged me to finish what I started. I am happy to share all my achievements with him because he is my pillar.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1   INTRODUCTION

1.1   Integrated Biorefinery

An integrated biorefinery is a processing facility that uses physical, chemical, thermal, and/or biological techniques (conversion technologies and equipment) to produce value-added chemicals, fuel and energy. According to Clark et al (2006) "a biorefinery can be considered as an integral unit that can accept different biological feedstocks and convert them to a range of useful products including chemicals, energy and materials." The structure of the biorefinery has been compared to the petroleum refinery but there are marked differences. The biorefinery uses biomass (plants and plant based materials) as a feedstock, utilizes renewable resources, and utilizes various established unit operations as well as some yet to be developed or adapted technology in order to derive various products and co-products. In comparison, the petroleum refinery uses crude oil as the sole feedstock, non-renewable carbon resources, and established unit operations in order to obtain a variety of products and co-products. A structural overview of the biorefinery is presented in Fig. 1.1.

_____

This dissertation follows the style of *Chemical Engineering Science.*
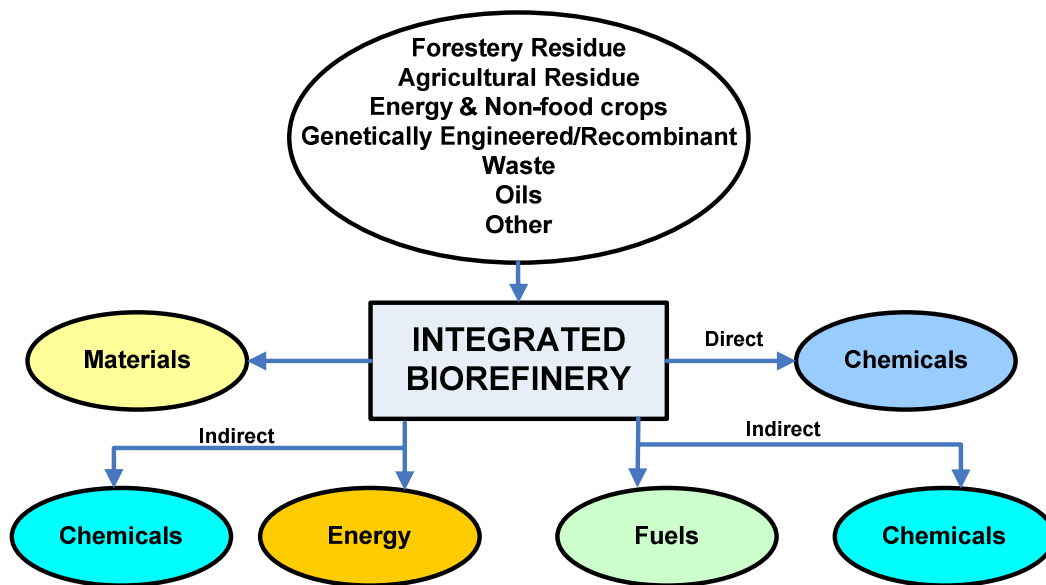
Fig. 1.1 Structural overview of the integrated biorefinery (adapted from Clark et al, 2006).

Major motivating factors for the development of integrated biorefineries are: 1. fossil based fuels are limited; 2. there is a growing interest and demand for sustainable fuel sources; 3. increased desire for more environmentally benign processing technologies or industries that contribute less to the emissions of Greenhouse gas and carbon. Fuels, chemicals, energy and other products form the biorefinery can provide alternative fuel and energy sources to supplement the current major fuel and energy sources. Key features of the biorefinery are the ability to incorporate for use diverse feedstock options, the availability of a number of conversion technologies and the variety of product possibilities (Carole et. al., 2004). In addition biorefineries use renewable resources and have the potential to contribute less to environmental pollution

compared with petroleum refining. There is an abundance of biomass feedstock resources.

Biorefinery feedstock include agricultural resources (including wastes and surpluses), forestry resources (namely residues), energy and non-food crops, wastes, genetically engineered and recombinant sources (such as plants and microorganisms), oils and other sources that do not fit into any of these categories. The focus for a sustainable biorefinery is agricultural, food industry and other "waste" and forestry residue. That which is considered waste or residue can be utilized as feed to generate chemicals and energy in the biorefinery (Clark et al, 2006). The use of renewable resources in the biorefinery is diagramed in Fig. 1.2.

Several processing technologies are available for converting biomass to products (Fig. 1.2). Not all portions of the biomass can be converted by all processing technologies, but different portions of biomass enter into the different processes. For example, oils, lipids, sugars or carbohydrates could be processed chemically. The sugars and carbohydrates would be processed via some form of acid hydrolysis while the oils and lipids would be process by chemical synthesis (i.e. transesterification). The products from acid hydrolysis are sugars and ethanol while the products from chemical synthesis include furfural derivative, fatty acid derivatives, esters, biodiesels, and glycerol.
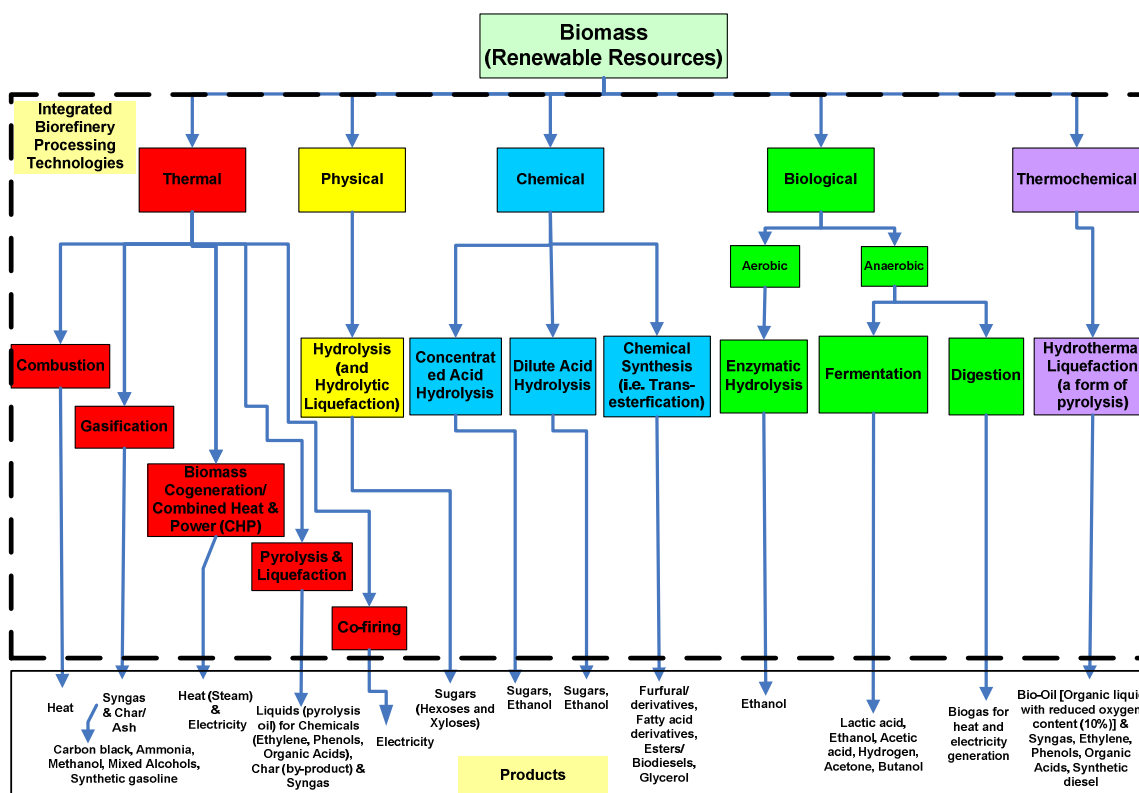
Fig. 1.2 Schematic representation of processing pathways in a biorefinery.

Thermal processes include combustion, gasification, biomass cogeneration and/or combined heat and power, pyrolysis and liquefaction and co-firing. Major products from thermal processing include heat, steam, electricity, liquid oils, syngas, chemicals and synthetic gasoline. Solid biomass (i.e. lignocellulosic feedstock, carbohydrates, and residues and waste) are major feedstock for the thermal processes. Hydrolysis is the main example of physical processing and products from hydrolysis are primarily sugars. Biological processing can be aerobic (such as enzymatic hydrolysis) or anaerobic (such as fermentation and digestion). Products from aerobic processing

include ethanol while anaerobic processing can yield a variety of products such as various acids, ketones, alcohols and hydrogen and biogas. Hydrothermal liquefaction is a form of thermochemical processing that can produce bio-oil, syngas, ethylene, phenols, organic acids and synthetic gasoline. This diversity of feedstock, processing technologies, and products are one of the greatest strengths of the integrated biorefinery.

In spite of all the potential benefits of the integrated biorefinery, there are still some challenges that need to be overcome. One such challenge is the need for decentralized biorefineries located closer to feedstock sources (Biocycle, 2005). Another is the need to develop processing technologies (Huber and Dumesic, 2006). New approaches for using biological material are also needed (Kamm et al, 2006). Feedstock currently used in biorefineries of different types contain mainly carbohydrates and lignin and to a much lesser extent other component (such as fats, oils and proteins) (Kamm et al, 2006). A major focus in biorefinery research is thus the processing of lignin and carbohydrate feedstock. Yet lipid (fat and oil) containing feedstock are not ignore as they can be readily converted to fuels. Current and future governmental policies, legislation, and incentives will undoubtedly present continued challenges for the integrated biorefinery.

1.2   Process Integration

"Process integration is a holistic approach to process design, retrofitting, and operation which emphasizes the unity of the process." (El-Halwagi, 1997). In utilizing process integration, it is important to recognize the chemical process as an integrated

system and that problem solving strategies must deal with root causes and not just symptoms of the problem. Traditional approaches to process development and improvement have been limited in applicability, can be time and cost intensive, do not guarantee the global solution, and do not reveal solutions that can be non-intuitive. Integration techniques can be used in process synthesis and conserve valuable resources (El-Halwagi, 2006). The holistic approach of process integration is of benefit in development of the integrated biorefinery because it provides a systematic and strategic approach for dealing with the associated challenges.

The focus will be on design, retrofitting and operation as these are key aspects for any process. Since the biodiesel production facility is a simple type of biofuels biorefinery and it is a potential component of large-scale integrated biorefineries, it is an adequate starting point for the investigation to follow. Increasing fuel demands, decreasing fossil fuel reserves, increasing costs of petroleum-based fuels and environmental concerns have propelled bio-based fuels to the forefront of the biorefinery scene. Bioethanol and biodiesel are currently the major biofuels being produced. Biodiesel production utilizes a variety of oils to produce biofuel, namely biodiesel, as its main product and glycerol as a by-product.

1.3 Dissertation Overview

Section 2 includes background information and a literature review pertaining to biodiesel, its significance, and the modeling of biodiesel processes.

Section 3 outlines the main aim of this work which is to develop a systematic approach for the design and operation of biodiesel production from various feedstock with a goal towards the development of a flexible multi-feedstock production process for biorefineries. The work is comprised of four case studies and the formal problem statement is presented to reflect this approach.

Section 4 details the first case study, the design and analysis of biodiesel production from algal oil. Algal oil was processed from algae grown through the use of sequestered carbon. Results from simulation, mass and energy integration, techno-economic analysis and sensitivity analysis of various algal oil cost, oil content and process design alternatives. Algal oil is a non-food feedstock investigated for potential inclusion into the integrated multi-feedstock biodiesel production process. Results are presented for the various scenarios for the profitable production of biodiesel from algal oil.

Section 5 describes the second case study, the multi-criteria design and analysis of biodiesel produced from lipids extracted from raw sewage sludge. Lipids from sludge are yet another non-food feedstock of interest for the use in the integrated multi-feedstock biodiesel process. Since there are possible safety hazards with the use of solvents for the extraction process, a safety metric is introduced for use with technical and cost metrics in designing and evaluating the sewage sludge to lipids to biodiesel process. The results of the multi-criteria analysis are presented along with a discussion of the trade-offs between cost and safety.

Section 6 presents the flexibility study. In this section, a systemic procedure for the design and operation of flexible biodiesel plants accommodating a variety of feedstocks is developed. The results of a process simulation of a base-case design for a multiple feedstock biodiesel plant, integration of energy and mass resources, optimization of process design and operation, and techno-economic assessment are utilized in retrofitting the base case plant for scenarios where additional units must be incorporated into the flexibility analysis. The developed optimization formulation is utilized to determine retrofitting cost for various throughputs for multiple feedstocks. Case study results are presented.

Section 7 describes a variation to the multiperiod flexible heat exchange network synthesis problem. A base case multifeedstock biodiesel production process that can accept soy, palm and algal oil is developed utilizing design and optimization strategies. An optimization formulation is introduced for the assembly of a flexible heat exchange network that incorporates the various heating and cooling requirements of various scenarios. The optimization results are presented.

Section 8 outlines the major conclusions for each of the four case studies and the work as a whole, as well as recommendations for future work.

2   BACKGROUND AND LITERATURE REVIEW

2.1   Biodiesel History and Comparison to Petrodiesel

2.1.1   History

Invention of the diesel engine was a precursor for the development of petroleum based diesel fuels and subsequently biodiesel. In the 19th century Rudolph Diesel developed the concept of an engine that ran on vegetable oils. The engine was patented in 1893 and a working engine was demonstrated in 1897. Vegetable oils were the predominant fuel source in diesel engines (Demirbas, 2008) until the early 20th century as petroleum gained in popularity. As early as the 1920s manufacturers, recognizing differences in the viscosity of vegetable oils and petroleum diesel, were compelled to alter engines to run on pertroleum diesel (Schmidt, 2007). In 1937, biodiesel made its debut in a Belgian patent was granted to G. Chavanne that described the use of ethyl esters of palm oil and methyl esters of other oils as diesel fuel (Knothe et al., 1997, Knothe, 2001).

Prior to World War II biodiesel continued to be developed and utilized but widespread use of biodiesel was deterred by the low cost of petroleum derived fuels. Biodiesel was used as fuel in heavy-duty vehicles in the Belgian Congo in South Africa (Knothe, 2001; Demirbas, 2008). In the period before World War II, increased demands for glycerol (or glycerin) for explosives (Van Gerpen, 2005) saw an increase in efforts to produce soap (a process with glycerol as the byproduct). By converting oils and fats to

methyl esters, glycerol could be obtained by centrifugation or settling. The methyl esters (major biodiesel components) were then used to produce soap by alkali reaction. Numerous patents for soap formation were issued in the 1940s mainly to researcher working for E.I. DuPont and Colgate-Palmolive-Peet.

The 1970s saw a renewed interest in biodiesel when crude oil prices skyrocketed in 1973 due to the Arab oil embargo (Schmidt, 2007). Research and development of production technologies for converting vegetable oils to fatty acid esters continued throughout the 1970s and 1980s. Oil prices jumped again in the 1990s due to the Gulf War, and with a national surplus of soybean oil, the developed transesterification technologies were used to domestically produce biodiesel fuel (Schmidt, 2007). In 1992, the National SoyDiesel Development Board was formed in order to become familiar with biodiesel production already well-established in Europe. By 1994, the group became the National Biodiesel Board, an organization that has been monitoring and reporting domestic biodiesel production since its onset.

2.1.2 Comparison to Petrodiesel

It has been mentioned that the rise in the cost of petroleum based fuels contributed to the development and widespread use of biodiesel as an alternative fuel. Biodiesel has numerous attributes that cause it to remain a popular fuel choice. Some attributes are that biodiesel can be incorporated into existing engines with little or no modification (Tyson et al., 2004), offers similar power and performance to petro-based

diesel and B100 offers up to 95% of the energy content of petroleum-based diesel (EPA, 2002).

Growth of biodiesel feedstock consumes CO_2 and thus biodiesel contributes less to Greenhouse gas emission and global climate change. Biodiesel contributes 78% less to CO_2 emissions and has lower tailpipe emission than petrodiesel (Sheehan et al., 1998) and has a lower emissions profile (Sheehan et al., 1998; Carraretto et al., 2004; Van Gerpen, 2005; Hill et al., 2006; Demirbas, 2009a). While petroleum-based diesel has no oxygen content, biodiesel has oxygen content between 10-12 wt % which means biodiesel undergoes more complete combustion and emits less carbon monoxide (CO), particulates and visible smoke (Carraretto et al., 2004; Lotero et al., 2005). Unfortunately, the higher oxygen content also contributes to a higher NO_x emission. NO_x emissions are predominantly tailpipe emissions with an overall of 13% increase in NO_x lifecycle emissions (Sheehan et al., 1998). Biodiesel also emits no sulfur and is blended with petrodiesel to meet sulfur requirements for ultra low sulfur diesel (ULSD). Long chain fatty acids that are found in the alkyl esters of biodiesel likely contribute to its high cetane number (CN). Cetane is a long unbranched hexadecane (16 carbons). Cetane number is a measure of ignition quality and a high cetane number corresponds to a shorter delay in ignition. In addition to a high CN, biodiesel is also non-toxic and non-flammable (Demirbas, 2003; Lotero et al., 2005; Demirbas, 2008). Cloud point (CP) and pour point (PP) are properties that are used to indicate the temperature at which diesel fuels are likely to gel. Biodiesel has a higher CP and PP than petroleum-based diesel and thus is more likely to lead to cold flow problems.

Much of the feedstock needed to produce biodiesel can be obtained domestically while a large percentage of crude oil used to produce petroleum diesel is imported. There are a wide range of feedstock options that include food and non-food derived choices. Vegetable oils and animal oils and fats can be virgin or recycled (used) oils and tallow is also available for use. One big step towards energy independence occurred in 2005 when the U.S. Navy adopted biodiesel as the fuel choice for all non-tactical diesel vessels (Arny, 2005).

2.2 Biodiesel Production in the U. S.

Biodiesel produced in US must meet the appropriate standards. Biodiesel can be blended with petroleum diesel to meet environmental and lubricity standards. Blends are denoted by BX where "B" denotes biodiesel and "X" denotes the percentage of biodiesel in the blend. Currently the specification for B100 it is ASTM D6751-09, and for blends B6-B20 it is ASTM D7467-09A (National Biodiesel Board, 2010). There are special rules and guidelines for low blends, B5 blends and blends above B20. Guidelines can be found on the National Biodiesel Board (NBB) website and are updated periodically.

Large-scale domestic biodiesel production saw its onset in the early 1990s as mentioned earlier. Domestic production has shown continued and marked growth especially since the Biodiesel Tax Incentive of 2005 (Schmidt, 2007; National Biodiesel Board, 2010). A tax credit of $1 per gallon of biodiesel produced is provided through the incentive. On December 31, 2009, the incentive expired but a decision to extend the incentive is currently under consideration (National Biodiesel Board, 2010; U.S.

Congress, 2009). Since 1999 U.S. biodiesel production has grown remarkably from 0.5 million gallons per year to 700 million gallons per year in 2008 (Fig. 2.1). This corresponds to 1400% increase in ten years.
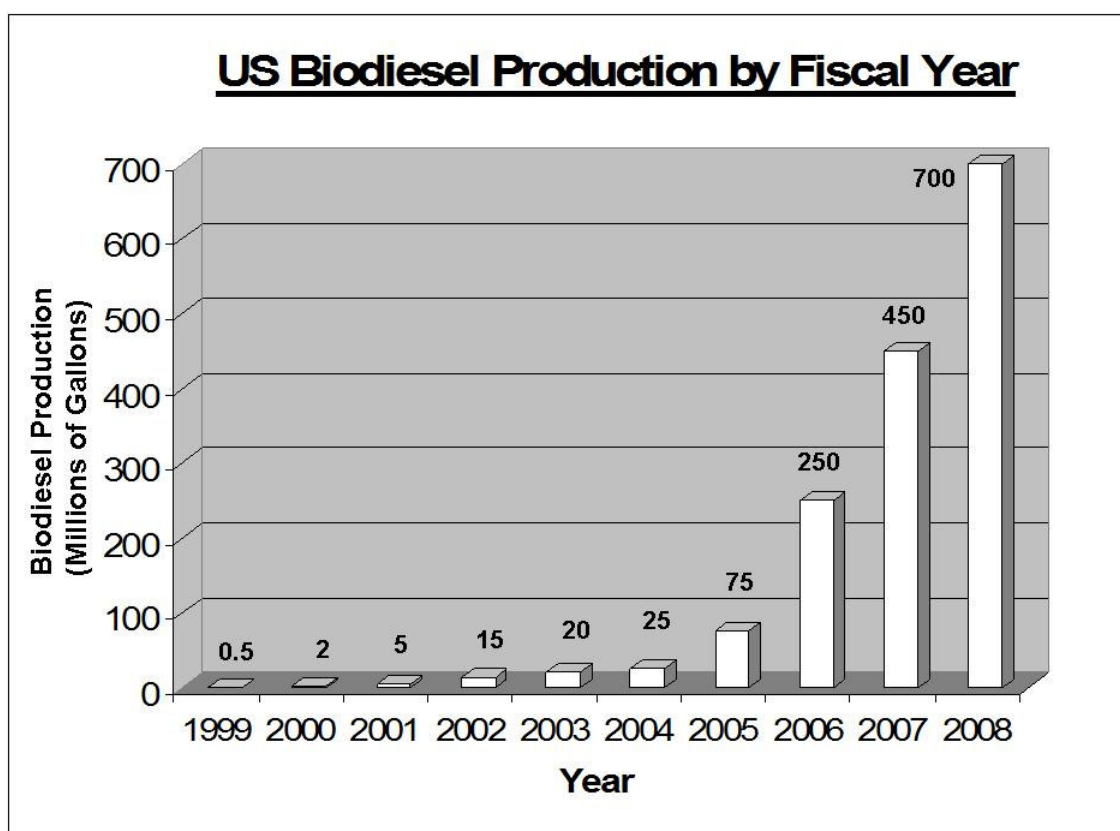
Fig. 2.1. Estimated US biodiesel production by fiscal year for 1999-2008 (National Biodiesel Board, 2009).

There are currently 183 biodiesel production facilities that are members of the National Biodiesel Board (National Biodiesel Board, 2010). These plants have a combined estimated capacity of 2.69 billion gallons per year (National Biodiesel Board, 2010). Non-NBB member plants exist. In addition, new biodiesel facilities are still being constructed. Thus national biodiesel production may exceed number reported by the NBB but the NBB goes through strict measures to report estimates that are as accurate as possible.

2.3   Feedstock

2.3.1   Building Blocks-Glycerol and Fatty Acids

2.3.1.1   Glycerol

Glycerol, also known as glycerin or glycerine is a common naturally occurring alcohol (a triol) composed of a three carbon chain with a hydroxyl group connected to each carbon. The structure of glycerol can be seen in Fig. 2.2. Glycerol is the backbone of all mono-, di- and triglylcerides and the major byproduct of biodiesel production.

$$H_2C \text{---} OH$$
$$HC \text{---} OH$$
$$H_2C \text{---} OH$$
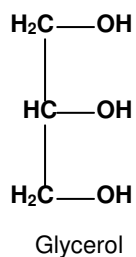
Glycerol

Fig. 2.2. Structure of glycerol.

2.3.1.2   Fatty Acids

Fatty acids and glycerol are the building blocks of a triglyceride molecule. The presence and position of various component fatty acids on a triglyceride molecule impact the physical and chemical properties of a fat or oil. A fatty acid molecule is composed of a carbon chain (usually with an even number of carbon atoms) with a carboxyl group at the head. The three main types of fatty acids are saturated fatty acids, unsaturated fatty acids, and polyunsaturated fatty acids. Saturated fatty acids contain only carbon-to-carbon single bonds in the carbon chain. They are the least reactive of the three types of fatty acids. Monounsaturated fatty acids contain one carbon-to-carbon double bond in the carbon chain. Oleic acid is the most common naturally occurring monounsaturated fatty acid. Polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds in the carbon chain (Plant Oils, 2007). The more saturated fatty acids an oil or fat contains, the lower the viscosity. Fig. 2.3 shows a general structural formula for a fatty acid with a saturated carbon chain. A more general representation of the fatty acid structure can be seen in Fig. 2.4. The R-group in the free (unbound) fatty acid represents the saturated or unsaturated carbon chain.

$$CH_3\text{-} (CH_2)_X\text{-}COOH$$

Saturated carbon chain   carboxyl group
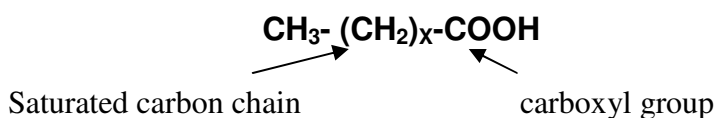
Fig. 2.3. General structural formula for a saturated fatty acid.

```
        O
        ‖
R —— C —— OH
```
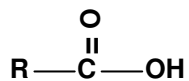
Free Fatty Acid

Fig. 2.4. General representation of a free fatty acid.

2.3.2 Oils, Fats, and Triglycerides

Fats and oils are composed mainly of triglycerides and both edible and inedible fats and oils exist. A triglyceride molecule is composed of one glycerol molecule with three fatty acids attached, one to the oxygen atom of each hydroxyl group through an ester bond. Simple triglycerides are those in which all three fatty acid groups are identical while "mixed" triglycerides are those in which two or three of the fatty acid chains differ. In this work, simple triglycerides were assumed in modeling biodiesel components in the simulation software. "Mixed" triglycerides are much more common than simple triglycerides. Fig. 2.5 depicts the structure of triglycerides. Mono- and diglycerides, free fatty acids, phosphatides, sterols, fat-soluble vitamins, tocopherols, pigments, waxes, and fatty alcohols are the minor components, and with the exception of free fatty acids, make up approximately two percent of crude vegetable oils and much less than two percent in animal fats. There is wide variation in the free fatty acid content of crude (unrefined) vegetable oils and animal fats (Food Fats and Oils, 2006).
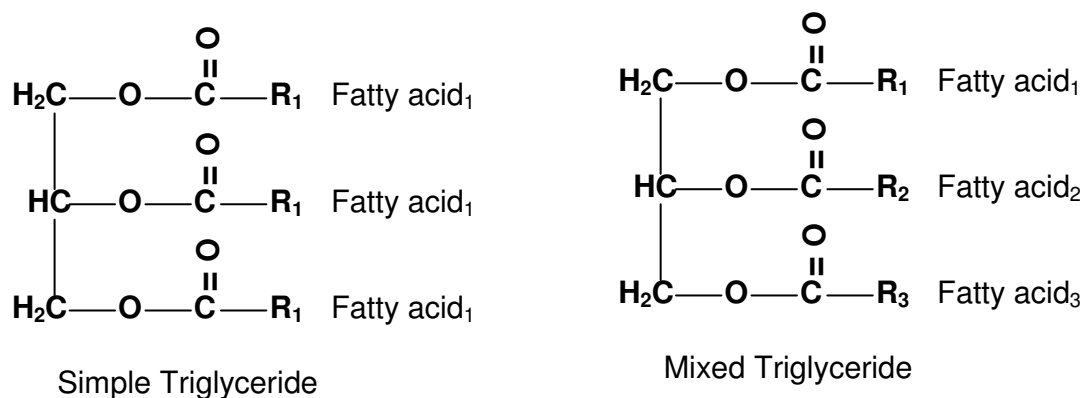
Fig. 2.5. Depictions of simple and mixed triglycerides.

Mono- and diglycerides occur naturally in plant oils and animal fats and are the mono- and diesters of fatty acids and glycerol. Fig. 2.6 depicts the structure of mono- and diglycerides. Free fatty acids are the fatty acids that are not attached to any glycerol molecule. Free fatty acids are more common in fats but some unrefined oils have free fatty acid content up to several percent. Fats and oils can be refined to greatly reduce the free fatty acid content (to less than 0.1%).
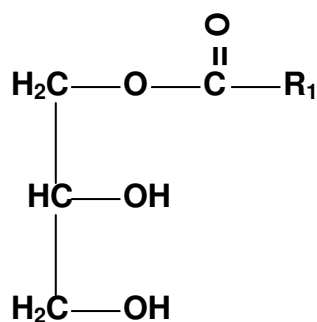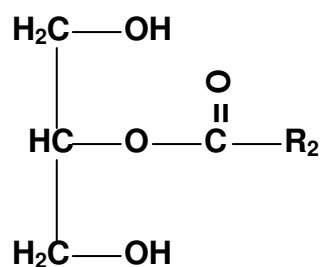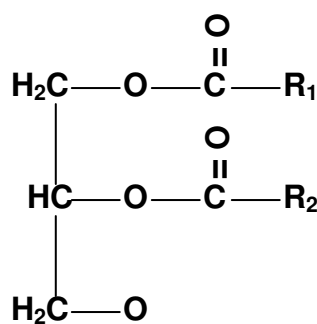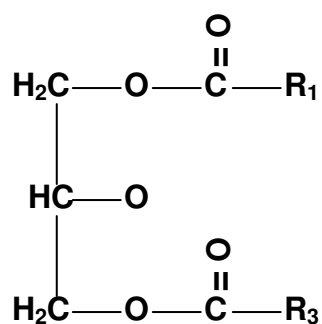
Fig. 2.6. Structures of mono- and diglycerides.

Under each structure the following labels appear:

1(α) - Monoglyceride

2 (β) - Monoglyceride

1, 2 (α, β) -Diglyceride

1, 3 (α, α') -Diglyceride

2.3.3 Other Components

Phosphatides, commonly known as phospholipids, are composed of an alcohol (usually glycerol), fatty acids and a phosphate ester and are almost completely removed by the refining process. Sterols (for example cholesterol) are more prevalent in animal fats than in vegetable oils (only trace amounts) and the types of sterols in animal fats and plant oils differ. Tocopherols and tocotrienols are antioxidants that slow rancidity and

contain vitamin E, thus are important minor components of vegetable fats, but fairly

absent in animal fats. They are partially removed during the refining process. Pigments

are naturally occurring color materials in fats and oils that are made up mostly of

carotenes (for example lycopene) and xanthopylls (for example lutein). Chlorophyll is

one of the most common pigments in plant material and is the source of the green

coloration. Most pigments are removed during the refining process. Fatty alcohols are

long chain alcohols that for edible fats are of little importance in most edible fats, less

prevalent in waxes (in an esterified form) but are more prevalent in marine oils. Table

2.1 summarizes some of the non-triglyceride components of crude fats and oils (Food

Fats and Oils, 2006).

Table 2.1   Some non-triglyceride components of crude fats and oils

Fat or Oil	Phosphatides (%)	Sterols (ppm)	Cholesterol (ppm)	Tocopherols (ppm)	Tocotrienols (ppm)
Soybean	2.2 ± 1.0	2965 ± 1125	26 ± 7	1293 ± 300	86 ± 86
Canola	2.0 ± 1.0	8050 ± 3230	53 ± 27	692 ± 85	---
Corn	1.25 ± 0.25	15,050 ± 7100	57 ± 38	1477 ± 183	355 ± 355
Cottonseed	0.8 ± 0.1	4560 ± 1870	68 ± 40	865 ± 35	30 ± 30
Sunflower	0.7 ± 0.2	3495 ± 1055	26 ± 18	738 ± 82	270 ± 270
Safflower	0.5 ± 0.1	2373 ± 278	7 ± 7	460 ± 230	15 ± 15
Peanut	0.35 ± 0.05	1878 ± 978	54 ± 54	482 ± 345	256 ± 216

Table 2.1   Continued

Fat or Oil	Phosphatides (%)	Sterols (ppm)	Cholesterol (ppm)	Tocopherols (ppm)	Tocotrienols (ppm)
Olive	<0.1	100	<0.5	110 ± 40	89 ± 89
Palm	0.075 ± 0.025	2250 ± 250	16 ± 3	240 ± 60	560 ± 140
Tallow	<0.07	1100 ± 300	1100 ± 300	---	---
Lard	<0.05	1150 ± 50	3500 ± 500	---	---
Coconut	<0.07	805 ±335	15 ± 9	6 ± 3	49 ± 22
Palm kernel	<0.07	1100 ± 310	25 ±15	3 ±	30 ± 30

2.3.4   Feedstock Considerations

Oils, fats, and greases are feedstock sources for biosiesel production (Fukuda, 2001; Van Gerpen, 2005; Demirbas and Karslioglu, 2007; Marchetti et al., 2007; Demirbas, 2008). Animals fats and oils (plant and/or animal) that have not been used previously for other purposes are labeled virgin fats and oils while fats, oils and grease that were used previously are considered recycled (Ginder, 2004). Animal sources of fats and oils include poultry, cattle, swine, and fish. Numerous authors have identified potential vegetable oil feedstock. Feedstock that have been studied include the following vegetable oils: canola (Singh et al., 2006), sunflower (Siler-Marinkovic and Tomasevic, 1998), palm (Kalam and Masjuki, 2002; Leevijit et al.; 2008), olive (Nelson et al., 1996; Dorado et al., 2004), jatrohpa (Shah et al., 2004), and camelina (Frohlich and Rice, 2005). Various other feedstock have been studied (Fukuda et al., 2001; Van Gerpen, 2005; Demirbas and Karslioglu, 2007; Marchetti et al., 2007; Demirbas, 2008)

and a non-exhaustive list of potential feedstock by type can found in Appendix A. The list is in no particular order and even includes extracted fat from meat and bone meal (Nebel and Mittelbach, 2006). Soy has been the predominant oil feedstock in the U.S. while rapeseed has dominated the European industry (Peterson and Scarrah, 1984). Used restaurant cooking oil, trap grease, and yellow grease are all examples of recycled or waste oils, otherwise known as waste cooking oil (WCO).

Algae are a potential biodiesel feedstock that has gained much attention in recent years. In "favorable" conditions algal organism synthesize compounds needed for growth such as sugars and proteins. In unfavorable conditions nitrogen deprivation or receiving an excess of certain nutrients, oil synthesis in algae increases markedly (Hu et al., 2008; Sharma and Singh, 2009). Miao and Wu (2006) grew microalgae heterotrophically to increase the oil content and subsequently successfully converted the algal oil to biodiesel. Ongoing research may lead to improvements in lipid content and thus make algae a more utilized feedstock (Huang et al., 2009; Gouveia and Oliveira, 2009). Algal oil for use in biodiesel production is attractive also because of the increased oil yield per acre compared to tradition terrestrial oil crops for biodiesel production (Chisti, 2008a).

Considerations for selecting biodiesel feedstock include:

- Cost
- %Oil content (dry weight)
- Chemical content of feedstock (i.e. Saturated fatty acid content (gelling) and Unsaturated fatty acid content (oxidation))

- Pretreatment Cost

- Purity

- Prevalence of crop domestically

- Expandable harvest areas/Flexibility to increase supply

- Regional availability (e.g. palm in tropical regions)

- Regional agricultural and political requirements (e.g. EU's iodine value parameter eliminates use of soy)

- Transportation Cost

- Quality

- Free Fatty Acid content

- Use as Food Source

- Biodiesel Yield (gallons per acre)

Feedstock cost comprises the major cost for biodiesel production (Myint, 2007; Singh et al., 2007; Sharma and Singh, 2009). In general, recycled feed cost less than virgin feedstock but can be more expensive to process and/or pretreat. Refined virgin feedstock may cost more than recycled feed but usually no additional pretreatment and can be processed directly.

Biodiesel feedstock composition varies between different feed types and even among a particular feed type. Feedstock composition is important because it can affect the processing of the feedstock and even impact the attributes of the resulting biodiesel. Chemical composition of feedstock is an important consideration for multiple feedstock processing.

2.4   Methods of Production

Currently, there are five main production methods. They are: 1.) Direct use and blending, 2.) Microemulsion, 3.) Pyrolysis, 4.) Esterification, and 5.) Transesterification (Demirbas and Karslioglu, 2007; Meher et al., 2006). Direct use and blending is a method that has waned in popularity since it was first proposed in the 1980s due to the various problems that vegetable oils cause to engines when use directly or as blends in the engines. Micoremulsions are defined as optically isotropic fluid microstructures (ranging from 1-50nm) that are formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles that are in a colloidal equilibrium dispersion (Ma and Hanna, 1999). Experiments have shown biodiesel produced via microemulsions to cause engine problems. Pyrolysis involves the use of heat (with or without a catalyst) in the absence of air and oxygen to convert one substance into another (Ma and Hanna, 1999). Pyrolysis also encompasses the processes of thermal and catalytic cracking. While these processes have shown reasonable yields in past experiments (73-88% yield), the equipment for the processes can be expensive (Ma and Hanna, 1999). Esterification is the process utilized in converting free fatty acids (FFAs) to alkyl esters. This is recommended for processes with FFA content greater than 5% (Gerpen, 2005). The two main types of transesterification are catalytic/non-supercritical transesterification and non-catalytic/supercritical transesterification (Demirbas, 2007). Catalytic/non-supercritical transesterification is the most common commercial process for producing biodiesel. Non-Catalytic/supercritical transesterification is a simpler alternative to the common commercial process that is gaining in popularity. In this work

the focus is on catalytic/nonsupercritical transesterification. There are two main types of catalytic/non-supercritical transesterification, acid catalyzed and alkali catalyzed transesterification.

Any of the five methods mentioned above can be used for either unrefined or refined oils, fats and greases but studies have shown that oils that have been pretreated to within accepted ranges are easier to handle for further processing by a selected method, the current method of choice being transesterification. Oils and fats with an FFA content less than one percent (<1.0%) can usually be processed without any problems but the accepted value is less than 0.5%. Yellow grease, being a standard commodity product, is an exception. The FFA content for yellow grease is <15%.[6] pg14 Most refined oils have an FFA content of less than 0.05 percent (<0.05%). The oils used in this study are assumed to have been refined and to have an FFA content of 0.5% or less. The amount of water present in feedstock should be kept as low as possible. Water content should be kept below point one percent (<0.1%) and the water content of feedstock is more important than the FFA content in regards to carrying out the transesterification process (Ma and Hanna, 1999; Gerpen, 2006).

2.5   Transesterification

Transesterification occurs when a triglyceride molecule reacts with an excess of alcohol in the presence of catalyst to produce glycerol and fatty acid alkyl esters (Myint, 2007). Fig. 2.7 illustrates the overall mechanism of transesterification, but in fact the process occurs through a series of reactions. Reaction temperature, alcohol to oil ratio,

oil used, catalyst type and amount appear to be the most important process variables for transesterification (Freedman et al., 1984, 1986; Fukuda et al., 2001; Demirbas and Karslioglu, 2007; Demirbas, 2008).
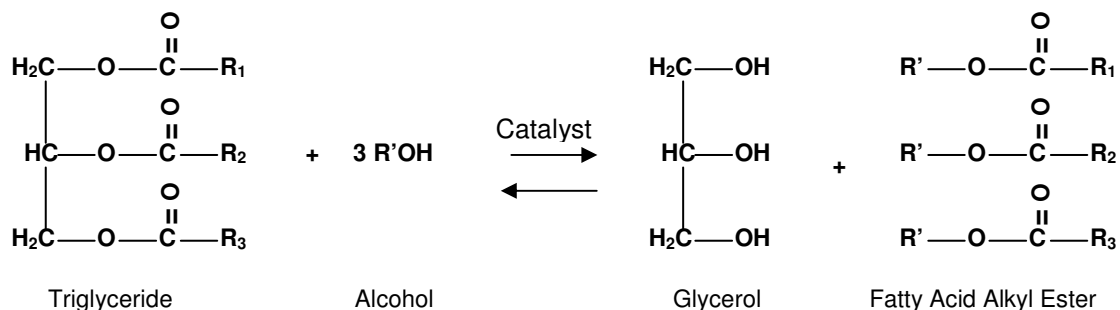
Fig. 2.7. Overall mechanism of transesterification.
(Where R is either a methyl group (for methanol) or a carbon chain linked to the appropriate hydrogen bonds, as in R_1, R_2 or R_3).

The process of transesterification actually occurs through a series of consecutive reversible reactions. In the first step the triglyceride is converted to a diglyceride. Next the diglyceride is converted to a monoglyceride. Finally, the monoglyceride is converted to glycerol. In each step, an alkyl ester is also released. Although the reactions are reversible, equilibrium is towards the production of glycerol and fatty acid alkyl ester (Ma and Hanna, 1999). Fig. 2.8 illustrates the stepwise reactions of transesterification.
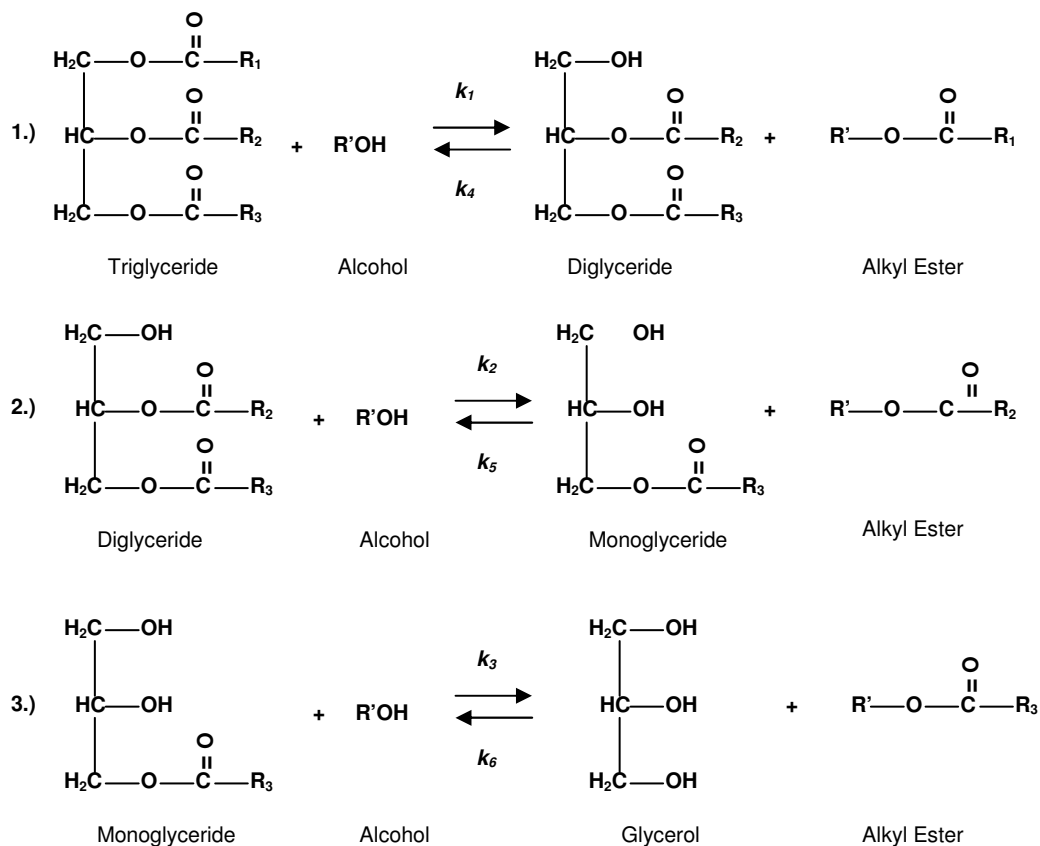
Fig. 2.8. The transesterification reactions of triglycerides with alcohol to esters and glycerol (adapted from Ma and Hanna, 1999).

Although the stoichiometric ratio for the overall oil transesterification is 3:1 (Fig. 2.7), in practice, however, an excess of alcohol is needed to ensure that the reaction goes to completion. As a result of numerous experiments, many sources (e.g. Rashid et al., 2008; Georgogianni et al., 2008; Meka et al., 2007; Leevijit et al., 2008) agree on the alcohol:triglyceride ratio of 6:1, which relates to 100% and a reaction temperature of 60°C. excess in order to ensure sufficient alkyl ester production. Freedman et al (1984)

conducted some of the earlier experiments that confirmed the 6:1 alcohol to triglyceride ratio.

Catalyst type is also an important consideration in transesterification. There are heterogeneous and homogeneous catalysts available for selection. Heterogeneous catalysts include enzymes, titanium silicates, alkaline-earth metal compounds, anion exchange resins, guanadines heterogenized on organic polymers. Heterogeneous catalysts have not been popular selections for transesterification. Homogeneous catalysts are preferred catalysts and include acid catalysts and base or alkali catalysts. Acid catalysts are preferred for transesterification of oils high in free fatty acids or moisture content because they are not greatly affected by the presence of these compounds (Freedman et al., 1984; Lotero et al., 2005) or for direct esterification of oils high in free fatty acids to methyl esters (Lotero et al., 2005). When used for transesterification, the acid catalyzed process proceeds more slowly that the alkali-catalyzed process. Acid catalysts include sulfuric acid, phosphoric acid, hydrochloric acid and organic sulfonic acids. Alkali catalysts include sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (NaOCH$_3$), and potassium methoxide (KOCH$_3$). Due to their low cost, NaOH and KOH are the most commonly used base catalysts (Akoh et al., 2007).

Methanol and ethanol are the two predominant alcohols used in transesterification. Methanol is favored due to its lower cost and lower molecular weight. Reaction type is also an important consideration for transesterification. Batch

reactions are preferred for small scale production but most commercial or large scale production of biodiesel via transesterification requires continuous production.

2.6 Pretreatment

Crude, unrefined plant oils are usually obtained from the seeds of oilseed plants (Vegetable Fats and Oils, 2007). Biodiesel feedstock includes vegetable oils (i.e. soybean, canola, palm, etc.), inedible oils (i.e. jatropha, crambe, linseed, tung, castor, etc.) (Vegetable Fats and Oils, 2007), rendered animal fats, rendered greases, and recovered material (trap grease, float grease, soapstock) (Gerpen, 2006). Feedstock vary greatly in regards to free fatty acid (FFA) content, water content, and other impurities. Pretreatment is necessary for all unrefined feedstock in order to reduce the FFA content, decrease water content, and remove impurities all of which can complicate or even hinder the processing of triglycerides into biodiesel. The greater the FFAs and water in a feedstock, the more alcohol and catalyst needed to process the triglycerides, the less effective the reaction (soap formation, reverse reaction, etc.), the lower the conversion and product yield, and the more expensive the product separation/purification. The FFA content common in biodiesel feedstocks has ranges as follows (Gerpen et al, 2004):

Refined vegetable oils < 0.05 %

Crude vegetable oil 0.3 – 0.7%

Restaurant waste grease 2 – 7%

Animal fat 5 – 30%

Trap grease 40 – 100%.

Methods of Pretreatment include esterification/acid catalysis, enzymatic methods, glycerolysis, acid catalysis followed by alkali catalysis (Gerpen et al, 2004). Of these methods, esterification or acid catalysis is preferred because of the capability of converting fatty acids in feedstock directly to methyl esters. A two-step process consisting of acid catalysis followed by alkali catalysis has also been employed with success for less refined feedstock with higher free fatty acid content (Lepper and Friesenhagen, 1986, 1987) such as waste cooking oil (Canakci and Van Gerpen, 2001, 2003; Zhang, 2003a, b; Wang et al., 2006, 2007).

2.7 Acid Value, Alcohol Ratio and Adverse Reactions

2.7.1 Acid Value

The acid value is the number of milligrams of KOH needed to neutralize the FFA in 1g of oil sample (Ma and Hanna, 1999). Triglycerides should have an acid value less than one with 0.8 being the maximum (ASTM D 6751 standard) (Gerpen, 2006).

2.7.2 Alcohol Ratio

Stoichiometrically alcohol to triglyceride ratio is 3:1 but experimentally, a ratio of 6:1 is widely accepted (Ma and Hanna, 1999).

2.7.3 Adverse Reactions: Soap and FFA Formation

Soap formation can occur when a free fatty acid reacts with the catalyst to form water (Gerpen et al, 2004; Lotero et al., 2005) (see Fig. 2.9) and soap or when water is

present the triglyceride can react with the catalyst to form glycerol and soap (Myint,

2007) (see Fig. 2.10). Soap formation can become a self-perpetuating cycle that can

consume all the triglyceride feedstock and catalyst and produce glycerol, fatty acids,

soap and water rather than biodiesel. The cycle is perpetuated by the presence of water.

The water can react with the triglyceride to form diglycerides and fatty acids (Gerpen et

al, 2004) (see Fig. 2.11). Adverse reactions decrease the yield of biodiesel and can

substantially increase the cost of glycerol separation.
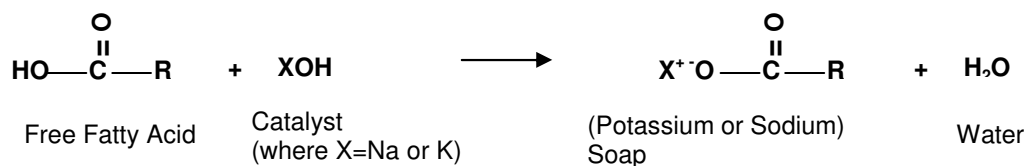
Fig. 2.9. Soap formation and water production from free fatty acid and catalyst.
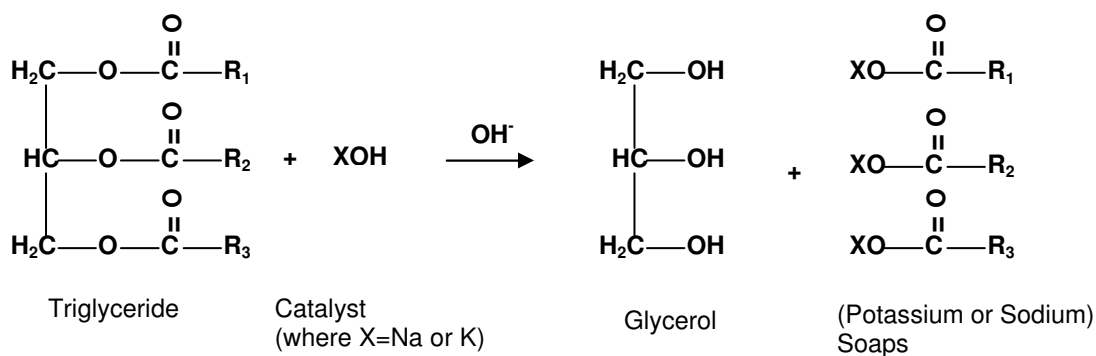
Fig. 2.10. Soap formation from triglyceride and catalyst.
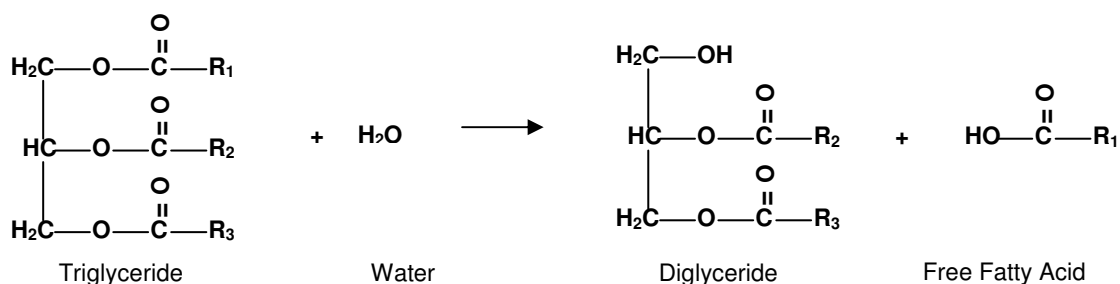
Fig. 2.11. Fatty acid and diglyceride production from water and triglyceride (Hydrolysis reaction).

2.8 Modeling Biodiesel Processes

Several researchers have modeled the biodiesel process. Simple spreadsheets and/or simulation software (i.e. ASPEN, HYSIS, ICARUS, etc.) have been used to evaluate the process for performance and economics. The majority of these process models have represented soy oil as the feed. A few have attempted representing other feedstock such as waste cooking oil (WCO). One on-going challenge for the representation of biodiesel feedstock in process models has been a lack of tools to properly represent the variety of biodiesel feedstock as feedstock compositions play an important role in biodiesel production. The challenge of representing biodiesel and more broadly, biomass feedstock must be overcome in order for analysis tools to be able to be utilized in pre-screening feedstock and synthesizing various portions of multi-feedstock processes. Some of the challenges pertaining to modeling biodiesel feedstock in simulations have been addressed in this work.

The major steps in biodiesel processing involve the transesterification reaction, subsequent separation of the glycerol and methyl ester streams, followed by individual purification of the glycerol rich stream and the methyl ester rich stream. Separation of the glycerol rich stream yields glycerol and recovered methanol. Purification of the methyl ester rich stream by acid neutralization followed by water washing yields a methyl ester stream and a water rich stream containing impurities. Most process models that have been developed for the transesterification incorporate variations of these key process steps.

Haas et al. (2007) utilized ASPEN PLUS software to model a continuous biodiesel production facility that utilizes soy as the feedstock. Crude, degummed soy oil was modeled as triolein and the process was assessed for economics in order to determine the cost ($/liter or $/gal) for biodiesel production for a 38MMGPY facility. Data from ASPEN PLUS were exported to EXCEL where cost calculations were conducted. The process model involved two transesterification reactions in sequence. The unreacted triglycerides from the first reactor were sent to the next reactor. 90% conversion was assumed through each reactor and an overall conversion of 99% was achieved. Subsequently glycerol and methyl ester streams were separated and purified. It was reported that the feedstock cost was a large portion of the production costs.

A two reactor system was also used by Tapasavi et al (2005) and soy and canola oils were modeled as the feed in the biodiesel transesterification model. The model for a continuous transesterification was developed using a spreadsheet and detailed mass balance calculations. Results for the process inputs and outputs were presented.

Four process configurations for the one-reactor alkali transesterification of soy oil were evaluated by Myint (2007) and Myint and El-Halwagi (2009). The process were designed, analyzed and optimized. Of the four scenarios, one scenario surpassed the rest and was selected for further evaluation. The scenario involved biodiesel and glycerol separation after the reaction followed by subsequent purification of glycerol rich stream to obtain glycerol and methanol and separate acid neutralization and purification of the methyl ester rich stream by water washing in order to obtain a very pure biodiesel product. ASPEN PLUS was the selected simulation software. Economic assessment was conducted with the aid of ASPEN ICARUS software and payback period and return on investment decreased with increase soybean oil cost. Feedstock cost was determined to be the bulk of the production cost.

A process utilizing vegetable oil and WCO as the feedstock was designed by Zhang et al. (2003a) using HYSIS process simulation tools. They evaluated four biodiesel production processes for the two feedstocks. While the alkali-catalyzed processing of virgin oil required fewer and smaller equipment demands, the high raw material cost was a deterrent. On the other hand, the process involving acid-catalyzed conversion of WCO feedstock yielded lower raw material cost and was more feasible than the alkali-catalyzed process. Economic analysis was then conducted by Zhang et al (2003b) for the four biodiesel process. They reported that while the alkali-catalyzed process utilizing virgin oil presented the lowest fixed capital cost, the acid-catalyzed WCO was more economically feasible.

Chongkhong et al (2009) presented a process model for the esterification of palm fatty acid distillate with high free fatty acid content. The feedstock contained 93% FFA and mono- and diglycerides as well as triglycerides. Acid catalysis utilizing sulfuric acid in the presence of methanol and sodium hydroxide was conducted to esterify the fatty acids directly to biodiesel. The process involved reaction of the feed, cooling the resulting stream, separation of methanol (by drying and evaporation) and neutralization of the methyl ester stream and subsequent purification of the methyl esters to biodiesel. High yields were reported (>90%) and raw material costs once again were reported as the bulk of the production costs.

3 PROBLEM STATEMENT

The overall goal of this work is to develop systematic procedures for the design, evaluation, and optimization of integrated biorefineries. Four categories are selected to address important classes of the biorefinery-design problem. In the first two problems, alternative feedstocks were modeled and simulated in biodiesel production. The two feedstock evaluated were algal oil and oils from sewage sludge. In the case of algae, an integrated system was considered to sequester carbon dioxide, grow algae, and synthesize a process flowsheet for biodiesel production. Next, the problem of using multiple criteria (cost, environmental, and safety) is considered. A design procedure is developed to use these criteria in guiding and screening the design. A case study is developed for the processing of sewage sludge, extraction of oils from sludge, and pretreatment of the extracted oils. The entire sludge process was then evaluated on the basis of technical, cost, and safety metrics. Sensitivity analysis is also presented for differing costs of oil production and algae of varying oil content. Next the problem of designing flexible biorefineries is addressed. The objective is to develop an optimization-based procedure for the design of biofuel-production facilities that are flexible enough to process multiple feedstocks. Finally, the problem of synthesizing flexible heat exchange networks is solved using a multi-period optimization formulation. More information on the statements of the four problems is given below.

3.1 Problem 1:   The Design of Algal Oil for the Sequestration of CO_2 and Production of Biodiesel

The problem to be addressed may be stated as follows:

Given an industrial source (e.g., power plant) which produces flue gas (flowrate M and composition Z), it is desired to sequester CO_2 from the flue gas to grow algae which is to be processed to produce biodiesel. For this case study a systems approach for the alternative process paths will be developed and a techno-economic analysis performed in order to determine the optimal design of a flue gas to biodiesel system through the cultivation of algae. The case study will also provide an analysis of the technical and economic metrics of the aforementioned steps.

3.2 Problem 2:   A Multi-Criteria Approach to the Design of Biorefineries with Application to the Production of Biodiesel from Sewage Sludge

The main aim in this problem is to develop a design procedure that uses multiple criteria (cost, environmental, and safety) to screen alternatives. The cases study is to design and optimize a process for extracting triglycerides and fatty acids from raw sewage sludge for use in biodiesel production while considering multiple criteria including cost, technical performance, and safety. Specific objectives can be identified as follows:

- Design an extraction process for obtaining lipids from sewage sludge.

- Optimize the process design.

- Utilize the design to simulate extraction of sludge using different solvents.

- Develop and apply a safety and cost metric for solvent selection.

- Simulate a process design for the pretreatment of fatty acids to biodiesel.

- Utilize the resulting triglycerides from the extraction process in a previously developed biodiesel production process.

- Evaluate and analyze the process economics and safety (using a newly introduced index).

3.3 Problem 3: Flexible Design for Multi-Feedstock Biorefineries

An increasing number of plants are being built as multi-feedstock facilities to accommodate for the variation in availability, economics, and environmental impact of feedstock alternatives. A base case process for a flexible plant must utilize pre-specified feedstocks to induce flexibility for biorefineries. Effective biorefineries need to be flexible in their capabilities to process a variety of feedstocks in a way that promotes sustainability and profitability. In order to do this, the goals are to:

1 Incorporate feedstock flexibility into the process design of the biodiesel production facilities.

2 Conduct a techno-economic study for the selected feedstock options.

The main aim of this case study is to develop a systematic approach for the flexible design of a biofuel production process. Formally stated, the problem is as follows:

Given is a biofuel production facility of with a certain base-case design handling a specific feedstock. A certain number (N_f) of alternative feedstock that can be used in conjunction with or in lieu of the current feedstock are available for consideration. It is desired to develop a systematic procedure for the design of a flexible biorefinery that accommodates all of the pre-specified feedstocks that may be utilized while maintaining a certain production level and quality constraints.

The following questions will be addressed:

• Should feedstocks be processed separately or co-fed?

• Which scenarios must be accounted for in the process design?

• What retrofitting changes are needed?

The following is a more detailed statement of the problem to be addressed.

Given a continuous process with:

- A set of pretreatment units $P = \{p | p = 1, 2, \ldots, N_{PT}\}$. Each pretreatment unit, p, has a set of input streams $\text{INPUT}_p = \{m_p \mid m_p = 1,2..., N_p^{in}\}$ and a set of output streams $\text{OUTPUT}_p = \{n_p \mid n_p = 1,2..., N_p^{out}\}$. Input stream m_p, has a flowrate, A_{m_p}, composition of component x as $Y_{m_p,x}$. Output stream n_p, has a flowrate, B_{n_p}, composition of component x as $Z_{n_p,x}$.

- A set of common process units $C = \{c | c = 1, 2, \ldots, N_{CP}\}$. Each process unit, c, has a set of input streams $\text{INPUT}_c = \{m_c \mid m_c = 1,2..., N_c^{in}\}$ and a set of output streams $\text{OUTPUT}_c = \{n_c \mid n_c = 1,2..., N_c^{out}\}$. Input stream m_c, has a flowrate, A_{m_c},

composition of component x as $Y_{m_c,x}$. Output stream n_c, has a flowrate, B_{n_c}, composition of component x as $Z_{m_c,x}$.

- A set of product discharges from the process R = {r|r= 1,2, …, N_R}.

- A set of intermediate streams I= {i|i= 1,2, …, N_I} that are redirected back into the process. Input stream m_i, has a flowrate, A_{m_i}, composition of component x as $Y_{m_i,x}$. Output stream n_c, has a flowrate, B_{n_i}, composition of component x as $Z_{m_i,x}$.

- A set of waste discharges from the process L = {l|l= 1,2, …, N_L}.

- A set of feedstocks (scenarios) SCENARIOS = {s|s = 1,2, …, N_s} . Within each scenario, s, there is a certain feedstock, pre-treatment units, processing units, production capacity, etc.

It is desired to form a systematic procedure that can be used to determine an optimal flexible process design that accommodates for a variety of feedstocks.

3.4 Problem 4: Flexible Heat Exchange Networks for Multi-Feedstock Biodiesel Processes

The use of multiple feedstocks in a biorefinery or the seasonal variation in capacity of biorefineries can lead to major differences in heating and cooling requirements for the process. It is, therefore, necessary to design heat exchange networks that can operate under the various conditions of anticipated changes. The objectives are to:

1 develop a flexible heat exchange network design that incorporates a variety of feedstock options

2 incorporate feedstock flexibility in the design of biodiesel processes

The main aim of this problem is to develop a systematic approach for the flexible heat exchange network design for a biodiesel production process. Formally stated, the problem is as follows:

A given biodiesel production facility has a known production and design process that utilizes a certain feedstock. Available for consideration are a number (N_f) of alternative feedstock that can be combined with or used instead of the current feedstock. It is desired to develop a systematic procedure for the design of a flexible heat exchange network that accommodates for the various feedstock that may be utilized while maintaining a specified production level and quality.

Questions to be addressed are:

• What retrofitting changes are needed?

• What is the minimum number of heat exchangers that can be used? Which heat exchangers should be used and with which feedstock? When?

The following is a statement of the problem to be addressed.

Given a continuous process with:

- A set of common process units C= {c|c= 1,2, …, N_{CP}}. Each process unit, c, has a set of input streams $INPUT_c = \{m_c \mid m_c = 1,2..., N_c^{in}\}$ and a set of output streams $OUTPUT_c = \{n_c \mid n_c = 1,2..., N_c^{out}\}$. Input stream m_c, has a flowrate, A_{m_c},

composition of component x as $Y_{m_c,x}$ and a temperature, T_{m_c}. Output stream n_c, has a flowrate, B_{n_c}, composition of component x as $Z_{m_c,x}$ and a temperature, T_{n_c}.

- A set of hot streams HS={h|h= 1,2,..., N_{HS}}, streams that need to be cooled or external heating utilities.

- A set of cold streams CS={k|k= 1,2,..., N_{CS}}, streams that need to be heated or external cooling utilities.

- Intervals over which residual heat exchange loads are passed (y).

- Residual heat exchange loads ($\delta_{h,y,s}$) for hot streams being transferred to cold streams for each scenario.

- A given scenario (s) in which there is a certain feedstock, processing units, production capacity, etc.

It is desired to form a systematic procedure that can be used to determine an optimal process design that accounts for heat integration and used to synthesize a flexible heat exchange network (HEN) that operates for a variety of scenarios by incorporating different feedstock.

4 DESIGN AND ANALYSIS OF BIODIESEL PRODUCTION FROM ALGAE GROWN THROUGH CARBON SEQUESTRATION[*]

4.1 Summary

This study addresses the design and techno-economic analysis of an integrated system for the production of biodiesel from algal oil produced via the sequestration of carbon dioxide from the flue gas of a power plant. The proposed system provides an efficient way to the reduction in greenhouse gas emissions and yields algae as a potential alternative to edible oils currently used for biodiesel production. Algae can be processed into algal oil by various pathways. The algal oil can then be used to produce biodiesel.

A flowsheet of the integrated system is synthesized. Then, process simulation using ASPEN Plus is carried out to model a two stage alkali catalyzed transesterification reaction for converting microalgal oil of Chlorella species to biodiesel. Cost estimation is carried out with the aid of ICARUS software. Further economic analysis is performed to determine profitability of the algal oil to biodiesel process. The results suggest that, for the algal oil to biodiesel process analyzed in this study, factors such as choosing the right algal species, using the appropriate pathway for converting algae to algal oil, selling the resulting biodiesel and glycerol at a favorable market selling prices, and attaining high levels of process integration can collectively render algal oil to be a competitive alternative to food based plant oils.

4.2   Introduction

Biodiesel is a transportation fuel that has grown immensely in popularity over the past decade. With the dwindling reserves of fossil fuels, it is now more important than ever to search for transportation fuels that can serve as alternatives to crude oil based fuels such as gasoline and diesel fuel. Common sources for biodiesel feedstock include soy, sunflower, safflower, canola, and palm. Lately there has been growing controversy about the use of potential food sources for the production of fuel. In attempt to address these concerns, researchers have turned their focus from the popular feedstock and are currently investigating the use of alternative, non-food related feedstock such as oil from algae.

Algae are a large and diverse group of simple plant-like organisms, ranging from unicellar to multicellar forms. These cells have the ability to convert carbon dioxide to biomass that can further be processed downstream to produce biodiesel, fertilizer and other useful products. Photosynthetic growth of algae requires carbon dioxide, water and sunlight. Temperature should be in the range of 20-30 degrees Celsius in order to have good growing conditions. Algae also need other inorganic nutrients like phosphorus and nitrogen in order to grow. The fact that micro algae grow in aqueous suspensions, allows for more efficient access to H_2O, CO_2 and other nutrients which explains the potential for the production of more oil per unit area than other crops currently used. The chemical composition of algae differs based on species. Algae have several characteristics that cause them to be a candidate biodiesel feedstock that deserves serious investigation.

The advantages of using algae for biodiesel production include:

- No competion for land with crops

- No competition with the food market

- Ability to grow in water with high levels of salt so there is no additional demand of fresh water. Also, areas with saline ground water that has no other useful applications can be targeted

- Overall use less water than oilseeds

- High oil yield: algae (of the aquatic species) require less land for growth than biodiesel feedstock from terrestrial plants because they are capable of producing

more oil per hectare (Chisti, 2008a). Table 4.1 shows the potential gallons of oil

per acre per year from different crops. Furthermore, the oil content in algae (per

dry weight) can reach as high as 80% (Chisti, 2008a). It is worth noting that the

oil from microalgae can be extracted with yields up to 80-90% (Grima et al,

1994; Fajardo et al, 2007; Belarbi et al, 2000).

- Efficient sequestration of CO_2: another reason why microalgae are attractive is

  that CO_2 (of about ½ of dry algae weight) is needed for growth (Chisti, 2008a).

  CO_2 is a common industrial pollutant, thus microalgae can contribute to reducing

  atmospheric CO_2 by consuming CO_2 wastes from industrial sources such as

  power plants.

Table 4.1   Gallons of Oil per Acre per Year (Chisti, 2008a)

Oil Feedstock	Gallons of Oil per Acre per Year
Corn	18
Soybeans	48
Safflower	83
Sunflower	102
Rapeseed	127
Oil Palm	635
Microalgae	5000-15000

There are nine major groups of algae which are cyanobacteria (Cyanophyceae), green algae (Chlorophyceae), diatoms (Bacillariophyceae), yellow-green algae (Xantophyceae), golden algae (Chrysophyceae), red algae (Rhodophyceae), brown algae (Phaeophyceae), dinoflagellates (Dinophyceae) and 'pico-plankton' (Prasinophyceae and Eustigmatophyceae) (Hu et al, 2008). Of these nine groups, the green algae are the largest taxonomic group. Microalgae have been known to survive under a wide range of conditions. Under optimal conditions, microalgae have lipid content between 5-20% dry weight while under unfavorable conditions lipid content increases to between 20-50% (Hu et al, 2008). Hence, it is ideal to cultivate microalgae under optimal conditions and later expose them to unfavorable conditions in order to increase lipid content.

Lab experiments utilizing green algae, diatoms, and oleaginous species from other eukaryotic taxa show that the microalgae have oil content of 26, 23, and 27 % dry weight, respectively, under optimal conditions and 46, 38, and 45 % dry weight, respectively under stress conditions (Hu et al, 2008). Depending on the species of microalgae, oil content can be further increased by limiting certain nutrients such as nitrogen, phosphorus or sulfur. For example, limiting sulfur content can increase lipid content in Chlorella sp. (Otsuka, 1961).

With the growing interest in growing algae for energy applications, different opinions have been expressed. The opinions range from concerns and skepticism about the energy efficiency, scaleup, and economic feasibility of microalgal use for transportation fuels and other energy needs (e.g., Anslow, 2008,; Sweeney, 2008,; Reijnders, 2008) to positive assessment of its efficiency and future industrial

applications in producing biodiesel meeting ASTM standards (e.g., Chisti, 2007; Chisti, 2008a; Chisti, 2008b; Miao and Wu, 2006).

The growth of algae requires carbon dioxide as one of the main nutrients needed. There is an opportunity to sequester CO_2 by using flue gas emissions from industrial sources as the CO_2 feed for algae cultivation. The objective of this case study is to develop a techno-economic analysis of a process for sequestering CO_2 from flue gas into growing algae which provides lipids that are processed to produce biodiesel. A combination of system synthesis, simulation, integration, and analysis is used to assess the technical and economic performance of the process. A case study is solved to discuss the various metrics of the process.

4.3   Problem Statement

The problem to be addressed in this case study may be stated as follows: Given an industrial source (e.g., power plant) which produces flue gas (flowrate M and composition Z), it is desired to sequester CO_2 from the flue gas to grow algae which is to be processed to produce biodiesel. The case study will develop a systems approach for the alternative process paths and perform a techno-economic analysis to determine the optimal design of a flue gas to biodiesel system through the cultivation of algae. The case study will also provide an analysis of the technical and economic metrics of the aforementioned steps.

4.4 System Overview

The overall system is composed of two main sections: an upstream processing section which is aimed at sequestering the CO_2, growing the algae, and producing the lipids and a downstream processing section which includes the pretreatment of the lipids followed by transesterification then separation and finishing, yielding the biodiesel. Fig. 4.1 illustrates these key steps.
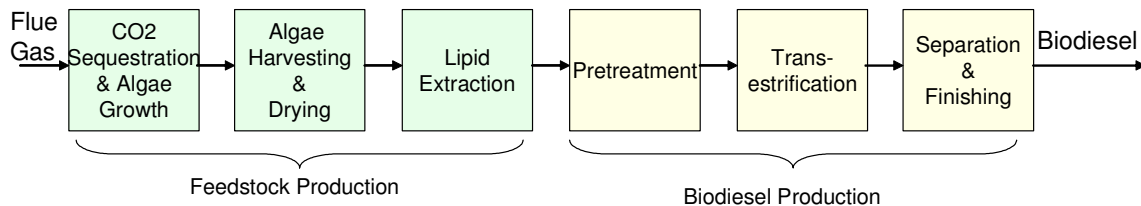
Fig. 4.1. Key elements of the algae-to-biodiesel production system

4.4.1 Algae Selection

The choice of algae species should address specific characteristics that allow the use of flue gas as the CO_2 source. Much research has been done on the tolerance of different species to flue gases. Several species were found to be suitable for the growth of algae using flue gas. One of these many species is Chlorella species. Hanagata et al (1992) found that Chlorella is tolerant to CO_2 concentrations of up to 40% by volume. Sung et. al. (1999) reported that chlorella grew in conditions of up to 40 degrees Celsius. These results indicate that Chlorella is a good choice for this study.

In this work, the Chlorella species is chosen. The oil content of Chlorella typically ranges between 28-32% dry weight (Chisti, 2007) but can reach 46% dry weight under stress conditions (Hu et al, 2008) and 55% dry weight when grown heterotrophically (Miao and Wu, 2006). Information about the fatty acid compositions of various microalgae (namely the green algae in the classes Chlorophyceae and Prasinophyceae) was published in 1992 (Dunstan et al). Chlorella is in the class Chlorophycea and the fatty acid compositions of three Chlorella species were listed. Chlorella sp. (CS-195) was used in this analysis because of its potential ease for use in simulation. It is interesting to note that the Chlorella protothecoides (CS-41) composition includes the same fatty acids present in the Chlorella sp. chosen (Dunstan et al, 1992) but in slightly different proportions. Another reason why Chlorella sp. was chosen is the availability of information about its growth, harvesting and extraction.

4.4.2   Feedstock Production

Algae can be cultivated via an open system or a closed system. Raceway ponds are the most commercially used open system for growing algae. Photobioreactors are a closed system for algae cultivation. Both raceway ponds and photobioreactors are described by Chisti (2007). Two systems are considered in this work: the use of an open pond system versus the Bio-King system (CleanTech, 2008) that uses a reactor to cultivate algae. The Bio-King process is utilized by a company in the Netherlands.

Methods for harvesting include centrifugation, filtration, and flocculation. Centrifugation is expensive but also one of the most effective ways to harvest algae.

The Alfa Laval PX series centrifuges will be used to harvest the algae. Centrifugation will result in the algae being 30% solid with 70% moisture content. As a result, further drying is required.

Drying is considered to be the most energy intensive part of this process. There are many ways to dry the wet paste slurry that comes out of the centrifuge. As mentioned the slurry contains 30% solids with the remaining 70% water. To try and save on energy costs for this process, the drying will be done using excess flue gas.

Extraction is the final step in the processing of algae for use in biodiesel production. Algal oil can be extracted physically, chemically or both. An expeller/press can be used to physically extract algal oil. The BK-oil press is capable of processing 20kg/h and will be used for this study.

Chlorella is an algal species that contains anywhere from 29-32% lipids (oil content). For this study it is assumed that Chlorella is about 30% oil and for sensitivity analysis purposes, the cost of producing algal oil assuming 50% oil content will also be evaluated.

4.4.3 Cost of Producing Algal Oil

An analysis was conducted assuming a process that utilized the BioKing Bioreactor for growing the algae, centrifugation for harvesting, excess flue gas for drying, and the BioKing oil press for extraction. Economic and sensitivity analyses were conducted for this process and used for estimating a range of costs for producing oil from algae. Specifically, two factors were varied: oil content in the algae and

performance. Two oil contents are considered: 30% and 50% (dry basis oil in algae).

The second factor is the performance of the drying and extraction units. For the high

performance case, low cost of electricity ($0.05/kWh), high production (100ton/day

plant), and the use of heat integration in drying using the hot flue gases were assumed.

For the low performance case, high cost of electricity ($0.20/kWh), low production

(1ton/day), and no heat integration for drying was assumed. The cost estimates are

presented in Table 4.2. These costs are used later in the economic analysis of the

production of biodiesel.

Table 4.2   **Estimated Costs for Producing Algal Oil**

	30% Oil Content	50% Oil Content	Units
Low Performance	1.14	0.63	$/lb
High Performance	0.21	0.07	$/lb
Average	0.68	0.35	$/lb

4.4.4   Biodiesel Process Description

Miao and Wu (2006) have shown that a species of Chlorella (Chlorella

protothecoides) can be used to produce biodiesel that meets ASTM standards. The

microalgae were grown heterotrophically to increase the oil content from 14.6% dry

weight to 55.2% dry weight. Acid transesterification was used since the acid value for the algal oil was reported as 8.97 mg KOH/g. The biodiesel yield was approximately 70% at 50°C and conditions of 60% H_2SO_4 catalyst, 5 hours reaction time, 160 rpm, 9.12g microalgal oil, and 30 to 1 methanol to oil ratio (Miao and Wu, 2006).

The design, integration, and economic assessment of the process are based on the procedure shown in Fig. 4.2. This approach is based on well-established procedures in the areas of process synthesis, simulation, and integration.

In this case study the algal oil is transesterified to biodiesel in a continuous process. Biodiesel can be produced by one of three common routes. They are: acid catalyzed transesterification, base catalyzed transesterification or acid catalyzed esterification of feedstock to fatty acids and then to alkyl esters (National Biodiesel Board, 2008). Base catalyzed transesterification is the well established means of processing biodiesel and the overwhelming option used in industry for economic and technical reasons. Rashid et al (2008) produced methyl esters from sunflower oil utilizing NaOH catalyst at 1% wt concentration in a 6:1 methanol to oil ratio at 60°C at yields of 97.1%. Georgogianni et al (2008) reported methyl ester yields from the processing of sunflower oil of 90% for conditions of 60oC, 7:1 methanol to oil molar ratio and 1%wt NaOH as catalyst. In the results and discussion it was later stated that "the highest conversion to ester (93-98%) was observed at a ratio of 6:1" (Georgogianni et al, 1008). Rashid and Anwar (2008) found that biodiesel could be produced from safflower oil with yields up to 98% for based-catalyzed transesterification utilizing sodium methoxide catalyst at 1%wt concentration, 60°C, and 6:1 methanol to oil ratio

and yields of above 90% could be achieved for the same conditions with the exception of the use of NaOH as a catalyst. Meka et al (2007) also synthesized biodiesel from safflower oil and found that at 60°C for 6:1 methanol to oil ratio and 1%wt NaOH cataslyst, yield of 96% could be obtained. Leung and Guo, (2006) performed experiments utilizing neat canola oil and used frying oil and found that for experiments exploring different parameters, a temperature of 60°C was optimum for a reaction time of 20 minutes used frying oil, that ester content was highest (98%) for canola oil for an alcohol to oil ratio of 6:1 (corresponding to a yield of 94%) and that for the three alkali catalyst explored sodium hydroxide was the cheapest and had an optimum concentration of 1.0 for neat canola oil and 1.1%wt for used frying oil. Foon et al (2004) in exploring the kinetics of the transesterification of palm oil, performed experiments utilizing base-catalyzed transesterification and found that formation of methyl esters was fastest for NaOH at 60°C for the parameters explored. Conversions above 97% were reported. Leevijit et al (2008) utilized alkali catalyzed transesterification in a 6-stage reactor to a fatty acid methyl ester product from palm oil. NaOH was used at 60oC in a methanol to oil ratio of 6:1. Gerpen et al (2004) describes the various possible routes for biodiesel production including alkali-transesterification.
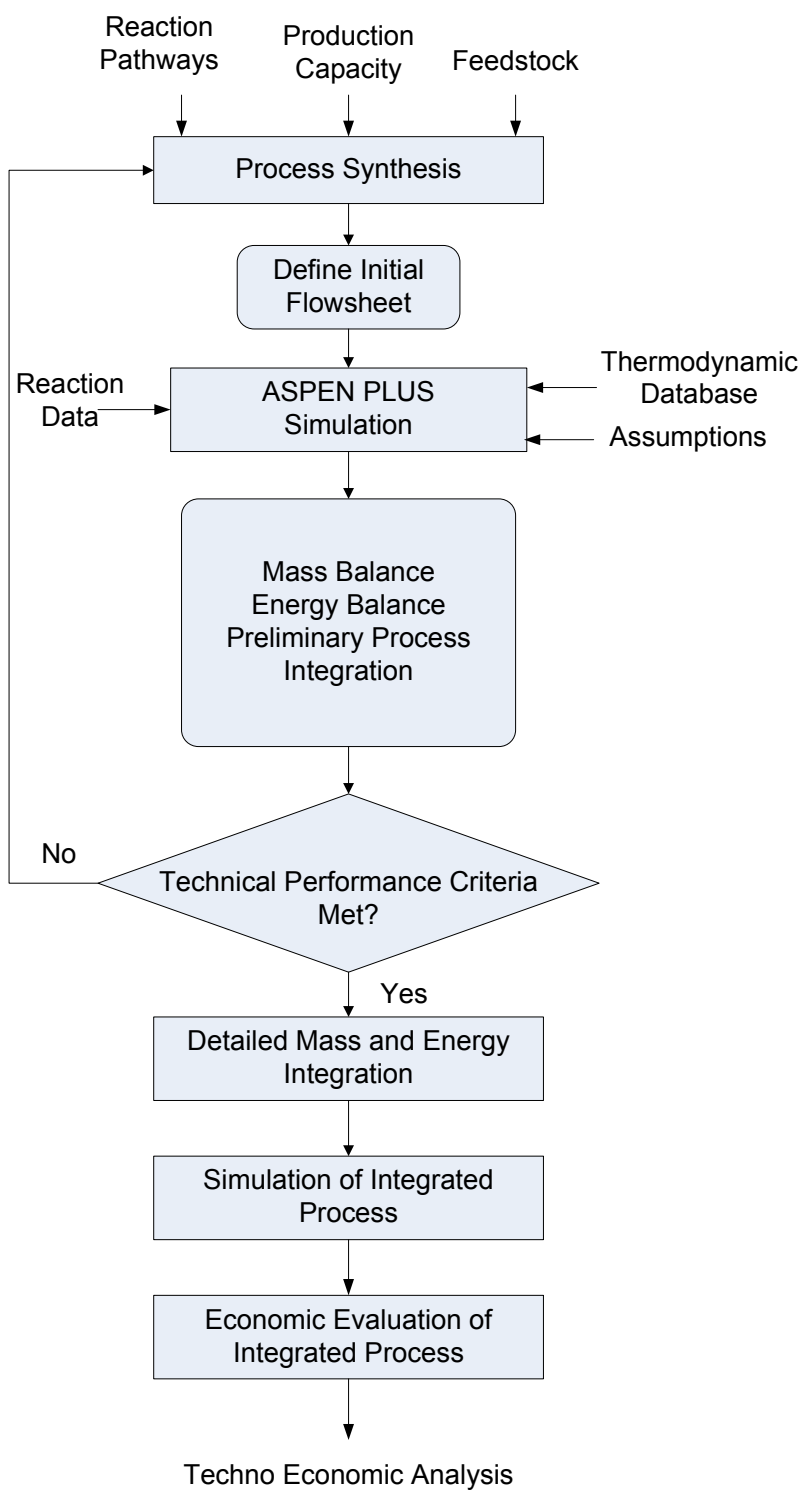
Fig. 4.2. Overall approach for algae-to-biodiesel.

For this reason, base catalyzed transesterification is used in this investigation. Pretreatment is required for feedstock with high free fatty acid (FFA) content (i.e. greater than 1%, such as waste cooking oils) as well as feedstock with substantial amounts of impurities (such as some algal oils). Feedstock with FFA content of 1wt% or less are generally required for base catalyzed transesterification. The algal oil used for the processing of biodiesel in this case study is assumed to have only trace amounts of impurities and to have FFA content of 0.05wt% therefore no pretreatment is required.

In general, the biodiesel process in this case study consists of seven sections:

- Feedstock composition

- Two-stage transesterification

- FAME and glycerol separation

- Methanol recovery

- Alkali removal

- Water washing (FAME purification)

- Glycerol purification

4.4.5 Feedstock Composition

The feedstock in this case study is algal oil from Chlorella sp. and is characterized in terms of the composition of the individual fatty acids and triglycerides. The free fatty acid content is assumed to be 0.05wt% and thus pretreatment is not necessary. Based on the data presented by Dunstan et al (1992) for Chlorella sp. (CS-

195), the fatty acid composition is distributed such that the total weight percent is 0.05. For the remaining 99.95wt%, the same data (Dunstan et al, 1992) is distributed such that it encompasses the triglyceride composition. For simplification, each triglyceride is represented as containing three identical component fatty acids, although in reality numerous possible combinations exist for the fatty acids comprising each triglyceride. Since the ASPEN Plus simulation software only has the thermodynamic data and other information for a limited number of fatty acids and the corresponding triglycerides and methyl esters that are found in plant oils, fats and algal oils (Myint, 2009), most of the components of the algal oil feedstock were entered manually using the user defined method and the structures of each compound were constructed using ISIS software.

4.4.6 Two-Stage Transesterification

The overall reaction between the triglycerides (algal oil) and methanol is given by:

Triglyceride   Methanol   Glycerol   Fatty Acid Alkyl Ester
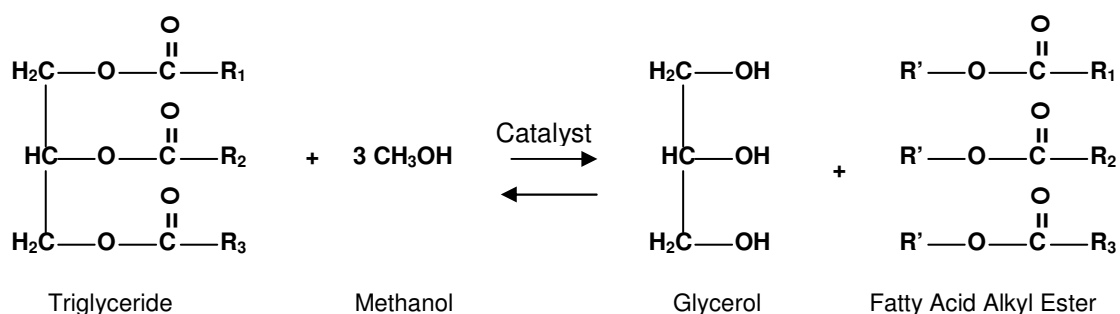
Consequently, one molecule of each triglyceride in the algal oil reacts with three molecules of methanol to produce three molecules of methyl esters, the biodiesel product, and one molecule of glycerol (Gerpen et al., 2004).

Based on several studies of alkali-catalyzed transesterification, the reaction will be carried out at the temperature near the boiling point of the alcohol (60°C for methanol). A molar ratio of 6:1, alcohol:oil, is also confirmed to be the optimal ratio by numerous studies (Ma et al., 1999; Tapasvi et al., 2005; Meher et al., 2006; Myint, 2009). In this study, the temperature of 60°C, methanol as the alcohol, a molar ratio of 6:1 methanol to oil, and NaOH as the base catalyst are the conditions used as a result of comprehensive literature review mentioned above in the section titled "Biodiesel Process Description."

In the first reactor, sodium hydroxide with a concentration of 1.0 wt % of the feed algal oil was used. The concentration of NaOH for the unreacted oil suggested in patent documents by Wimmer (1995) and Tanaka et al. (1981) for the second reactor is 0.2 wt % of inlet oils. For the process where 97.7% conversion is assumed through each reactor, no additional NaOH is needed in the second reactor. For the process where 70% conversion is assumed through each reactor, additional NaOH that is only 0.14 wt % of inlet oils is needed in the second reactor as a result of mass balance calculations, to bring the total NaOH to 1.0 wt% of the inlet to the second reactor. The purity of algal oil is assumed to be 99.95 wt % while the free fatty acid (FFA) content was assumed to be 0.05wt%.

In order to increase the conversion of the algal oil, two transesterification reactions are conducted in sequence. Conversion of feedstock have been documented by Tanaka et al. (1981) to reach up to 99.5 wt % using this two step process. In this work, the conversion is set to the same percent in each reactor. In the first scenario, the conversion through each reactor is set at 97.7% and in the second scenario the conversion through each reactor is set at 70%. The reaction products biodiesel and glycerol from the first reactor (REACT1) are separated in a decanter (DECANT4) with the byproduct glycerol sent to a distillation column (MET-DIST2) for purification. The unreacted triglycerides (algal oil) is transesterified in the second reactor (REACT2), followed by a further separation of glycerol from biodiesel in another decanter (DECANT1).

4.4.7 FAME and Glycerol Separation

The transesterification products (Fatty acid methyl esters or FAME, and glycerol) are cooled to 92^oF (33.3^oC) in the first reactor from 60^oC, and pumped to a decanter (DECANT4) where FAME and byproduct glycerol are separated. The biodiesel and glycerol from the second reactor are further separated in another decanter (DECANT1). FAME and glycerol are separated at a temperature below the reaction temperature and at atmospheric pressure simply because of their immiscibility and gravity difference. Since the glycerol phase is much denser than biodiesel phase, the two can be gravity separated. The glycerol is drawn off the bottom of the settling vessel.

4.4.8 Methanol Recovery

FAME or biodiesel is the main component of the lighter products. It is separated in a decanter (DECANT1), is heated to 60°C and then sent to a distillation column (MET-DIST1) with theoretical stages of 6, a total condenser and a kettle reboiler. In this distillation column, methanol is separated and recovered from the biodiesel phase through the overhead as a vapor. The reflux ratio is set at 1.5 in order to obtain a good separation between methanol and other components.

4.4.9 Alkali Removal

The bottom effluents from the distillation column (MET-DIST1) are cooled to 25°C and then sent to another decanter (DECANT2), where the excess sodium hydroxide is neutralized with hydrogen chloride. Hydrogen chlorides is added not only to remove residual sodium hydroxide catalyst but also to split any soap that may form during the reverse saponification reaction given by:

$$
\underset{\text{Hydrochloric Acid}}{\text{HCl}} + \underset{\text{Soap}}{\text{R-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-O-Na}} \longrightarrow \underset{\text{Free Fatty Acid}}{\text{R-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-OH}} + \underset{\text{Sodium Chloride}}{\text{NaCl}}
$$
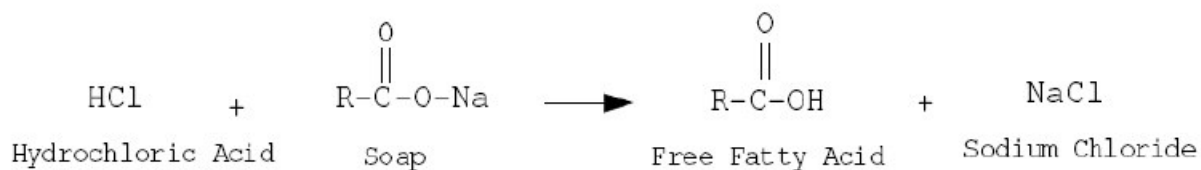
Neutralizing the stream before the water washing step aids in reducing the water required for purifying the FAME and in minimizing the chances of emulsion formation when the wash water is added to the FAME.

4.4.10 Water Washing (FAME Purification)

Once separated from other components such as sodium hydroxide and triglycerides in the decanter (DECANT2), FAME (the biodiesel) is purified by washing gently with warm water to remove residual catalyst, salts, methanol, free glycerol and soaps. A biodiesel purity of 99.65 wt% is required to meet ASTM D 6751 of biodiesel specification. Waste water exiting the water washing unit can then be recycled.

4.4.11 Glycerol Purification

After separation in decanter (DECANT4), the glycerol stream is heated to 60°C and then sent to glycerol distillation column (MET-DIST2) with 5 theoretical stages, a total condenser and a kettle reboiler. Residual FAME exits via the overhead column in terms of vapor, while the glycerol exits through the bottoms, is cooled and can be used commercially.

4.4.12 Process Simulation and Design of Biodiesel Production

In this simulation, NRTL and RK-Soave thermodynamic properties were used. Although the thermodynamic data for some triglycerides, fatty acids and methyl esters are available in ASPEN Plus, certain crucial thermodynamic properties (i.e. ideal gas heat capacity) for the components available in the ASPEN Plus databanks are not present. Most of the components were not available in the ASPEN Plus databanks at all. Thermodynamic properties not available in ASPEN Plus must be either entered by a user-defined method or estimated by ASPEN Plus upon providing the molecular

structure of the compounds (Myint, 2009). The molecular structure of all the triglycerides, fatty acids and methyl esters were created using ISIS draw software and exported as .mol files and then imported to ASPEN Plus. Furthermore, ASPEN Plus UNIFAC group contribution method was used based on the molecular structures. Since the component database in ASPEN Plus does not automatically distinguish between cis and trans compounds, there are some expected deviations between the actual thermodynamic data and the data estimated from the imported molecular structure. (Myint, 2009).

Na+ and OH- ions were used instead of solid NaOH because the simulation does not support the use of the solid form in the reaction (Myint, 2009). Similarly, H+ and Cl- ions were used instead of the HCl in the ASPEN Plus databank. Electrolyte properties must be defined for the Na+, OH-, H+ and Cl- ions.

Feed wash water amount was determined by performing the water sensitivity analysis in order to achieve methyl esters purity higher than 99.65 wt% as required by the ASTM D 6751 standards for biodiesel purity. In addition, a sensitivity analysis was performed of distillate mass flow rate in distillation column (MET-DIST2) in order to guarantee that the purity of glycerol is higher than 90% the temperature of glycerol is lower than its decomposition temperature 554^oF (290^oC given by Material Safety Data Sheet of glycerol, available at http://avogadro.chem.iastate.edu/MSDS/glycerine.htm).

Similarly, sensitivity analysis of distillate mass flow rate in column (MET-DIST1) was performed as well in order to keep the biodiesel stream temperature below its decomposition temperature 482°F (250°C).

4.5   Results and Discussion

For the processing of the algal oil to biodiesel, two simulations were conducted. Figures 4.3 and 4.4 depict the processes.   In the first simulation, there was 70% conversion through each reactor and an overall conversion of 90%.   In the second simulation, 97.7% conversion was assumed through each reactor and an overall conversion of 99.7% was achieved.   Both simulations used the same initial amount of methanol and sodium hydroxide.   Also both simulations have the same initial free fatty acid (FFA) and triglyceride composition.

In the simulation with 70% conversion through each reactor, there is a substantial amount of unreacted triglycerides (7,920 lb/h), and much additional methanol (1,901 lb/h) and additional sodium hydroxide (80 lb/h) required.   The overall conversion is 90%.   Some of the methanol that is utilized cannot be recovered.   In contrast, the

simulation with 97.7% conversion through each reactor has much less unreacted triglycerides (607 lb/h) and needs no additional methanol or sodium hydroxide in the second reactor.   The overall conversion is 99.7%.   For both cases, the resulting biodiesel is 99.7% pure and the density is calculated to be 6.4 lb/gal.

4.5.1   Heat Integration via Pinch Analysis

Data for the hot and cold streams for the cases of 90% and 99.7% overall conversions are presented in Tables 4.3 and 4.4. Next, the thermal pinch analysis (e.g., Linnhoff and Hindmarsh, 1983; Papoulias and Grossmann, 1983) is used to carry out heat integration and to determine minimum heating and cooling utility requirements. The grand composite curves (Linnhoff, 1993) are illustrated by Figures 4.5 and 4.6 and show the utility saving for 90% and 99.7% overall conversion, respectively. The results are summarized by Tables 4.5 and 4.6. The second simulation (99.7% overall conversion) has greater utility savings (63% for heating and 53% cooling) than the first simulation (90% overall conversion) (39% for heating and 37% for cooling).   Additionally, mass integration for recycling methanol and water was carried out using source-sink mapping techniques (e.g., El-Halwagi, 2006; 1997).
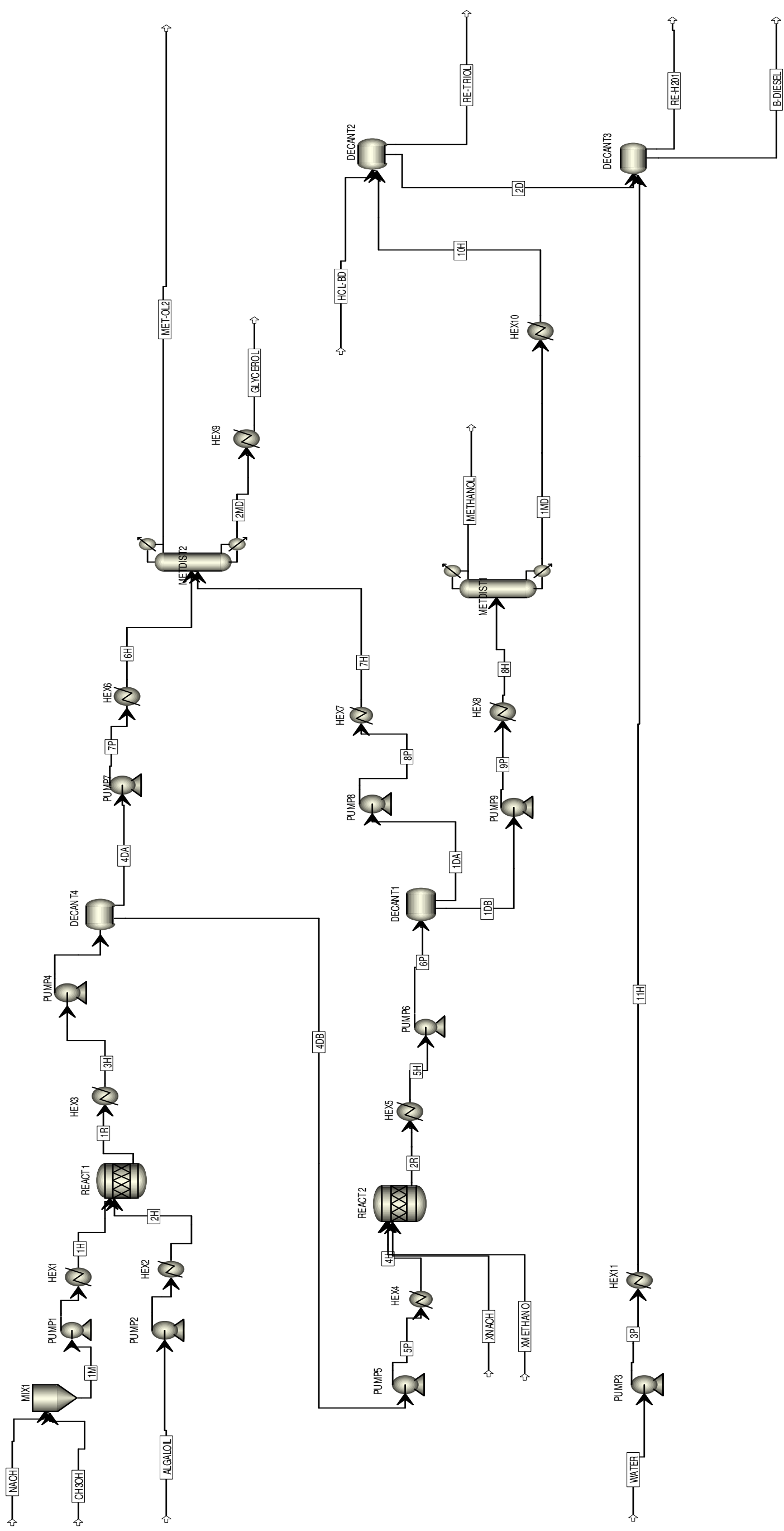
Fig. 4.3. Process Flow Diagram of biodiesel production for 70% conversion through each reactor, the overall conversion is approximately 90%.
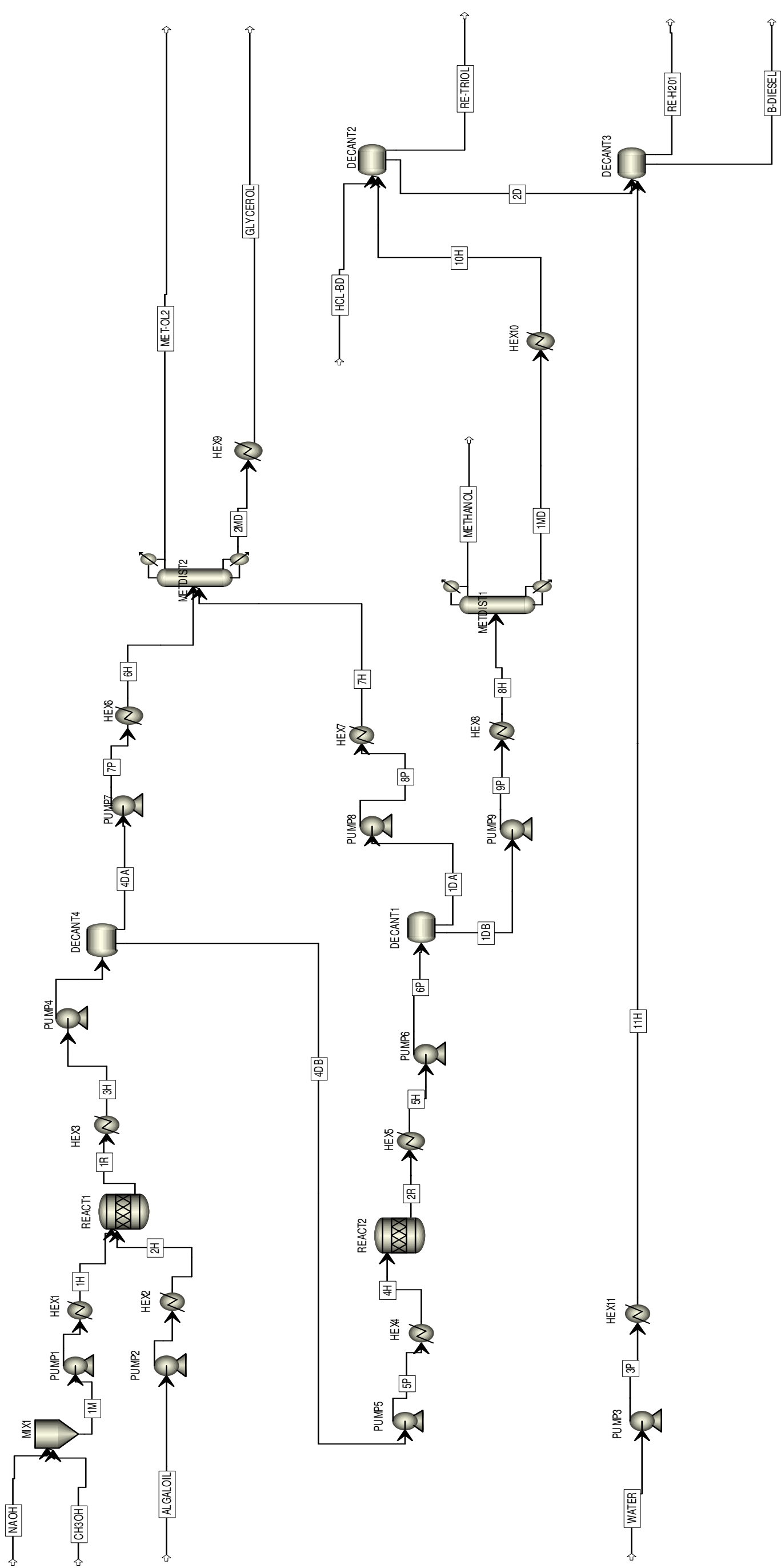
Fig. 4.4. Process Flow Diagram of biodiesel production for 97.7% conversion through each reactor, the overall conversion is 99.7%.

90% Overall Conversion

Table 4.3   Hot and cold streams for heat integration for 90% overall conversion

Cold Streams	Supply Temp (^{O}F)	Target Temp (^{O}F)	Enthalpy Change 10^3 Btu*h^{-1}	Specific Heat 10^3 Btu*h^{-1}*^{O}F^{-1}
HEX1	77	140	50	1
HEX2	78	140	2598	42
HEX4	92	140	700	15
HEX6	92	140	344	7
HEX7	77	140	80	1
HEX8	77	140	982	16
MET-DIST1 (Reboiler)	191	192	157	157
MET-DIST2 (Reboiler)	128	129	8045	8045
Total Heating Utility			12957	

Hot Streams	Supply Temp (^{O}F)	Target Temp (^{O}F)	Enthalpy Change 10^3 Btu*h^{-1}	Specific Heat 10^3 Btu*h^{-1}*^{O}F^{-1}
HEX3	140	77	1223	19
HEX5	140	77	1041	16
HEX9	128	77	980	19
HEX10	192	77	854	7
HEX11	78	77	1	1
MET-DIST1 (Condenser)	62	61	374	374
MET-DIST2 (Condenser)	62	61	7473	7473
REACT1	140	139	695	69
REACT2	140	139	1018	1018
Total Cooling Utility			13659	

99.7% Overall Conversion

Table 4.4   Hot and cold streams for heat integration for 99.7% overall conversion

Cold Streams	Supply Temp (^{O}F)	Target Temp (^{O}F)	Enthalpy Change 10^3 Btu*h^{-1}	Specific Heat 10^3 Btu*h^{-1}*^{O}F^{-1}
HEX1	77	140	50	1
HEX2	78	140	2598	42
HEX4	92	140	794	16
HEX6	92	140	312	6
HEX7	77	140	6	0.09
HEX8	77	140	1043	16
MET-DIST1 (Reboiler)	207	208	1666	1666
MET-DIST2 (Reboiler)	111	112	4800	4800
Total Heating Utility			11269	

Hot Streams	Supply Temp (^{O}F)	Target Temp (^{O}F)	Enthalpy Change 10^3 Btu*h^{-1}	Specific Heat 10^3 Btu*h^{-1}*^{O}F^{-1}
HEX3	140	77	1353	21
HEX5	140	77	1051	17
HEX9	112	77	1054	30
HEX10	208	77	1955	15
HEX11	78	77	1	1
MET-DIST1 (Condenser)	62	61	860	860
MET-DIST2 (Condenser)	62	61	4125	4125
REACT1	140	139	2611	2611
REACT2	140	139	309	309
Total Cooling Utility			13320	
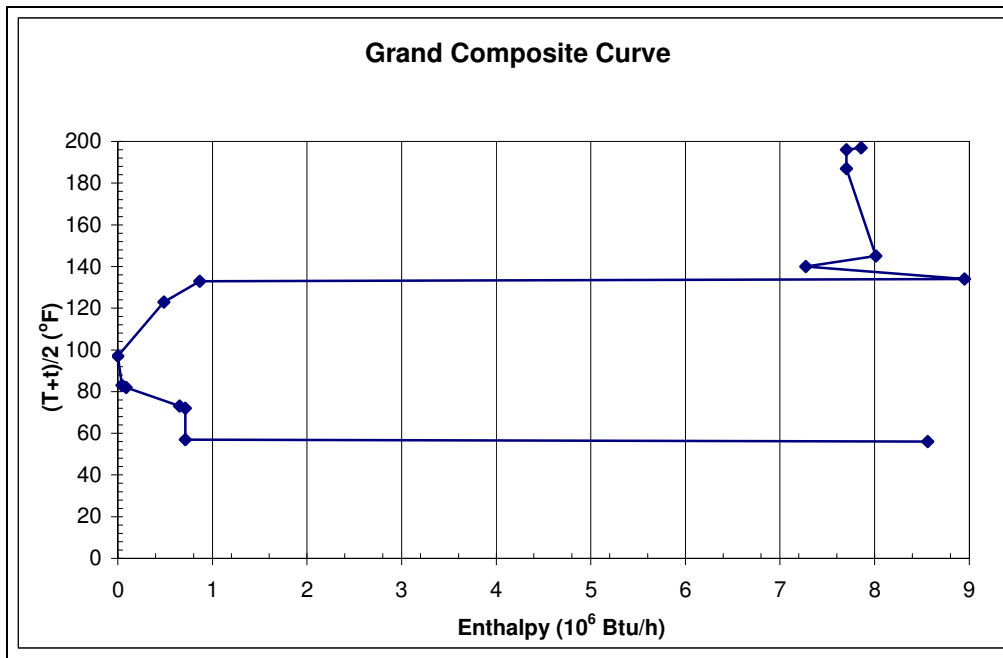
Fig. 4.5. GCC for 90% overall conversion.
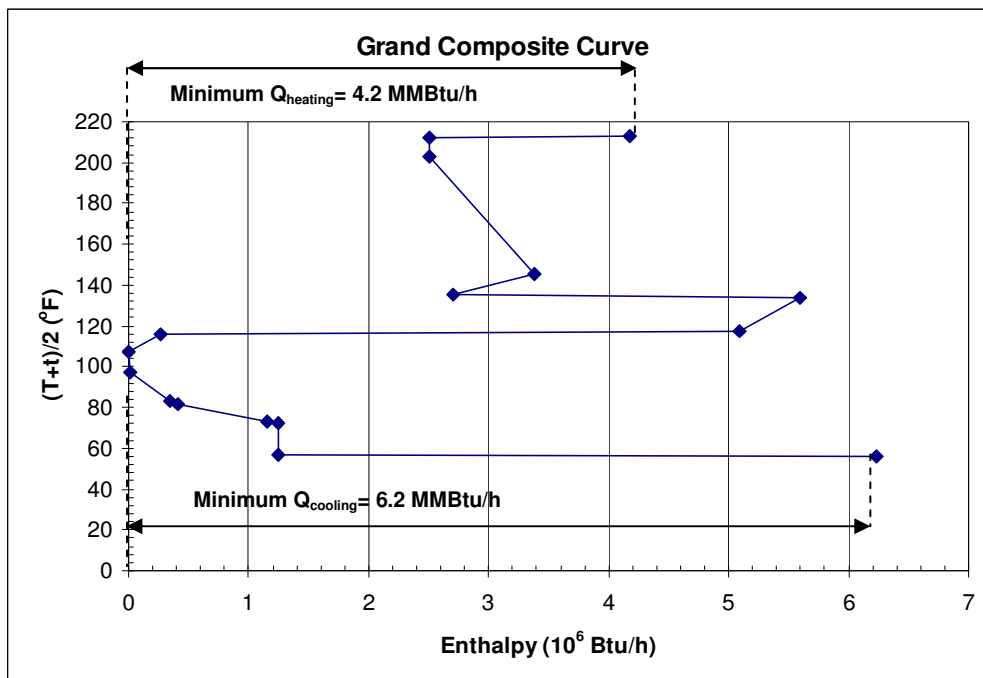
Fig. 4.6. GCC for 99.7% overall conversion.

Table 4.5   **Utility Savings for 90% Overall Conversion**

	Heating Utility	Cooling Utility
Utility without integration (Btu/h)	12957	13659
Utility after integration (Btu/h)	7859	8561
Savings from heat integration	5098	5098
Percentage of savings	39%	37%

Table 4.6   **Utility Savings for 99.7% Overall Conversion**

	Heating Utility	Cooling Utility
Utility without integration (10^3 Btu/h)	11269	13320
Utility after integration (10^3 Btu/h)	4175	6226
Savings from heat integration (10^3 Btu/h)	7094	7093
Percentage of savings	63%	53%

4.5.2   Economics

ASPEN ICARUS has been used to compute project capital and equipment cost. Once the simulation has been completed and ASPEN Plus is run, the information from ASPEN Plus can be exported into ICARUS. For the algal oil to biodiesel process, the total capital investment is $10.9 million for 99.7% overall conversion and $10.5 million for 90% overall conversion). The total direct equipment costs estimated from ASPEN ICARUS are $2.6 million for the 90% overall conversion process and $2.8 million for the 99.7% overall conversion process. Raw material costs are presented in Table 4. 7 for the 90% overall conversion case and in Table 4. 8 for the 99.7% overall conversion case. Cost of algal oil comprises the bulk of the raw material costs in each case.

Table 4.7   Raw Material Costs for 90% Overall Conversion

Raw materials	30% Oil Content			50% Oil Content		
	cost per unit ($/lb)	units (lb/h)	annual cost (1000 $/yr)	cost per unit ($/lb)	units (lb/h)	annual cost (1000 $/yr)
Algal oil (Low Performance)	1.14	37298	340,008	0.63	37298	186,606
Algal oil (High Performance)	0.21	37298	63,605	0.07	37298	21,981
Methanol	0.3	10262	24,629	0.3	10262	24,629
NaOH	1.8	198	2,859	1.8	198	2,859
HCl	0.63	60	302	0.63	60	302
Water	0.0012	5404	51	0.0012	5404	51
Total Low Performance			367,851			214,449
Total High Performance			91,448			49,824

Table 4.8   Raw Material Costs for 99.7% Overall Conversion

Raw materials	30% Oil Content			50% Oil Content		
	cost per unit ($/lb)	units (lb/h)	annual cost (1000 $/yr)	cost per unit ($/lb)	units (lb/h)	annual cost (1000 $/yr)
Algal oil (Low Performance)	1.14	37298	340,008	0.63	37,298	186,606
Algal oil (High Performance)	0.21	37298	63,605	0.07	37,298	21,981
Methanol	0.3	8538	20,491	0.3	8,538	20,491
NaOH	1.8	186	2,683	1.8	186	2,683
HCl	0.63	60	302	0.63	60	302
Water	0.0012	5404	51	0.0012	5,404	51
Total Low Performance			363,538			210,137
Total High Performance			87,135			45,511

Profit (P), payback period (PP), return on investment (ROI) and breakeven (BE) analysis calculations were done for the low performance and high performance scenarios for the cost of producing algal oil and for the assumptions of 30% and 50% oil content of algae for both the 90% and the 99.7% overall conversion processes. The same for calculations (P, PP, ROI, BE) were repeated for the assumptions of 30% and 50% oil content but this time for the cost of producing algal oil that is an average of the low performance and high performance values. This was done for both the 90% and the 99.7% overall conversion processes. In addition, for all of these calculations, a low selling price of $3.69/gal and a high selling price of $4.20/gal for biodiesel were assumed for all the calculations (P, PP, ROI, BE) mentioned previously. The selling prices were obtained or assumed based on data from the Clean Cities Alternative Fuel Price Report (2008) from January to October 2008. The assumptions of glycerol selling price ($0.60/gal and $0.88/gal) were made based on information from ICIS Pricing (2008) for the same period.

Based on the results of the economic and sensitivity analysis, the most profitable results where those utilizing process integration. For the cases assuming oil content of 50%, the high performance and average cases were profitable and the low performance case was not highly profitable or unprofitable in some cases. When assuming 30% oil content, only the high performance cases were profitable. Return on investment results are presented in Figures (4.7-4.18) for the cases assuming 50% oil content with heat integration and in Figures (4.19-4.30) for the cases assuming 30% oil content with heat integration.
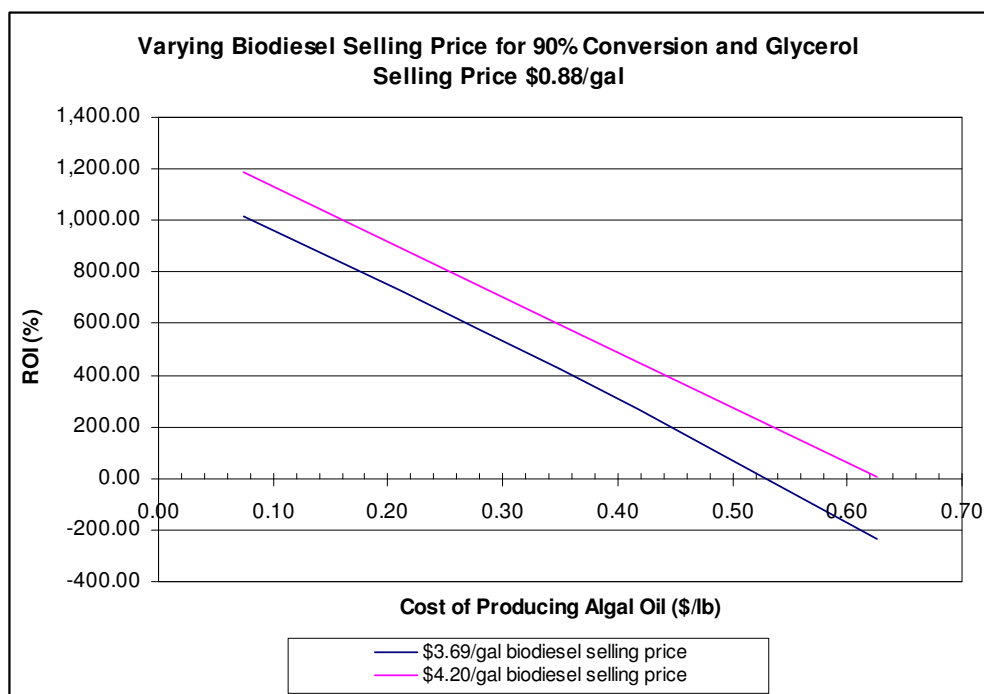
Fig. 4.7. Varying biodiesel selling price at constant conversion (90%) and constant glycerol selling price ($0.88/gal) for 50% oil content, with process integration.
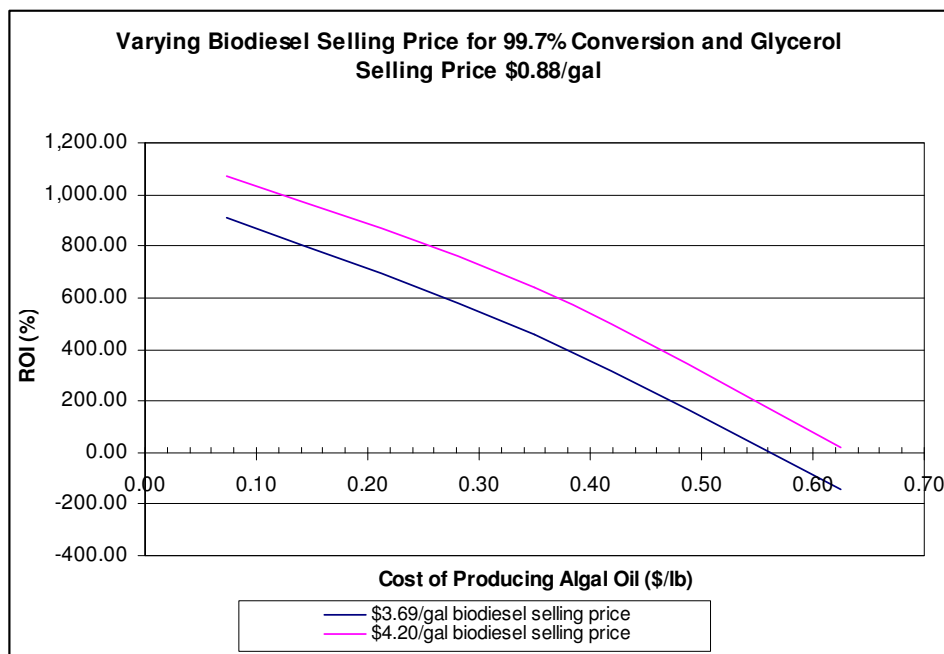
Fig. 4.8. Varying biodiesel selling price at constant conversion (99.7%) and constant glycerol selling price ($0.88/gal) for 50% oil content, with process integration.
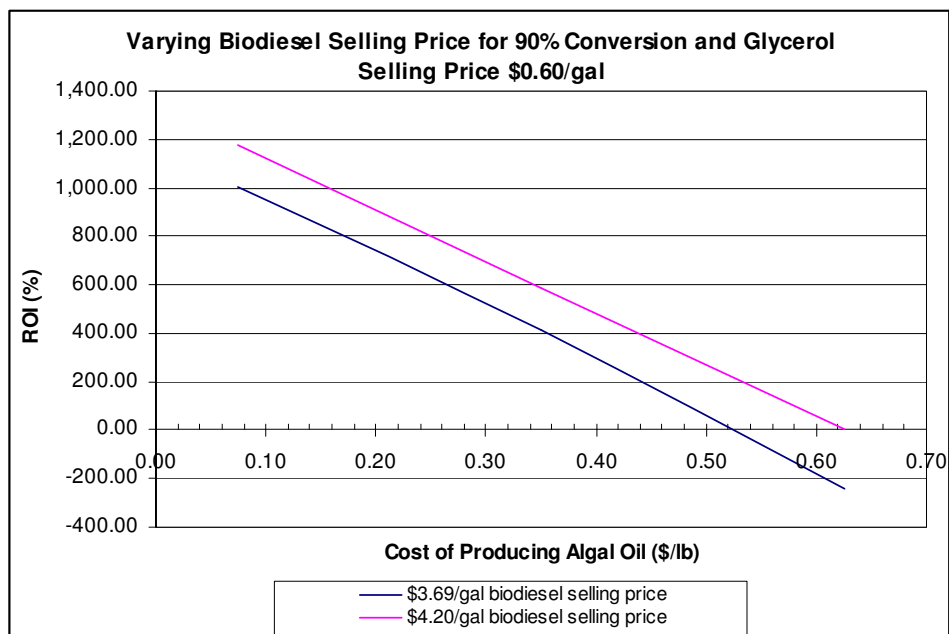
Fig. 4.9. Varying biodiesel selling price at constant conversion (90%) and constant glycerol selling price ($0.60/gal) for 50% oil content, with process integration.
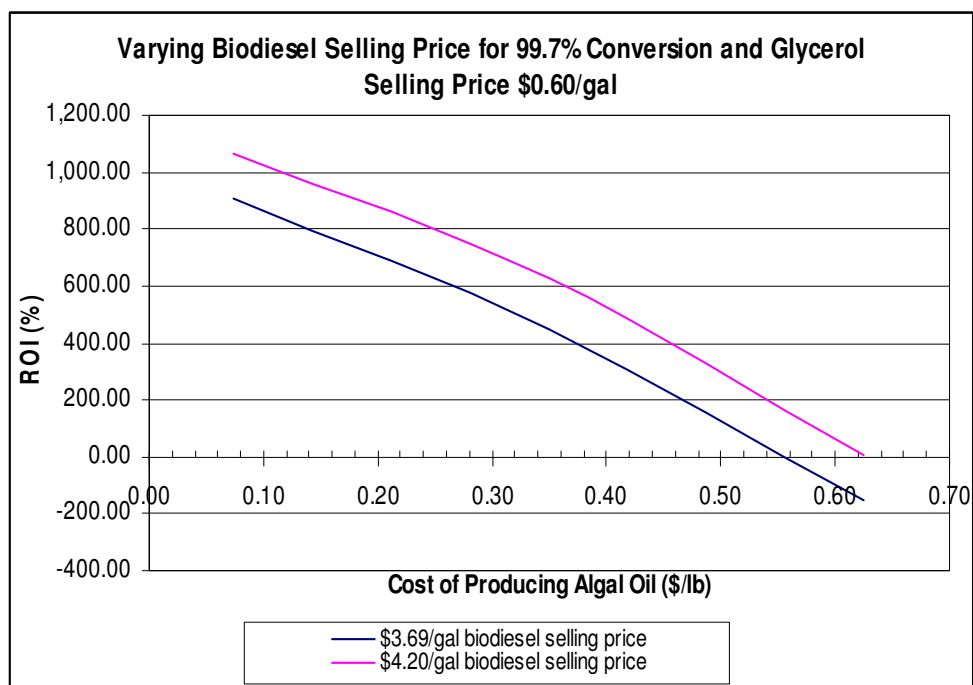
Fig. 4.10.   Varying biodiesel selling price at constant conversion (99.7%) and constant glycerol selling price ($0.60/gal) for 50% oil content, with process integration.
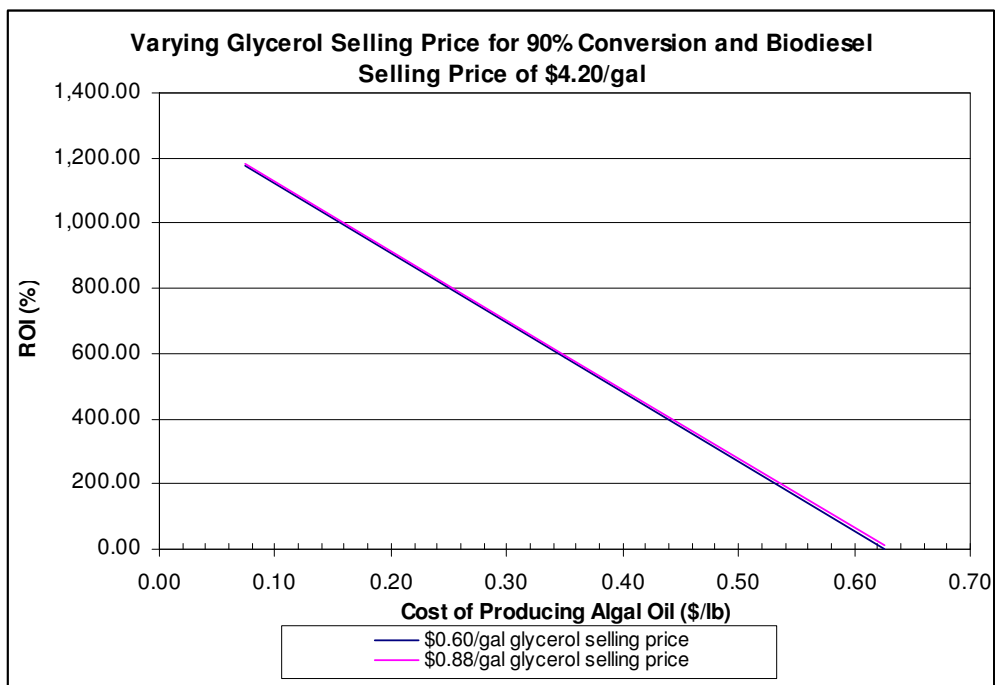
Fig. 4.11. Varying glycerol selling price at constant conversion (90%) and constant biodiesel selling price ($4.20/gal) for 50% oil content, with process integration.
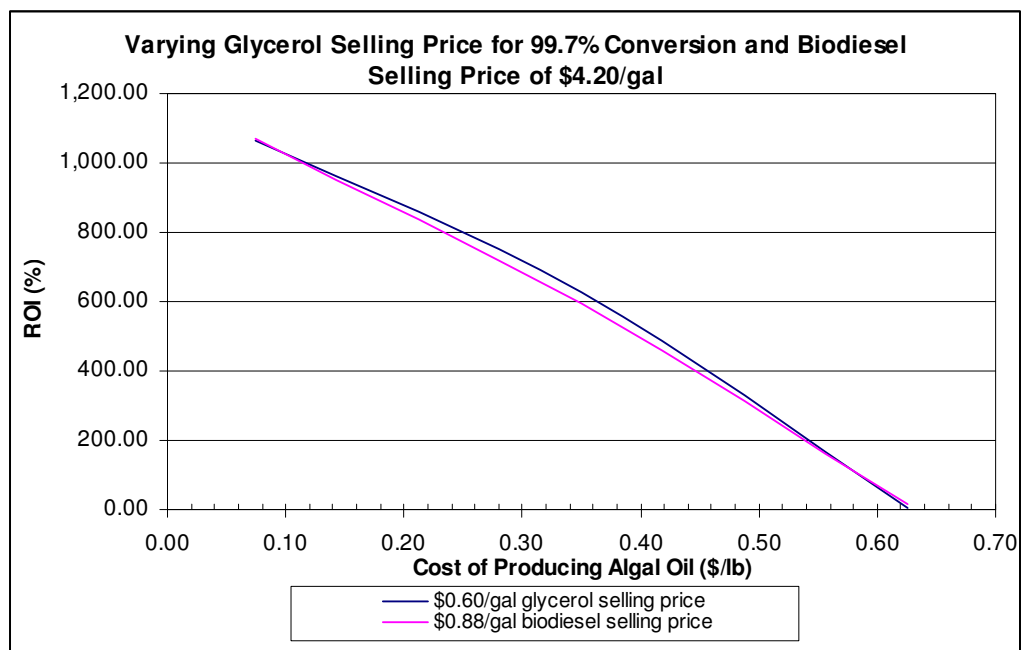
Fig. 4.12. Varying glycerol selling price at constant conversion (99.7%) and constant biodiesel selling price ($4.20/gal) for 50% oil content, with process integration.
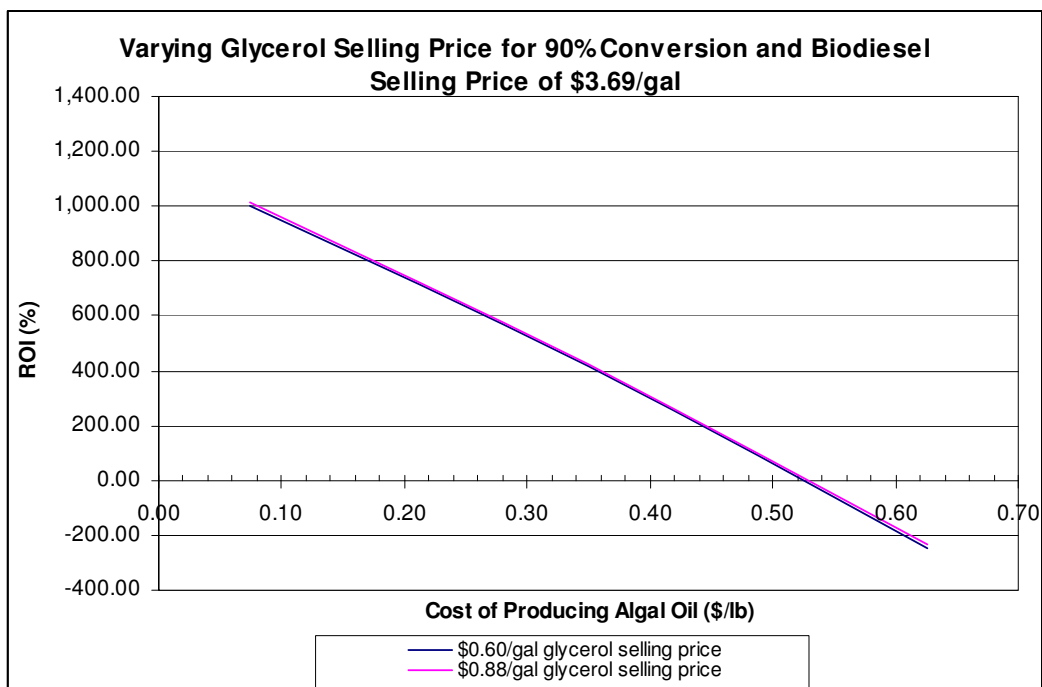
Fig. 4.13. Varying glycerol selling price at constant conversion (90%) and constant biodiesel selling price ($3.69/gal) for 50% oil content, with process integration.
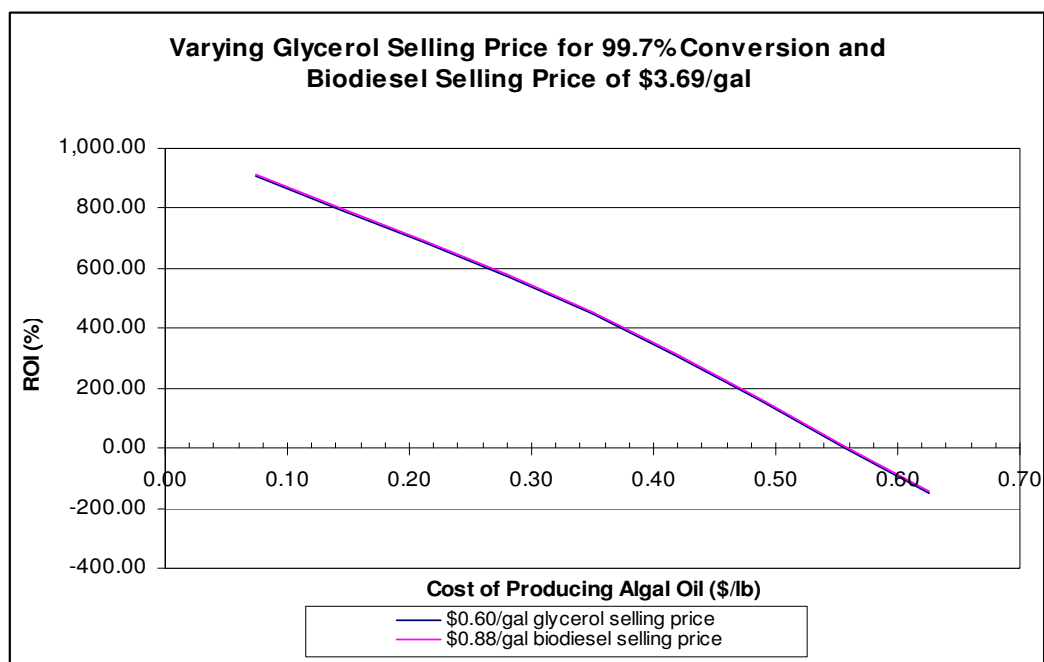
Fig. 4.14. Varying glycerol selling price at constant conversion (99.7%) and constant biodiesel selling price ($3.69/gal) for 50% oil content, with process integration.
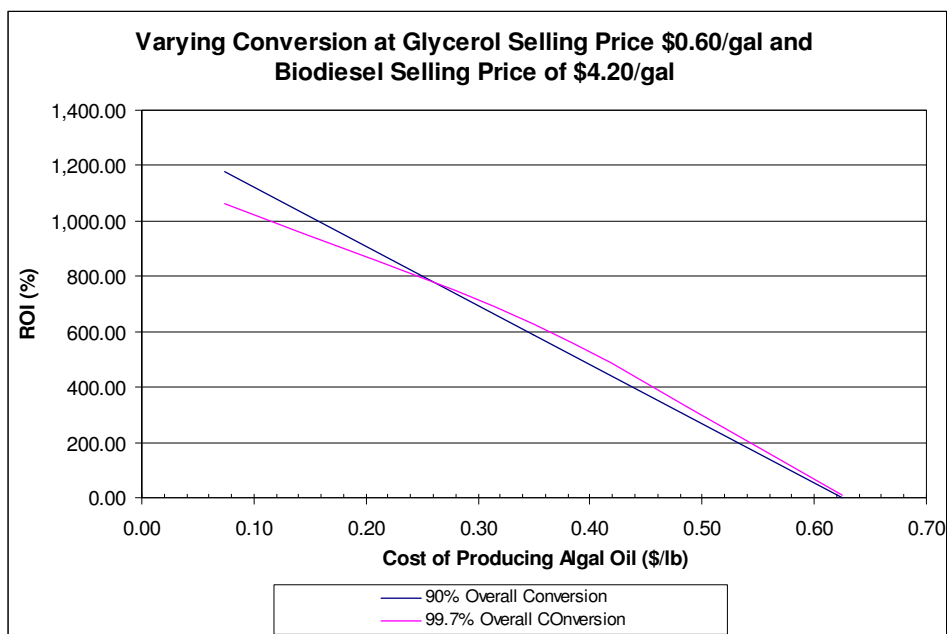
Fig. 4.15. **Varying conversion at constant glycerol selling price ($0.60/gal) and constant biodiesel selling price ($4.20/gal) for 50% oil content, with process integration.**
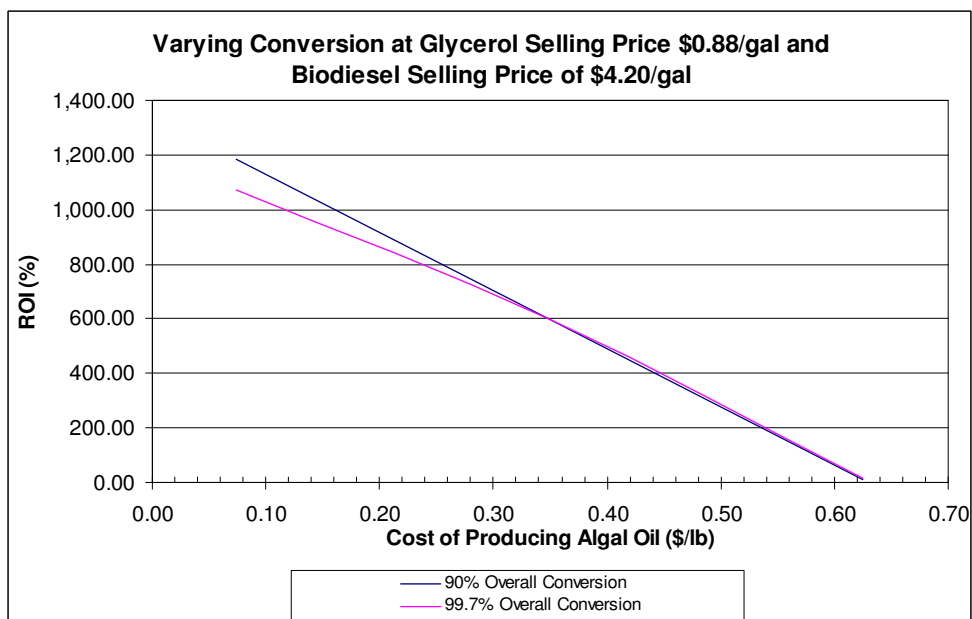
Fig. 4.16. **Varying conversion at constant glycerol selling price ($0.88/gal) and constant biodiesel selling price ($4.20/gal) for 50% oil content, with process integration.**
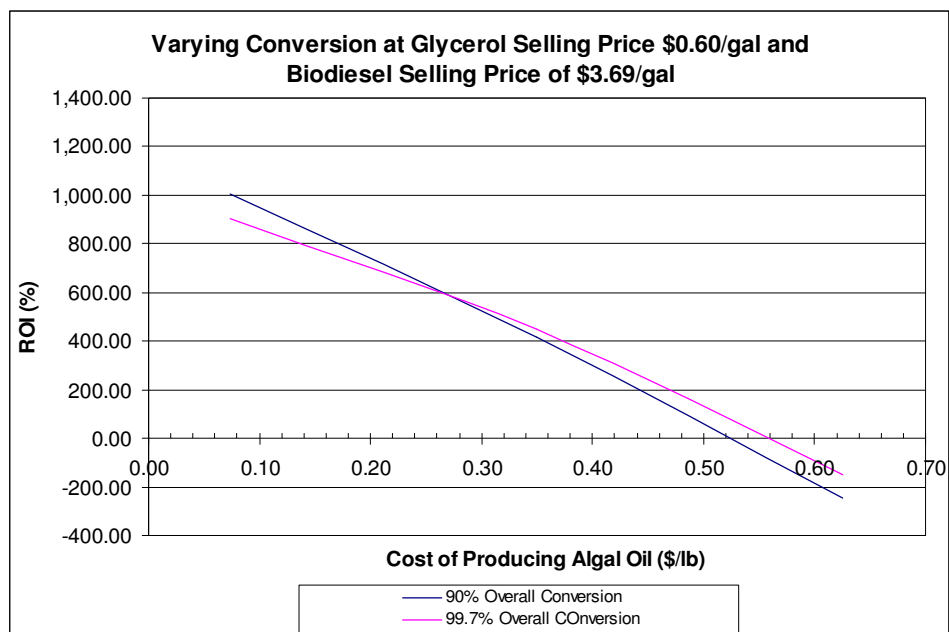
Fig. 4.17. Varying conversion at constant glycerol selling price ($0.60/gal) and constant biodiesel selling price ($3.69/gal) for 50% oil content, with process integration.
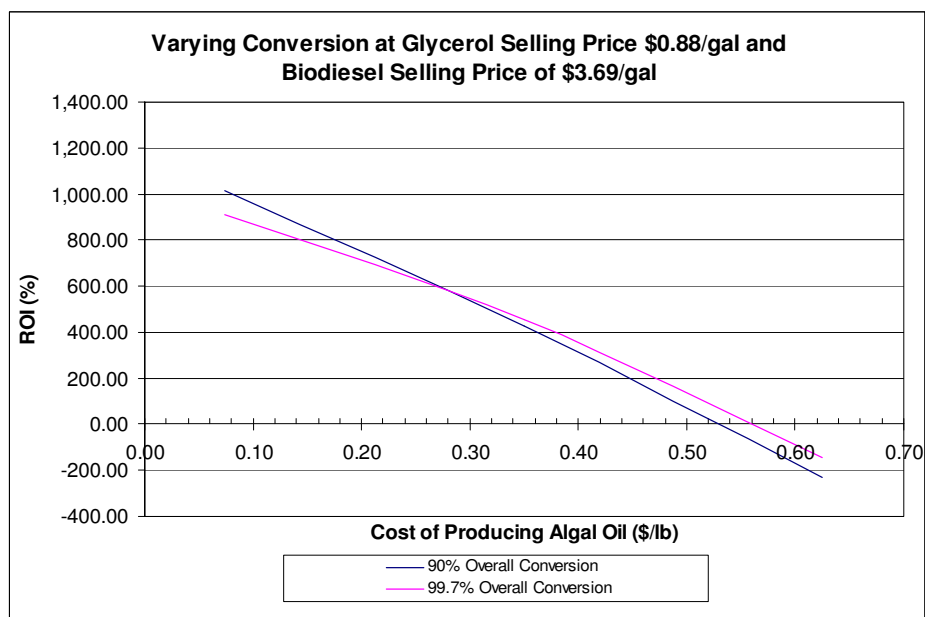
Fig. 4.18. Varying conversion at constant glycerol selling price ($0.88/gal) and constant biodiesel selling price ($3.69/gal) for 50% oil content, with process integration.
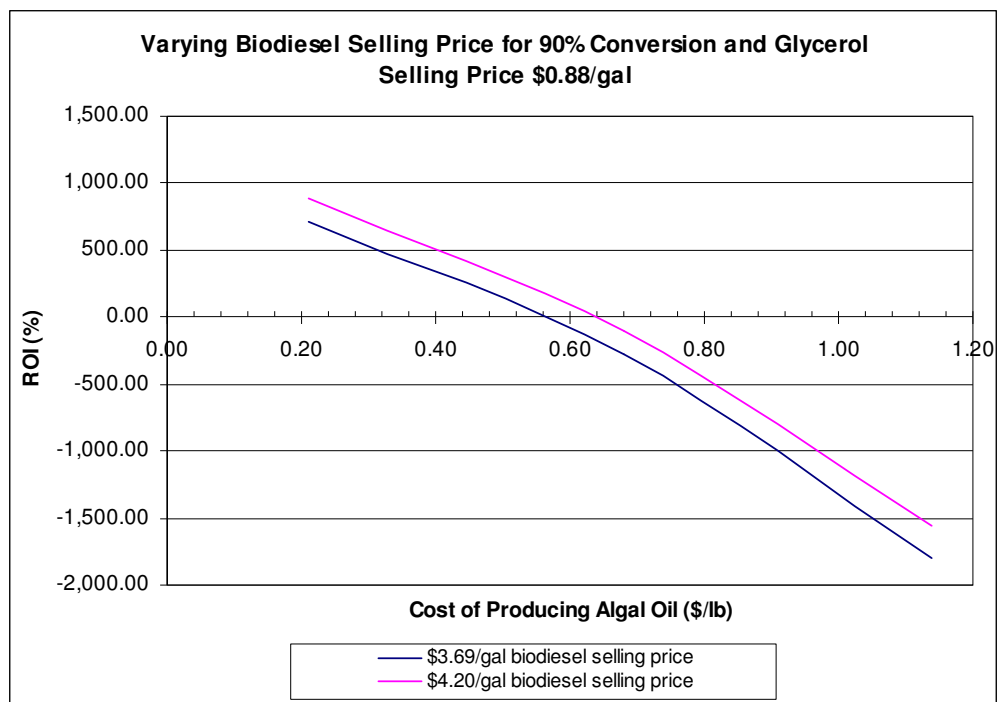
Fig. 4.19. Varying biodiesel selling price at constant conversion (90%) and constant glycerol selling price ($0.88/gal) for 30% oil content, with process integration.
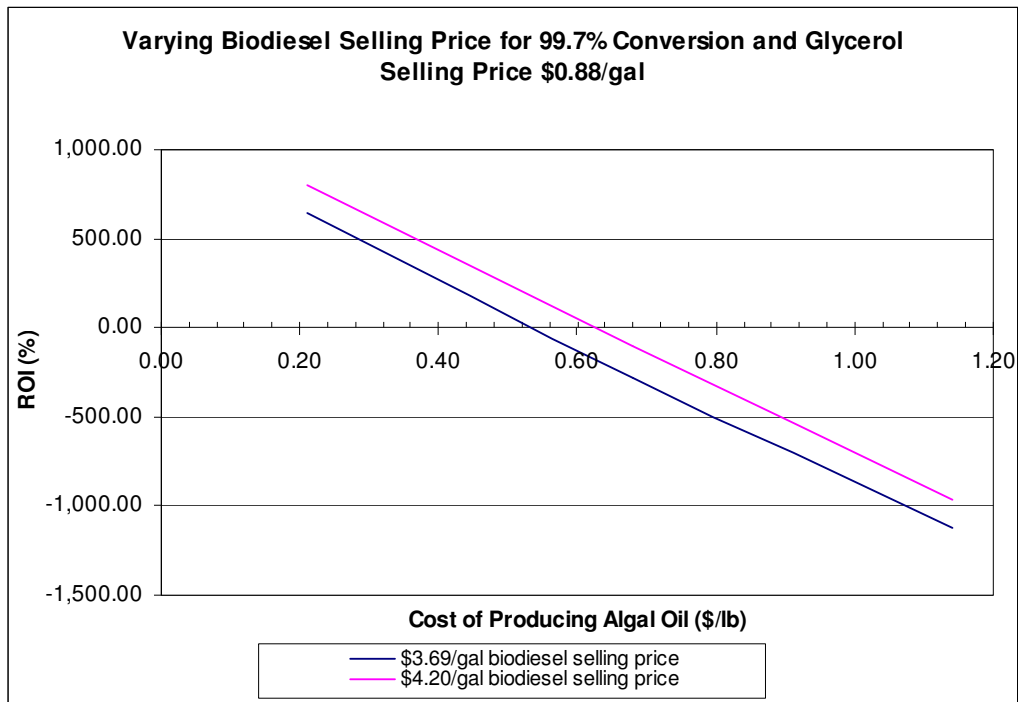
Fig. 4.20. Varying biodiesel selling price at constant conversion (99.7%) and constant glycerol selling price ($0.88/gal) for 30% oil content, with process integration.
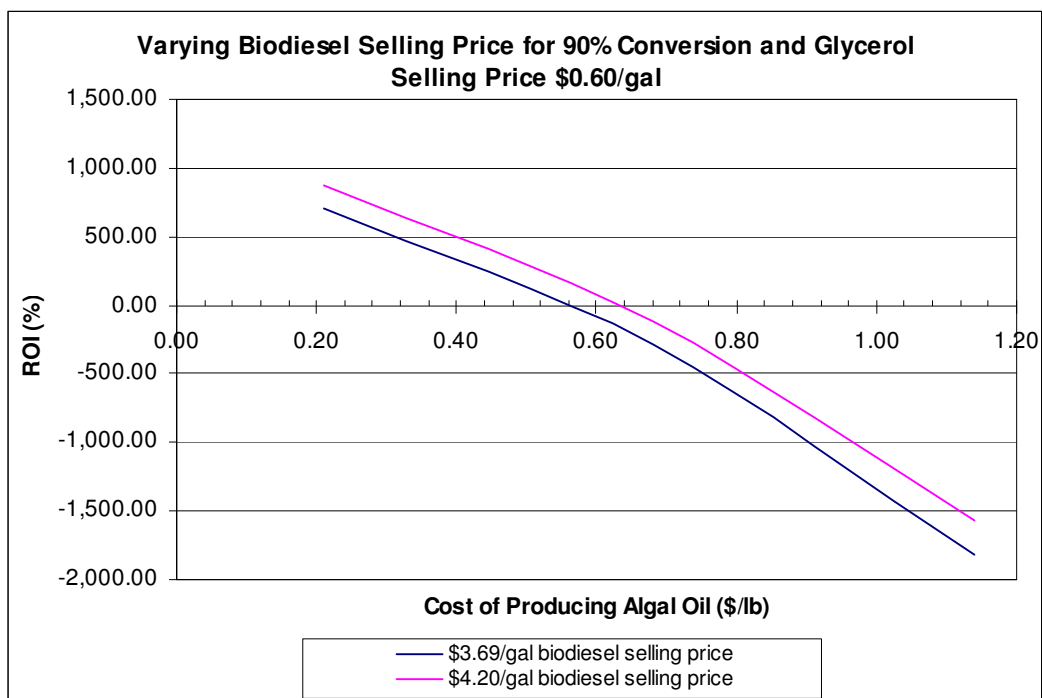
Fig. 4.21. Varying biodiesel selling price at constant conversion (90%) and constant glycerol selling price ($0.60/gal) for 30% oil content, with process integration.
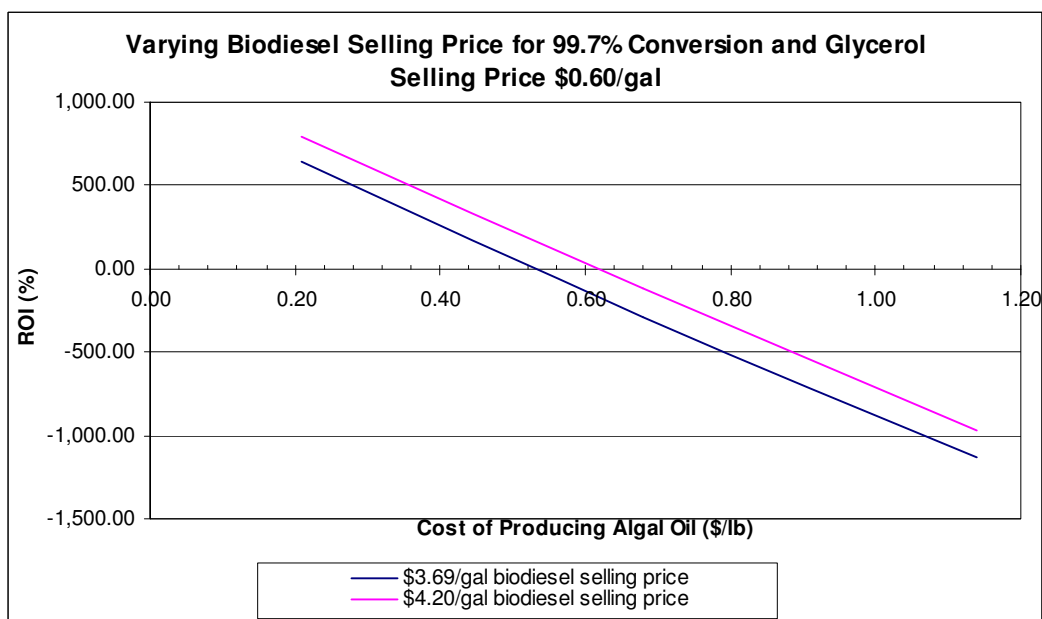
Fig. 4.22. Varying biodiesel selling price at constant conversion (99.7%) and constant glycerol selling price ($0.60/gal) for 30% oil content, with process integration.
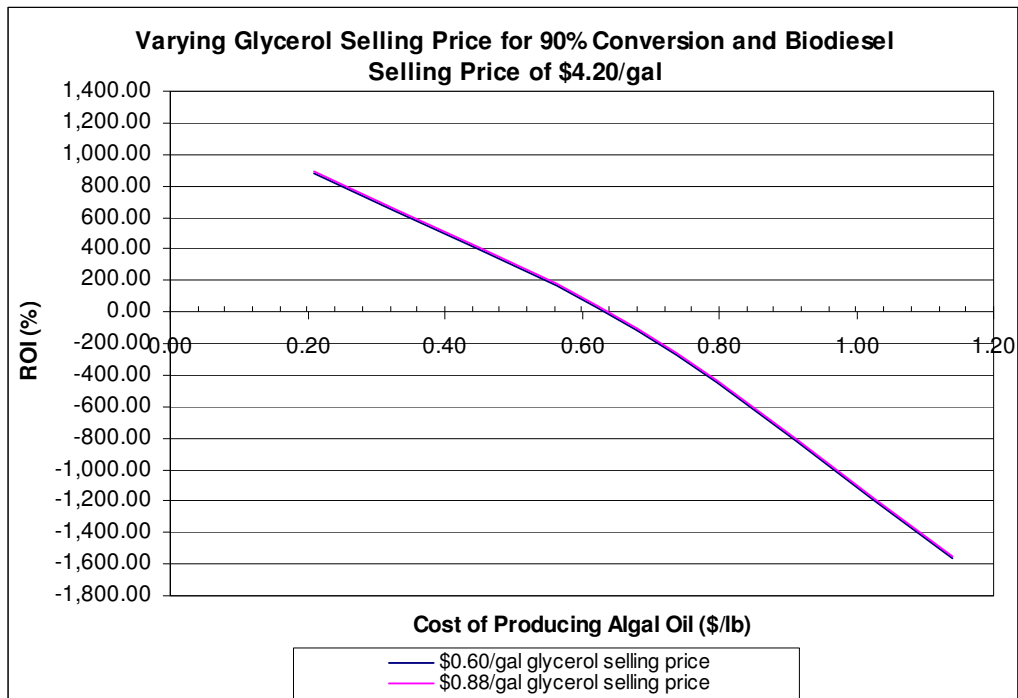
Fig. 4.23. Varying glycerol selling price at constant conversion (90%) and constant biodiesel selling price ($4.20/gal) for 30% oil content, with process integration.
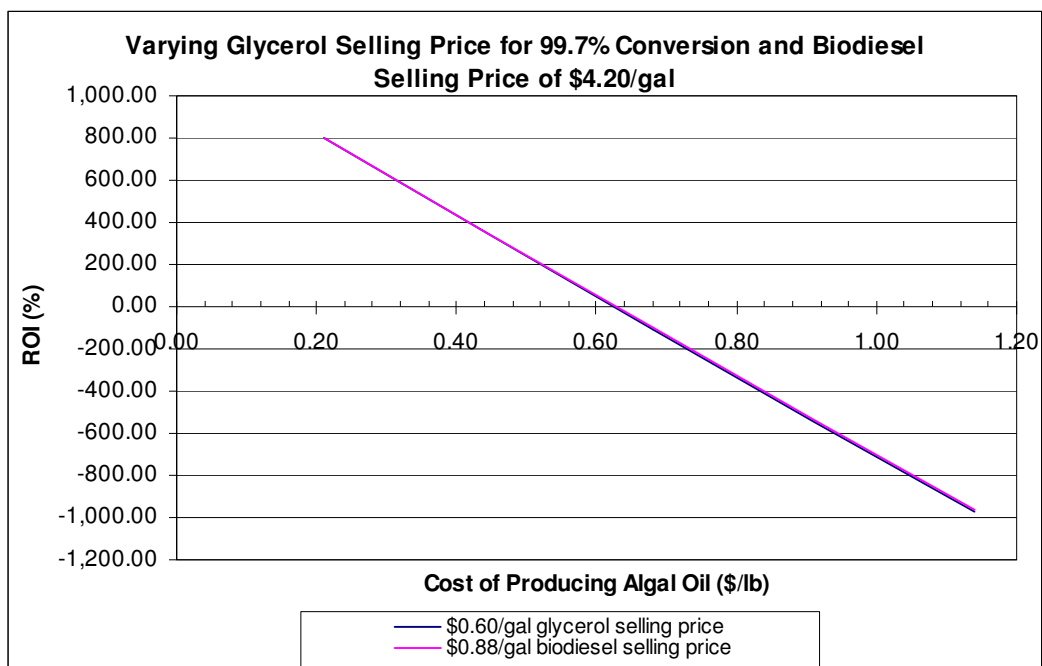
Fig. 4.24. Varying glycerol selling price at constant conversion (99.7%) and constant biodiesel selling price ($4.20/gal) for 30% oil content, with process integration.
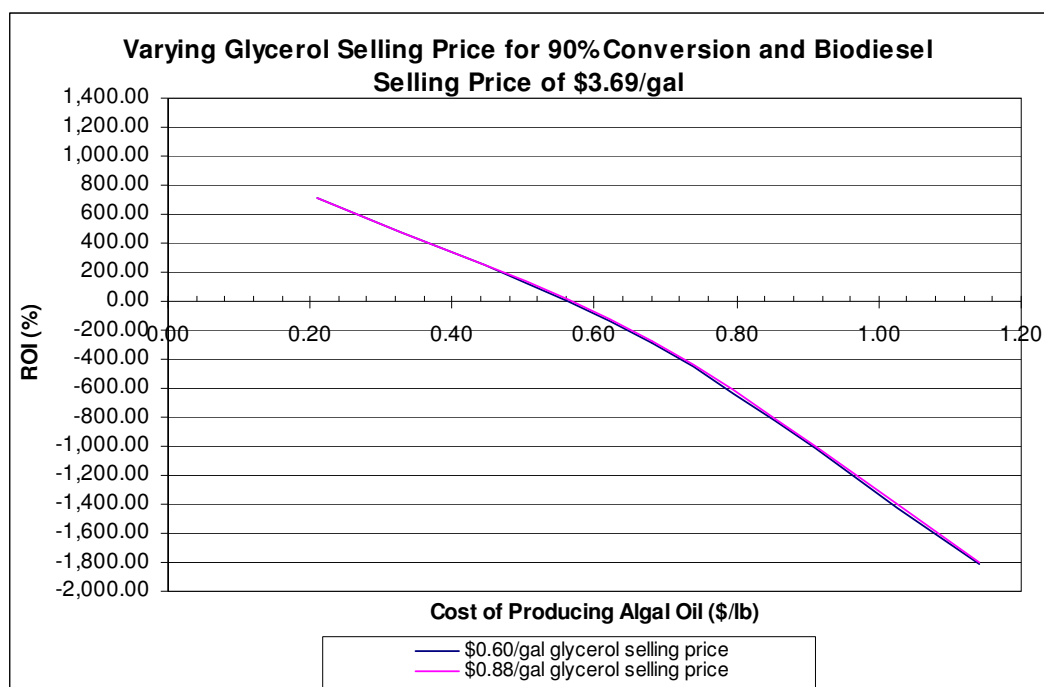
Fig. 4.25. Varying glycerol selling price at constant conversion (90%) and constant biodiesel selling price ($3.69/gal) for 30% oil content, with process integration.

88
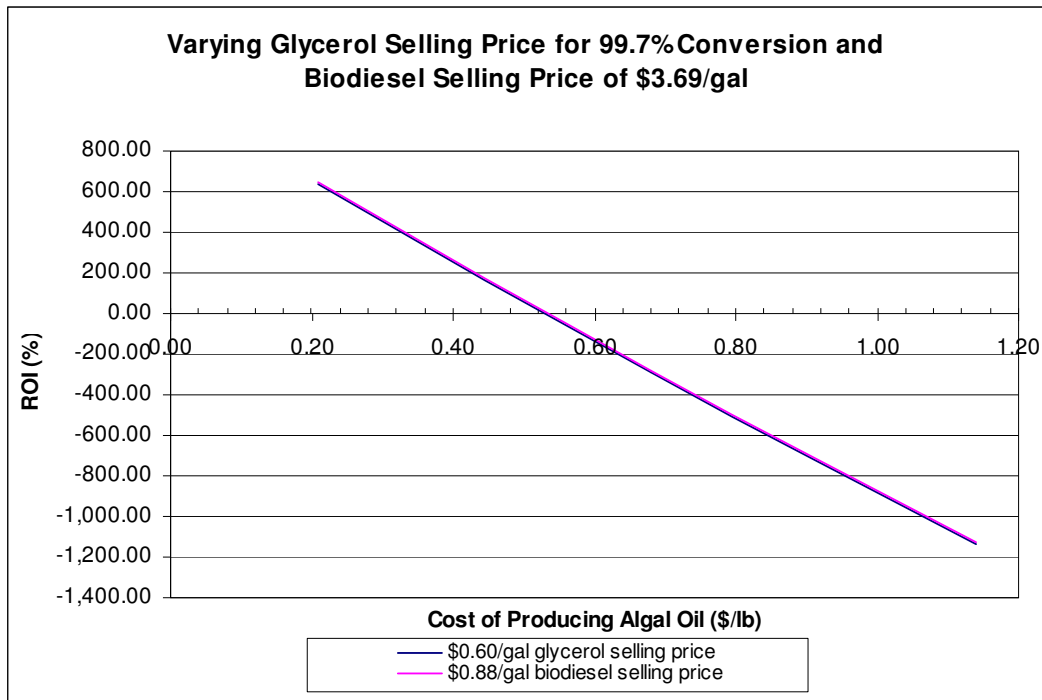
Fig. 4.26. Varying glycerol selling price at constant conversion (99.7%) and constant biodiesel selling price ($3.69/gal) for 30% oil content, with process integration.
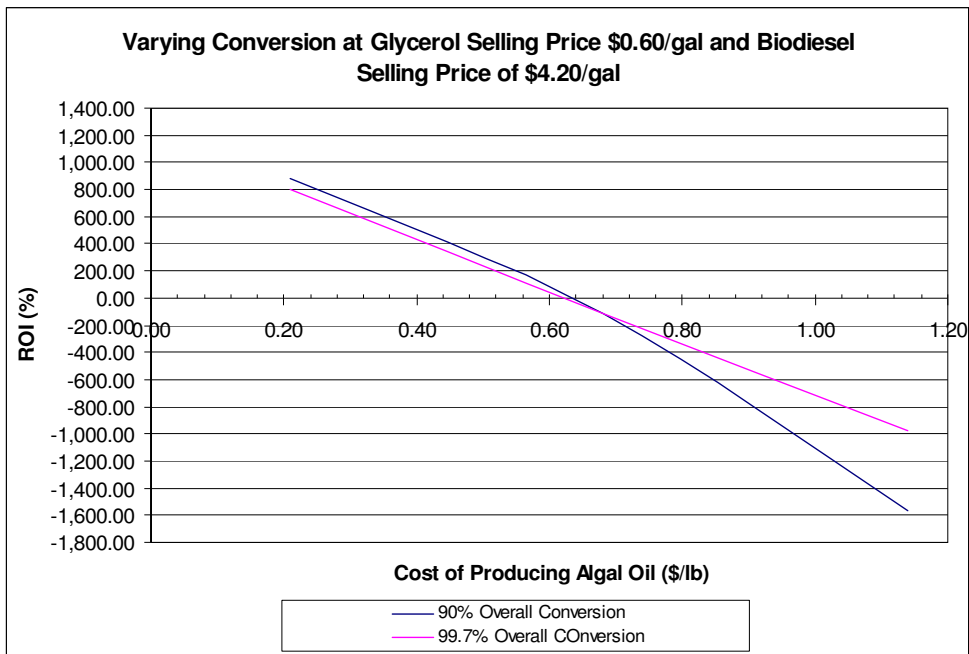
Fig. 4.27. **Varying conversion at constant glycerol selling price ($0.60/gal) and constant biodiesel selling price ($4.20/gal) for 30% oil content, with process integration.**
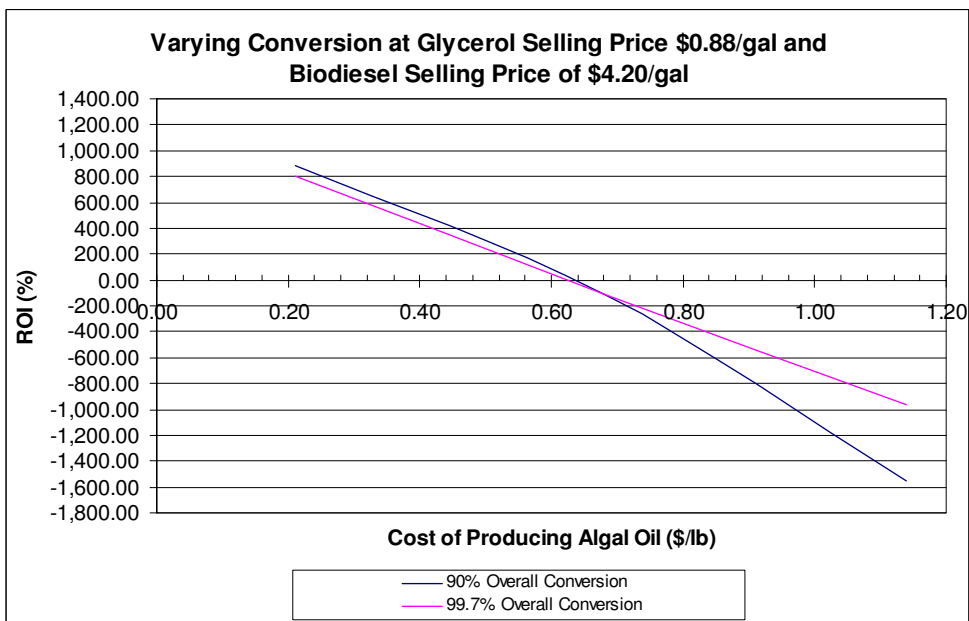
Fig. 4.28. **Varying conversion at constant glycerol selling price ($0.88/gal) and constant biodiesel selling price ($4.20/gal) for 30% oil content, with process integration.**
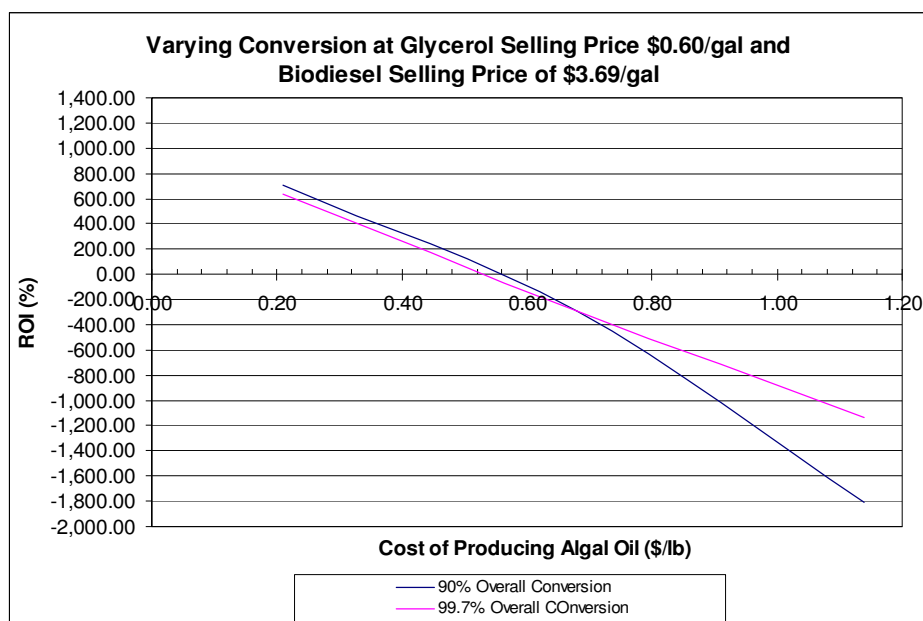
Fig. 4.29. Varying conversion at constant glycerol selling price ($0.60/gal) and constant biodiesel selling price ($3.69/gal) for 30% oil content, with process integration.
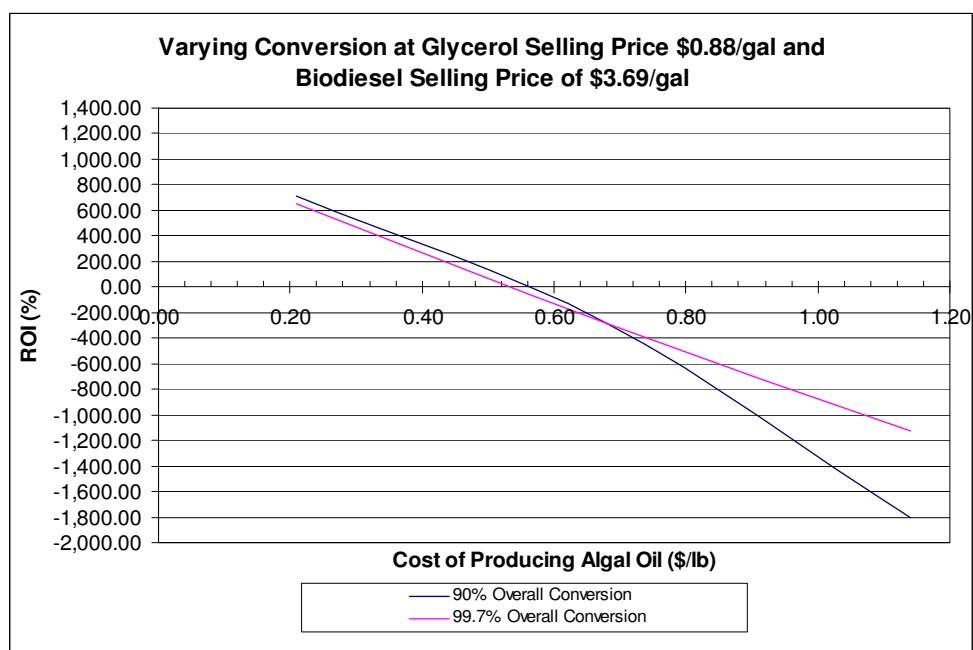
Fig. 4.30. Varying conversion at constant glycerol selling price ($0.88/gal) and constant biodiesel selling price ($3.69/gal) for 30% oil content, with process integration.

4.6   Conclusion

In this study the use of microalgal oil from the Chlorella species to produce biodiesel via a two step alkali catalyzed reaction was investigated and simulated in ASPEN Plus. The oil content of the algae was assumed as 30% and 50%. Using a previously analyzed cultivation process, it deemed possible to obtain algal oil from high performance and low performance alternatives that could be analyzed for both the 30% and 50% oil content cases. The transesterification reaction simulation was performed twice for two cases: 70% conversion through each reactor and 97.7% conversion through each reactor. Economic analysis was performed on ASPEN ICARUS utilizing both simulation results. The economic analysis included sensitivity analyses incorporating the various aspects that were investigated (30% and 50% oil content, high performance and low performance cases, an average of the high and low performance cases, and the two simulation results). As a outcome of analyzing the results of the calculations for profit, payback period, return on investment and breakeven analyses, it was found that the most profitable scenarios for producing biodiesel from Chlorella species microalgal oil are those assuming 50% oil content and incorporating heat integration. These results reveal that the production of biodiesel from microalgal oil will indeed prove profitable and will be a competitive alternative to food derived plant oils under the appropriate conditions (selection of algae, algal growth and processing, selection of a high yield biodiesel process, and achieving high levels of process integration).

5 A MULTI-CRITERIA APPROACH TO SCREENING ALTERNATIVES FOR CONVERTING SEWAGE SLUDGE TO BIODIESEL[*]

5.1 Summary

The search for cheaper feedstock for use in the production of biofuels such as biodiesel has turned attention to various forms of waste products including animal fats, waste oils and now lipids in sludge. With the potential of obtaining sludge at a reduced cost, free, or possibly with incentives, sewage sludge is being investigated as a potential feedstock for biofuel production. For the extraction of oils from the sewage sludge and the subsequent processing, there are various alternatives that should be designed, analyzed, and screened. In developing and screening these alternatives, it is necessary to have a consistent basis for comparing alternatives based on key criteria.

While most of the design studies focus on techno-economic criteria, it is also important to include safety metrics in the multi-criteria analysis. In this work, a detailed economic analysis and a safety evaluation are performed on a process involving extraction of triglycerides and fatty acids, pretreatment of fatty acids (direct conversion to biodiesel), and transesterification of triglycerides to biodiesel. Four solvents, toluene, hexane, methanol and ethanol, are individually used in the extraction process. The resulting triglycerides and fatty acids from each extraction are modeled in the pretreatment process. ASPEN Plus software is used to simulate the detailed process. Economic analysis is performed using ASPEN ICARUS, and scale-up of a previously analyzed process is used to estimate the cost of the biodiesel portion of the process. A new safety metric (referred to as the Safety Index "SI") is introduced to enable comparison of the various solvent extraction processes. The SI is based on solvent criteria as well as process conditions. A case study is presented to demonstrate the insights and usefulness of the developed approach. The results of the techno-economic analysis reveal that of the four solvents used for the initial extraction, hexane and toluene were least costly (2.89 and 2.79 $/gal, respectively). Conversely, the safety analysis utilizing the SI reveals that methanol and ethanol are the safer solvent options. The issue of cost/safety trade-offs is also discussed.

5.2   Introduction

Sewage sludge is an abundant by-product from wastewater treatment facilities. Solids and grease, the main components of untreated sludge, are screened to remove grit and then sent to a primary clarifier from which the primary sludge is obtained. The untreated wastewater from the primary clarifier is treated in an aerobic bio-oxidation unit and sent to a secondary clarifier from which the secondary (activated) sludge is obtained (Mondala, Liang, Toghiani, Hernandez and French, 2009). Sludge treatment comprises a substantial portion (~50%) of the wastewater treatment costs (Boocock, Konar, Leung and Ly, 1992). Handling and disposing of sewage sludge also pose economic and environmental challenges for wastewater treatment facilities. Incineration, land application (i.e., use in fertilization) or landfill disposal of sewage sludge have the potential of releasing toxins and heavy metals into the environment. Therefore, there is a need to identify cost-effective and sustainable solutions to the utilization of raw untreated sewage sludge. Given the lipid content of sludge, there is a promising potential in extracting these oils and converting them to a biofuel (e.g., biodiesel).

Traditional biodiesel feedstocks have primarily been oils from potential food sources (e.g., Haas et al., 2006; Myint and El-Halwagi, 2008). With a growing food versus fuel debate, non-food biodiesel feedstocks are growing in popularity. Feedstocks such as algae have been investigated previously (e.g., Pokoo-Aikins et al., 2009). As mentioned earlier, sewage sludge is another non-food feedstock that offers significant potential for biodiesel production. The feedstock cost is typically the major cost items

for the biodiesel process. As sludge disposal poses a challenge for wastewater treatment plants, the cost of sewage sludge as a biodiesel feedstock is projected to be less than the cost of traditional seed oils.

The purpose of this case study is to develop and apply a systems approach to the assessment of process alternatives for converting sewage sludge to biodiesel. In order to extract oils and fatty acids from sewage sludge, several solvents are considered for extraction. The associated processes are simulated and analyzed. The solvent extraction alternatives are screened based on economic, technical, and safety metrics. The extracted oil is processed via a transesterification process. Computer-aided simulation is used to analyze the process. Sensitivity analysis is also used to evaluate the overall process under different conditions.

5.3   Background

Solvents have been used to extract lipids from sewage sludge. As noted by Boocock et al (1992) such solvents should be selected based on various properties (e.g., polarity, volatility, non-miscibility with water, boiling point, cost, and environmental consideration). Examples of these solvents include toluene (Boocock et al, 1992), methanol, ethanol, and hexane (Dufreche et al, 2007). Once the oils are extracted from the sludge, they can be converted to biodiesel. Dufreche et al (2007) conducted in-situ transesterification of dried sludge and reported a yield of 6.23%. Upon evaluating the cost of the in-situ transesterification process and determined that the cost for producing biodiesel was $3.11 per gallon. A slightly higher but comparable biodiesel cost of $3.23

per gallon was reported by Mondala et al (2009) for another in-situ transesterification process. In both of these studies, acid-catalyzed transesterification was used, because the reactions were occurring directly in the sludge, and the lipid portion of the sludge has high free fatty acid (FFA) content with regard to transesterification. If the lipids (FFAs and TGs) can be separated prior to transesterification, then alkali-catalyzed transesterification can be used to obtain FAMEs. It is anticipated that a higher yield than that obtained by Dufreche et al (2007) (6.23%) and Mondala et al (2009) (between 11.5% and 15.5%) can be achieved with extraction and conversion to biodiesel in separate steps rather than in-situ transesterification.

In addition to the triglycerides in the lipid portion of sewage sludge, there is a fatty acid portion that in general is the bulk ($\sim$ 60%) of the lipid content of the sludge (Higginset al., 1982). When extracted and separated from the other lipids, the fatty acid portion will be significantly greater than 1 wt% free fatty acid (FFA) (Van Gerpen, Shanks, Pruszko, Clements and Knothe, 2004) and thus unacceptable for conversion to biodiesel by traditional alkali transesterification methods. A separate pretreatment method can be employed to convert the fatty acids to biodiesel. Pretreatment is used to reduce the amount of free fatty acid in a feedstock. There are various pretreatment methods such as enzymatic methods, glycerolysis, acid catalysis or acid catalysis followed by alkali catalysis (Van Gerpen et al, 2004) but of particular interest is the acid catalyzed esterification of high free fatty acid feedstock because of the capability of converting free fatty acids directly to methyl esters which can then be purified to obtain biodiesel.

Marchetti and Errazu (2008) esterified free fatty acids in the presence of triglycerides using sulfuric acid as the catalyst to achieve high (>90%) conversion of free fatty acids in a high FFA feedstock (~11% FFA, ~89% TG). Chongkhong, Tongurai, Chetpattananondh and Bunyakan (2007) conducted experiments in which they evaluated conditions that would influence the conversion of FFAs in palm fatty acid distillate (PFAD) to fatty acid methyl esters (FAME). It was found that the weight percent of FAME increased with increased methanol to PFAD ratio, with increased reaction time and with increased reaction temperature. A detailed process for converting PFAD to FAME was presented by Chongkhong, Tongurai and Chetpattananondh (2009). At conditions of 8.8:1:0.05 molar ratio of methanol to PFAD to sulfuric acid catalyst, 60 minutes residence time, 75°C reaction temperature, ~133kPa reaction pressure, an esterification yield of 97% could be achieved from a continuous process (Chonkhong et al, 2009). When the fatty acids in a feedstock are greater than 1 wt% but are not the major portion of the feedstock, acid catalysis followed by alkali catalysis is another pretreatment method that can be used. In this analysis, depending on the feedstock composition of the fatty acid portion from the extraction process, either acid catalysis will be used to lower the FFA content followed by alkali catalysis, or acid catalysis will be used to convert the FFAs directly to methyl esters.

While much attention has been given to the chemistry and economics of biodiesel production, significantly less effort has been dedicated to the inclusion of safety metrics in the design and assessment stages, The need for a method for comparing the inherent safety of conventional chemical processes has been identified for several

years, and many process safety researchers have developed versions of an inherent safety index for use in comparing alternatives. Heikkila et al.(1996) developed an inherent safety index (ISI) for evaluating the inherent safety of process alternatives. Indices were designated for evaluating chemical and process safety. Parameters considered in the evaluation of chemical safety included heat of main reaction, heat of side reaction, flammability, explosiveness, toxicity, corrosiveness, and chemical interaction. Rahman et al. (2005) compared three safety index methods (Prototype ISI, ISI and i-Safe index) by applying them to a methyl methacrylate process case study. Edwards and Lawrence (1993) evaluated the possible relation between plant cost and inherent safety. They investigated the Dow Fire and Explosion Index (FandE I) and the Mond Fire and Explosion Index in developing an index, which they applied to a methyl methacrylate example. Safety index methods can be applied for one unit or for a whole process (e.g., Suardin et al., 2007) or in evaluating different alternative processes (e.g. Prototype ISI, ISI and i-Safe).

5.4   Problem Statement

The main aim in this case study is to design and optimize a process for extracting triglycerides and fatty acids from raw sewage sludge for use in biodiesel production while considering multiple criteria including cost, technical performance, and safety.

Specific objectives can be identified as follows:

- Design an extraction process for obtaining lipids from sewage sludge.

- Optimize the process design.

- Utilize the design to simulate extraction of sludge using different solvents.

- Develop and apply a safety and cost metric for solvent selection.

- Simulate a process design for the pretreatment of fatty acids to biodiesel.

- Utilize the resulting triglycerides from the extraction process in a previously
  developed biodiesel production process.

- Evaluate and analyze the process economics and safety (using a newly
  introduced index).

5.5   Approach

In the overall approach, the first step is to synthesize the process utilizing
information about reaction pathways, production capacity and feedstock from literature
search and other sources (i.e., MSDS, property databases). The process is comprised of
three portions: extraction, pretreatment of fatty acids and biodiesel production. Once the
process is synthesized, the initial flowsheet is defined and simulated using ASPEN Plus.
Mass and energy balances and preliminary process integration are conducted from the
simulation results. Preliminary integration and mass and energy balance results are used
to decide whether or not technical performance criteria are met. If technical criteria are
not met, the previous steps are repeated until they are met. Once the technical criteria
are fulfilled, detailed material and energy integration are performed and the integrated
process is simulated. Next, the integrated process is evaluated to determine economics
and profitability. Subsequently, a newly-introduced safety metric is used to assess the

process. Finally, the alternatives can be screened using multiple criteria to generate a detailed analysis of the process. The overall approach is detailed in Fig. 5.1.
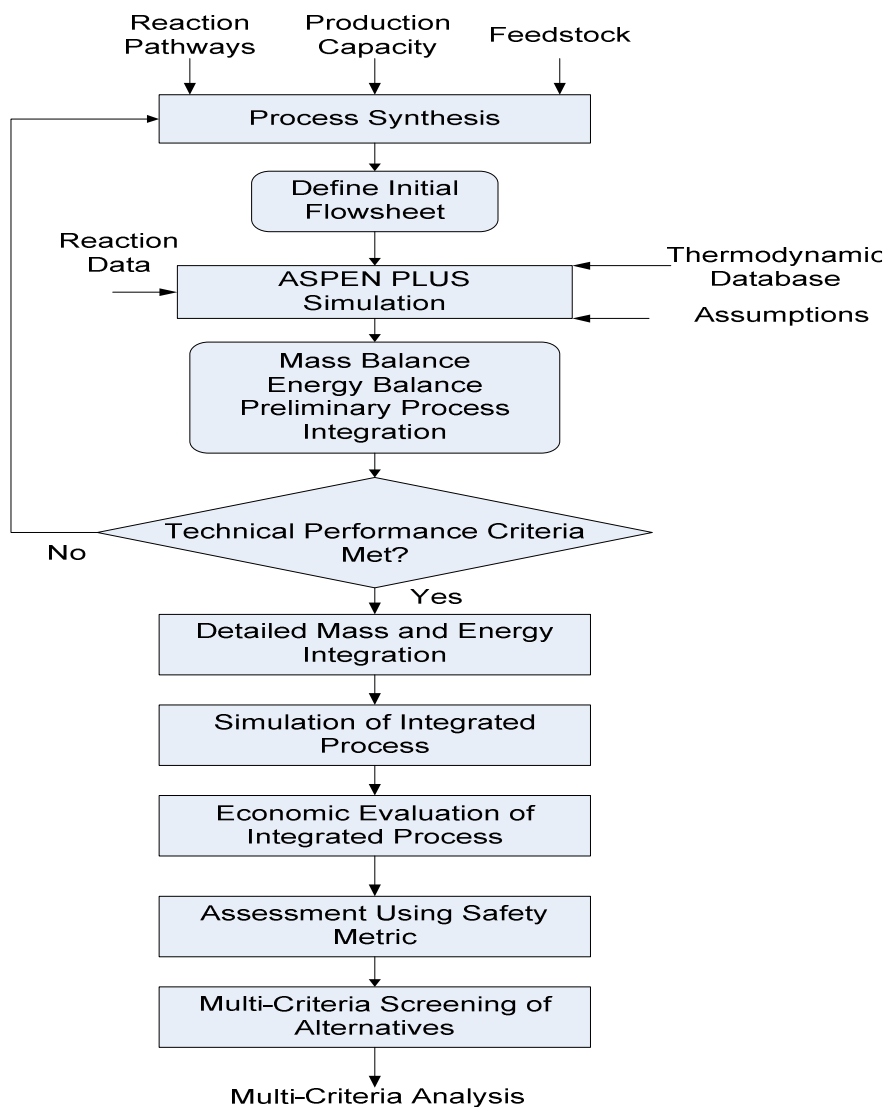
Fig. 5.1. Overall approach for multi-criteria analysis sludge-to-biodiesel.

5.6 Overall Process

The overall process consists of several steps that include three main portions: extraction, pretreatment, and transesterification (Fig. 5.2). The following sections detail these steps.
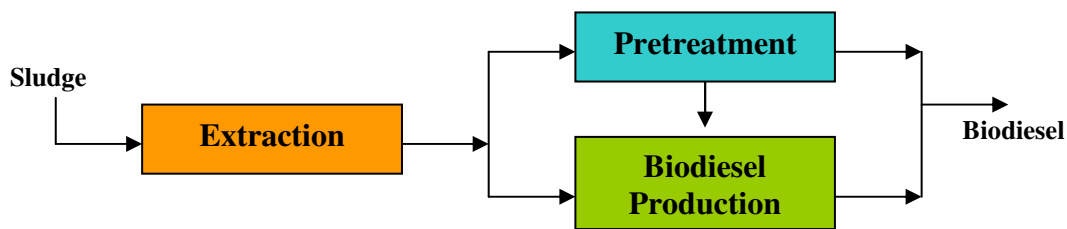
Fig. 5.2. Schematic of main processes for sludge-to-biodiesel.

5.6.1 Extraction

Lipids and oils can be extracted from sewage sludge. Four different solvents were evaluated for use in lipid extraction from sludge and they are toluene, hexane, ethanol and methanol. The first step in the extraction process is to mix sludge and solvent and pump to a filter where solids are removed. Fluids obtained from the filtration process are then distilled to obtain the bulk of the triglycerides (oils) and recover most of the solvent (>98 wt%). Solvent is separated from the triglycerides in a decanter after the stream exiting the distillation column is cooled. In the decanter the

heavier triglycerides (oils) settle to the bottom, are recovered and then are stored in a tank. The recovered solvent is recycled to the process. The fatty acid rich stream from the bottoms of the distillation process includes some residual ash and some valuable triglycerides. Three flash operations are used to remove ash and obtain free fatty acids (FFA). Ash is removed in the first flash operation. The fatty acid rich stream from the top of the flash operation is cooled and enters a decanter where the remainder of the triglyceride is recovered. In extraction processes where methanol and ethanol are used as the solvents, an additional decanter is required in this step to remove residual xylose and obtain the triglycerides (oils). The triglycerides (oils) obtained from the latter decantation process(es) are stored in the same tank as the triglycerides from the first decantation process. Two flash operations are used to separate the free fatty acids from the remaining lipids in the stream. The free fatty acids (FFA) obtained are cooled and stored for use in the pretreatment process. Schematics of the extraction process are depicted for the process utilizing hexane or toluene as solvent (Fig. 5.3) and for the process utilizing methanol and ethanol (Fig. 5.4).
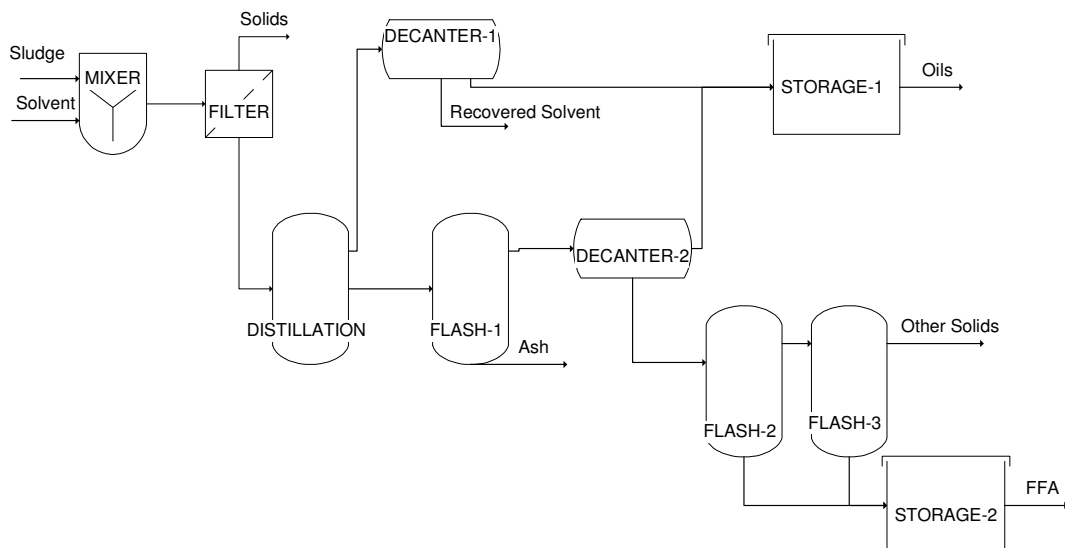
Fig. 5.3. Sewage sludge extraction process with hexane or toluene as solvent.
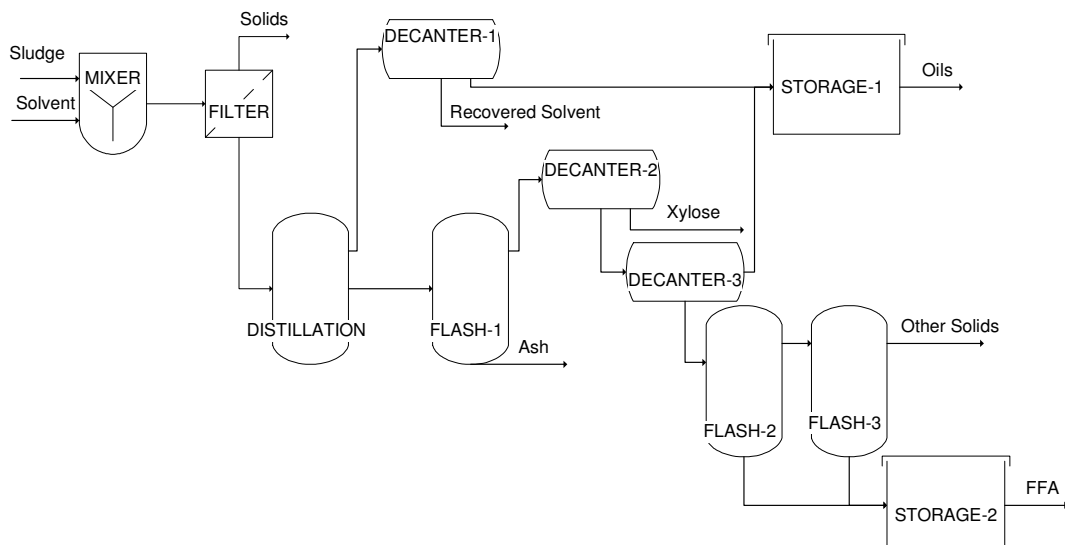
Fig. 5.4. Sewage sludge extraction process with methanol or ethanol as solvent.

Several assumptions were made in order to carry out the process. The amount of solvent required was based on the ratio of sludge to solvent calculated from information from Boocock et al (1992). Ratios of solvent to dried sludge were essentially the same for both the Soxhlet extraction method and the boiling extraction method. For the Soxhlet extraction method, 300ml of solvent was used for 50g of dried sludge, and for the boiling extraction method, 600ml of solvent was used for 100g of dried sludge. By approximating the density of toluene to be 0.8669g/mL, the ratio of solvent to sludge was determined to be 5:1. In the filter used to separate the solids from the fluids, it was assumed that the solid particle size for all solids was 0-2cm and a screen opening of 0.001mm was used.

The composition of the sludge was determined based on the information presented by Higgins et al (1982) for raw dried primary sewage sludge. The composition was then modified to favor the lipids portion based on the fact that composition of sewage sludge varies and that the lipid fraction of sludge can reach up to 35% (Mara and Horan, 2003; Richardson, 1996). The composition of ash was obtained from a paper by Lin (2006). For simplification and to accommodate modeling in ASPEN Plus, only SiO_2, Fe_2O_3, CaO, and MgO were represented. Also, pectins, tannins and carbohydrates were not considered part of the composition because they could not be modeled in ASPEN Plus simulator. Since to composition of sewage sludge varies, this is a reasonable assumption. Table 5.1 presents the composition of sewage sludge that was assumed for the analysis.

Table 5.1 **Composition of raw dried primary sewage sludge**

Component	%total sludge (wt%)
Hemicellulose	1.5
Cellulose	19.3
Lignin	8.2
Ash	22.0
Water	0.8
Amino Acids	13.2
Grease	35.0
Total	100.0

5.6.2 Pretreatment

The FFAs extracted from sludge can be converted to biodiesel via pretreatment, namely acid catalyzed esterification. In the process, one mole of fatty acid reacts with one mole of methanol to form one mole of methyl ester and one mole of water. A process was simulated using ASPEN Plus based on the process used by Chongkhong et al (2009). Conditions specified by Chongkhong et al (2009) were used and comparable results were achieved for a continuous process. These conditions are 8.8:1:0.05 molar ratio of methanol to water to sulfuric acid, reaction temperature of 75°C, reaction pressure of 133kPa, and for every 100g of FAME phase, 10.24g of NaOH- H_2O solution was used for neutralization. A stoichiometric reactor was used in ASPEN Plus for both the esterification and neutralization reactions. In the esterification reactor, a fractional

conversion of 0.97 was assumed. Neutralization is conducted so that the remaining fatty acids are converted to soap and the soap can then be removed. The neutralization reaction is as follows:

```
    O                                       O
    ||                                      ||
  R-C-O-H      +      NaOH           →     R-C-O⁻ Na⁺    +      H₂O
  Fatty Acid        Sodium Hydroxide        Soap                 Water
```
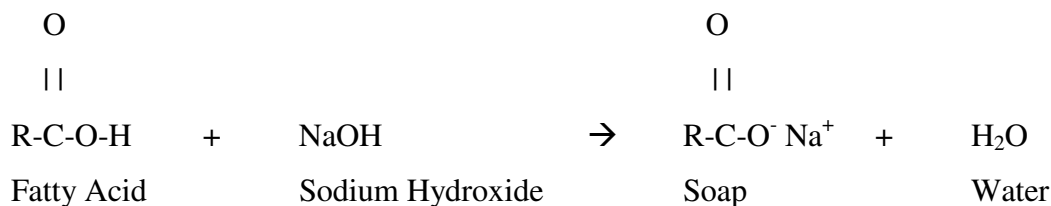
Components of the soap resulting from the neutralization reaction were modeled as ions in ASPEN. Since NaOH- H_2O was used rather than NaOH, two moles of water appear on the products side.

The methyl ester containing stream from the esterification reactor is fed to a separator, which was modeled in ASPEN Plus as a distillation column. Much of the methanol can be removed in this first separator. The stream is cooled and sent to an evaporator (modeled in ASPEN Plus as a flash separator), where almost all the remaining methanol is removed as well as most of the water. Sodium hydroxide is then used to neutralize the remaining product stream. Neutralization is modeled in a stoichiometric reactor at $80^{\circ}C$ and 1 atm. A general separator was used to model the second separation process. In this separator, it was assumed that all of the methyl esters are recovered and only 1% of the soap and water remain with the methyl esters.

Next, the product stream is washed with water. Water needed in the washing process is determined to be 1.2 times the mass flowrate of the FAME phase by linear scaling of that used by Chongkhong et al (2009). The washed FAME phase is sent to yet another separator (also modeled as a distillation column), where some of the water is removed. The remainder of the water is removed in an evaporator (modeled as a flash column), and the purified biodiesel product is obtained.

5.6.3   Transesterification

Triglycerides obtained from the sewage sludge extraction process can be transesterified to biodiesel. Cost and performance data for the transesterification process can be obtained by scaling the processes, as presented by Myint and El-Halwagi (2009). The annual operating cost was scaled linearly, and the fixed cost was scaled utilizing the six-tenths factor rule (Peters et al., 2003).

5.7   Solvent Selection

5.7.1   Safety Metric

As indicated earlier, several index methods exist for evaluating the inherent safety of process alternatives. For ease of application to the process being developed in this work, a simplified matrix was developed. The matrix includes a process or operations specific and a chemical specific category. Chemical specific categories

included here are toxicity and vapor density, and process specific categories consist of temperature and pressure. The elements of the matrix and index are described.

5.7.1.1   Chemical Specific and Operations Specific Categories

The indexing categories under the priority ranking category "Extent of Chemical Hazards" were separated into two sections delineating which categories deal more with the chemical (Chemical Specific) and which categories deal more with the process or operation (Operations Specific). The "Chemical Specific" categories are LC_{50} and Vapor Density, and the "Operations Specific" categories are Temperature Factor and Pressure Factor.

5.7.1.2   Priority Indexing

The selected priority index range is 1-5. For each chemical, a priority index is assigned for each indexing category. The index value assigned depends on the properties of the chemical or the process. In general, the higher priority index is associated with a higher safety risk or an increased hazard, and the lower priority index is linked to a lower hazard.

5.7.1.3 Chemical Specific Categories

5.7.1.3.1. Toxicity- LC_{50}

LC_{50} is a measure of inherent toxicity that is defined as the lethal concentration that would kill fifty percent of the affected population. LC_{50} was chosen for use in the Safety Index (SI), because it is a toxicity measure for which data can be obtained easily for the solvents.   Other toxicity values were considered but rejected during the development of the SI. IDLH, AEGL and ERPG were all considered, but IDLH and AEGL were dismissed due to inconsistencies in their literature values, and ERPG values were dismissed because the LC_{50} values are more applicable for the solvents. The 4-hour inhalation exposure for rats is used as a base measure. An equation is needed for estimation of the LC_{50} for an animal other than a rat and for a time period different from 4 hours. For example if the time is 8 hours rather than 4 hours, the concentration can be divided by 2 (following Haber's rule). Even though concentrations often do not obey Haber's rule, if the chosen equations are applied consistently throughout the assessment, the resulting concentrations should be comparable and valid for use in relative ranking.

5.7.1.3.2. Vapor Density

Toxic chemicals should also be ranked based on other intrinsic properties such as vapor density (compared to STP air =1). Vapor density was chosen, because if the vapor form of the density of the chemical is greater than that of the density of air, the chemical is more likely to disperse close to ground level and affect the population. Therefore, the

greater the vapor density is than air, the higher the priority index assigned to the chemical. It should also be noted that chemicals with a greater density may also be less likely to travel long distances and more likely to affect the immediate population, recognizing that the distance traveled and population affected depend on the specific conditions. The purpose of including the property vapor density is not to address these scenarios but to use a general property for comparing the chemicals aside from other specific conditions. If the basis for the vapor density differs from the specified STP air=1, the data for the vapor pressure should be adjusted for the specific conditions.

Vapor pressure and boiling point are two other properties that were initially investigated for inclusion as chemical specific categories but were eventually used in the operations specific categories. It was chosen to relate vapor pressure at a certain temperature to the operating pressure, and to relate boiling point at a certain pressure to the operating pressure.

5.7.1.4 Operations Specific Categories

5.7.1.4.1. Temperature Factor

The temperature factor (T_f) is based on boiling point and maximum operating temperature (MOT, in Kelvin). The equation for the temperature factor is:

$$T_f = \frac{MOT - BP}{BP} \tag{5.1}$$

where MOT is the maximum operating temperature for a process involving the chemical of interest, and BP is the boiling point of the chemical at standard conditions (one atmosphere). For the temperature factor, a higher priority index corresponds to an increased value for T_f and an increased hazard. T_f is unitless.

5.7.1.4.2. Pressure Factor

The pressure factor (P_f) is based on vapor pressure (VP, in atm) and maximum operating pressure (MOP, in atm) for a process involving the particular chemical being investigated. The equation for the pressure factor is:

$$P_f = \left| \ln\left(\frac{MOP}{1atm} \right) \right| + \left| \ln\left(\frac{VP_{MOT}}{VP_{ST}} \right) \right| \tag{5.2}$$

where ST is standard temperature. The equation for calculating pressure factor differs from the one for calculating temperature factor, because in the event that the vapor pressure at the MOT (VP_{MOT}, in atm) approaches the vapor pressure at standard temperature (VP_{ST}, in atm) and the MOP approaches 1 atm the pressure factor approaches zero. Since pressure behaves in more of a logarithmic fashion, the equation chosen for P_f is more suited for evaluating pressure. For the pressure factor, a higher priority index corresponds to the absolute value of P_f moving further from zero and an increased hazard. P_f is unitless.

5.7.1.5 Safety Index, Safety Ranking Matrix and Equation

An overall inherent safety index (SI) table should be prepared for each chemical in question, and the results of the safety and security analysis can be used to rank each chemical. An SI value can be obtained by applying the Safety Ranking Equation (SRE), Equation 3, to each of the priority indices obtained using the Safety Ranking Matrix (SRM). An overall SI value (Equation 4) can then be obtained by summing the SI values for each chemical being evaluated.

The Safety Ranking Equation for use in calculating the SI is as follows:

$$SI_{i,k} = a_{i,1} * LC_{50 i,k} + a_{i,2} * VD_{i,k} + a_{i,3} * T_{f_{i,k}} + a_{i,4} * P_{f_{i,k}} \tag{5.3}$$

where LC_{50} = lethal concentration for 50% of population, VD = Vapor Density, T_f = Temperature Factor, P_f = Pressure Factor and $a_{i,j}$ is a weighting factor for each index parameter, where i corresponds to a chemical, k corresponds to a particular process step (in this case the extraction process step), and where j=1,corresponds to LC_{50}, j=2, corresponds to VD, j=3 corresponds to T_f, j=4 corresponds to P_f.

The overall SI for a given process alternative is calculated as follows:

$$\text{Overall SI}_k = \sum_{i=1}^{n} SI_{i,k} \tag{5.4}$$

Below is an SRM (Table 5.2) for priority categories and indices for ranking the safety levels associated with process chemicals.

Table 5.2   **Safety ranking matrix**

	Extent of Chemical and Process Hazards			
	CHEMICAL SPECIFIC		OPERATIONS SPECIFIC	
Priority Index	LC_{50} (4hr Inhalation- ppm)	Vapor Density (Air =1)	T_f (Temperature Factor)	$|P_f|$ (Pressure Factor)
1	>2,000	<1	<0.2	0-3
2	1001-2000	1-1.9	0.2-0.9	4-6
3	500-1000	2-2.9	1-2	7-9
4	4-500	3-4	3-4	10-12
5	<=3	>=4.1	>5	>12

5.7.1.6   Weighting Factors

Weighting factors can be applied to emphasize index parameters that contribute significantly to the SI. Weighting factors should be applied based on the difference between the largest and smallest index values (ΔI_j), and $a_{i,j}$ is equal to $\Delta I_j + 1$. For a difference in index value of 0, $\Delta I_j = 0$, the weighting factor ($a_{i,j}$) is 1, for a difference in index value of 1 ($\Delta I_j = 1$) the weighting factor is 2, for $\Delta I_j = 2$, the weighting factor is 3, and for $\Delta I_j = 3$, the weighting factor is 4. In this way, the parameters that vary more are weighted more heavily. The difference in index values and corresponding weighting factors are listed in Table 5.3. Data used to determine the Safety Indices for the four solvents are presented in Tables 5.4 and 5.5.

5.7.1.7 Application of Index

In this analysis, the processes are very similar and the main differences arise from the type of solvent used. In order to focus on the differences among the processes, the safety analysis was only conducted for the extraction step, because the solvents are introduced and used almost exclusively in this step. As a result, equations 1-3 are applicable and useful for comparing the chemicals used in the process. Equation 4 is also applicable, but because only one process step is being evaluated, k=1, equations 3 and 4 are the same.

Table 5.3   Change in index values and corresponding weighting factors

Difference in Index values, ΔI_j	Weighting factor, $a_{i,j}$
0	1
1	2
2	3
3	4
4	5

Table 5.4   **Chemical specific data used for safety ranking of extraction solvents**

Chemicals of Interest	MW	LC_{50} (ppm) (time-mode-animal) mode:I=inhalation,O=oral	Vapor Density (Air = 1, unless otherwise indicated)
Ethanol	46.0	20,000ppm (10h)-I (rat)[1]	1.6
Hexane	86.2	48,000ppm (4h) -I (rat or mouse) [2]	3
Methanol	32.0	64,000ppm (4h) -I (rat) [3]	1.1
Toluene	92.1	49000mg/m3(4h) (rat) [4] -I; 400ppm-I (24hr) (mouse) [4,5]	3.1

[1](Fisher Ethanol MSDS, 2009)

[2](HSDB n-Hexane, 2009)

[3](Sysmex MSDS, 2009)

[4](Fisher Toluene MSDS, 2009)

[5](HSDB Toluene, 2009)

Table 5.5   Operations specific data used for safety ranking of extraction solvents

Chemicals of Interest	Boiling Point (^{o}C), @760mmHg	BP (K)	Vapor Pressure (mmHg), @25°C	VP_{MOT} (atm)	VP_{ST} (atm)	Operating Temperature of Unit (K)	Operating Pressure of Unit (atm)	T_f (Temperature Factor) (MOT-P)/BP	P_f (Pressure Factor) $|\ln(VP_{MOT}/VP_{ST})|$ + $|\ln(MOP/1atm)|$
Ethanol	78	351	59.3	180	0.078	588	1	0.675	8
Hexane	69	342	129.3	61.7	0.170	570.5	1	0.668	6
Methanol	64.7	337.7	128	226	0.168	588	1	0.741	7
Toluene	110.6	383.6	28.5	39	0.038	560	1	0.460	7

5.7.2   Cost Analysis

For the raw materials 99.9% of the solvent used in extraction is recovered; therefore, the solvent cost is only assessed for the approximately 1% needed to make up the lost solvent. Water treatment plants incur a cost for sludge handling and processing. It is assumed that plants will be willing to give away or pay an incentive to get rid of raw sludge to avoid the associated costs of dealing with sludge. As a result, it is assumed that the sewage sludge can be obtained for free. An economic analysis was conducted for sewage sludge obtained at no cost.

With the exception of the raw materials and the cost of utilities, information for calculating the annual operating cost, as well as the total capital cost, were obtained from ASPEN ICARUS. A salvage value of 10% and useful life period of 10 years were assumed in calculating the annualized fixed cost.

Feedstock and solvent prices were obtained from the Internet. For the extraction process, the price of each solvent was found through ICIS pricing. Ethanol can be obtained at a cost of $0.27/lb (ICIS Pricing Ethanol, 2009), hexane at $0.45/lb (ICIS Pricing Hexane, 2009), methanol at $0.23/lb (ICIS Pricing Methanol. 2009), and toluene at $0.30/lb (ICIS Pricing Toluene, 2009). Sewage sludge, the feedstock into the extraction process and the main feedstock overall, can be obtained at a cost of $0.03/lb (WDEL News, 2009), for free (Hope, 1986), or with an incentive (of $0.025/lb) (Israel21c, 2009). For the pretreatment process, the price for sodium hydroxide ($0.20/lb) was obtained from ICIS (ICIS Pricing Sodium Hydroxide, 2009), and the price of sulfuric acid ($0.03/lb) was obtained from The Innovation Group (The

Innovation Group, 2009). All items of the operating cost have the same time basis (March 2009).

5.8   Results and Discussion

5.8.1   Extraction

For all extraction processes, the maximum yield of 3.4% was obtained for the triglyceride stream. The yield of fatty acids for extraction using toluene and hexane was 24.8% and 24.9%, respectively. Extraction utilizing methanol and ethanol resulted in a slightly higher fatty acid yield of 25.5% for either process.

5.8.2   Pretreatment

Biodiesel of 99.6% purity and overall yield of 95% was achieved from the pretreatment of fatty acids from the extraction process using various solvents.

5.8.3   Heat Integration of Extraction and Pretreatment Processes

It was found that the heating and cooling duties for toluene and hexane were very similar. The heating and cooling duties were also similar for methanol and ethanol. Heat integration tools (e.g., El-Halwagi, 2006) were used twice, once for toluene and hexane, and again for methanol and ethanol. It was found that the minimum heating utilities and cooling utilities are 9.31 and 8.86 MMBtu/hr, respectively, for the extraction

with toluene and hexane. The minimum heating utilities and cooling utilities are 31.91 and 31.54 MMBtu/hr, respectively, for the extraction with methanol and ethanol. Considerably more heating and cooling utilities are needed for the extraction with methanol and ethanol than for the extraction with toluene and hexane. As was observed in the calculations for heat integration of the extraction process, integration could be performed once for the pretreatment of free fatty acids resulting from toluene and hexane extraction and once for the pretreatment of free fatty acids resulting from methanol and ethanol extraction. The minimum heating and cooling utilities are 9.66 and 2.07 MMBtu/hr, respectively, for pretreatment of free fatty acids from toluene and hexane extraction. For the pretreatment of free fatty acids from methanol and ethanol, the minimum heating and cooling utilities are 8.96 and 1.66 MMBtu/hr, respectively. The minimum heating and cooling utilities for the pretreatment processes are similar. Slightly more heating and cooling utilities are needed for the pretreatment of free fatty acids from toluene and hexane extraction.

Two processes for the extraction of lipids from sewage sludge were developed using ASPEN PLUS. The processes differ primarily in the use of an additional decanter for extraction utilizing methanol and ethanol as solvents.

5.8.4　Economics Results

5.8.4.1　Extraction

Economic analysis results are presented for the extraction processes (Tables 5.6-5.8). It is possible to receive sludge for free an thus the case for sewage sludge received at no cost was evaluated and is labeled as "Free Sludge". Two other cases for obtaining sewage sludge, paying for sewage sludge and receiving an incentive for taking away the sludge, were also evaluated but were not presented here. The cost for utilities includes the savings from integration.

Raw materials costs are essentially the same for all processes and differ only in the cost for the solvent (Table 5.6). Hexane was found to be the most costly solvent, followed by toluene, followed by ethanol, and the least costly solvent is methanol. Although the solvent costs for hexane and toluene are higher than methanol and ethanol for the extraction process, the utilities cost for using methanol and ethanol ($3,556,000/year) are significantly greater than for toluene and hexane ($1,021,00/year) (Table 5.7). The annualized fixed costs are similar for extraction with all solvents but are slightly higher for extraction with methanol and ethanol (Table 5.8).   Annual operating costs and total annualized costs (Table 5.8) for methanol and ethanol are considerably higher, primarily due to the higher utilities costs.

Table 5.6   Raw material costs for extraction processes using free sewage sludge

Raw Materials (Extraction)	Amount (lb/hr)	Unit Price ($/lb)	10^3 $/yr
Toluene – Total	33,333	0.3	800
Hexane – Total	33,333	0.45	1,200
Ethanol –Total	33,333	0.27	720
Methanol –Total	33,333	0.23	613

Table 5.7   Total utilities for extraction processes

Utilities for Toluene or Hexane Extraction	Amount (MMBtu/hr)	Unit Cost ($/MMBtu)	10^3 $/yr
Heating (steam)	18.29	8	1,171
Cooling (Water)	17.85	6	857
Utilities with Integration			
Heating (steam)	9.31	8	596
Cooling (Water)	8.86	6	425
Savings with Integration			*1,006*
Total			*1,021*
Utilities for Ethanol or Methanol Extraction	**Amount (MMBtu/hr)**	**Unit Cost ($/MMBtu)**	**10^3 $/yr**
Heating (steam)	40.96	8	2,621
Cooling (water)	40.58	6	1,948
Utilities with Integration			
Heating (steam)	31.91	8	2,042
Cooling (water)	31.54	6	1,514
Savings with Integration			*1,013*
Total			*3,556*

Table 5.8   **Annual operating cost, annualized fixed cost, and total annualized cost for extraction processes**

Annual Operating Cost (Extraction)	10^3 $/yr
Toluene Extraction Total	2,495
Hexane Extraction Total	2,898
Ethanol Extraction Total	4,969
Methanol Extraction Total	4,886
Annualized Fixed Cost	**$10^3$$**
Toluene Extraction	463
Hexane Extraction	469
Ethanol Extraction	506
Methanol Extraction	522
Total Annualized Cost	**$10^3$$/yr**
Toluene Extraction	2,958
Hexane Extraction	3,367
Ethanol Extraction	5,474
Methanol Extraction	5,389

5.8.4.2   Pre-treatment Economics

Economic analysis results are presented for the pre-treatment of free fatty acids from extraction. The unit operations and equipment for the pretreatment process are the same regardless of the stream entering the process from the extraction process. The stream from the extraction process containing fatty acids (FFA) are very similar in composition, and the raw materials used to process the fatty acid stream are also very

similar, thus the results for the pretreatment costs are also very similar. The raw materials costs for pretreatment are $4.9 MM per year. Cost for utilities including savings from integration is approximately $0.7 MM per year. Annual operating costs are approximately $6.7 MM. The annualized fixed cost for pretreatment is $0.544 MM regardless of which solvent was used in the extraction process. Pre-treatment of the process streams from extraction with toluene and extraction with hexane ($7.251 MM) are slightly more costly than pretreatment of streams from extraction with ethanol and extraction with methanol ($7.239 MM) when comparing the total annualized cost for an annual production rate of 3.5 MM gallons per year.

5.8.4.3   Conversion of Triglycerides to Biodiesel

Based on the work by Myint and El-Halwagi (2008), the biodiesel production process was scaled down for the triglycerides extracted from sewage sludge. The annual operating cost was scaled linearly while the fixed cost was scaled according to the six-tenths rule (Peters, Timmerhaus, and West, 2003). The annual operating cost for biodiesel regardless of the solvent used in extraction is $1.3 MM per year for the conversion of triglycerides from extraction. Annualized fixed cost for the biodiesel production from toluene, hexane, methanol, or ethanol extraction is $52,000/year. Total annualized cost for the biodiesel production from any of the four solvents is $1.3 MM per year. For the biodiesel processing, it is assumed that the process equipment and procedures are the same for the streams regardless of which solvent was used in the initial extraction step. Moreover, the flowrate and composition of the triglyceride stream

entering the biodiesel step are very similar. For this reason, the total annualized cost for the biodiesel process is essentially the same ($1.34 MM) regardless of which solvent was used for extraction.

5.8.4.4 Economics for Overall Process

For the overall process, the resulting economics vary when different solvents are used in the initial extraction step. From the results for the total annualized cost for the overall process, using methanol or ethanol as the initial solvent leads to a higher total annualized cost ($14 MM per year) than for the case of using toluene or hexane ($12 MM). Annual production rates for the overall process are very similar (4.1 MM gallons per year). Although toluene and hexane were the more costly solvents for biodiesel production, the overall processes utilizing methanol and ethanol in the extraction steps have a higher cost. The resulting prices (in $/gal) for biodiesel production from oils from the solvent extraction of sewage sludge are (for free sludge) 2.79 when using toluene, 2.89 when using hexane, 3.37 when using methanol and 3.39 when using ethanol.

5.8.4.5 Safety Metric

A greater index value corresponds to a higher safety risk. Based on the assessment utilizing the Safety Index (SI), toluene has the greatest index value, followed

by hexane, followed by methanol, and finally ethanol. Parameter values for the solvents

are listed in Table 5.9. The resulting index values can be seen in Table 5.10.

Table 5.9   Values for the safety index categories

Chemical Alternatives	LC_{50} (ppm)	Vapor Density (Air =1)	Tf (Temperature Factor)	|Pf| (Pressure Factor)
Ethanol	20,000	1.59	0.68	8
Hexane	48,000	3	0.67	6
Methanol	64,000	1.11	0.74	7
Toluene	>400	3.1	0.46	7

Table 5.10   Index values for the safety index

Chemical Alternatives	LC_{50}	Vapor Density (Air =1)	Tf (Temperature Factor)	|Pf| (Pressure Factor)	Total Safety Index (without weighting factor)	Total Safety Index (with weighting factor)
Ethanol	1	2	2	3	8	18
Hexane	1	4	2	2	9	22
Methanol	1	2	2	3	8	18
Toluene	5	4	2	3	14	45

In Table 5.9, the category values used to calculate the safety index values are presented. The toxicity values (LC_{50} in ppm), vapor density, boiling point temperature and vapor pressure at standard temperature were found in Material Safety Data Sheets (MSDS) and are presented in Tables 5.4 and 5.5. Vapor pressure at maximum operating temperature was extrapolated using Antoine's Equation. Antoine's Coefficients were found in Yaw's Handbook (Yaws, Narasimhan and Gabbula, 2005). Boiling point temperature and the operating temperature for the unit with the highest temperature and Eq. (1) were used to calculate the temperature factor (Tf). Vapor pressure at maximum operating temperature, vapor pressure at standard temperature and maximum operating pressure of the extraction process were used along with Eq. (2) to calculate the pressure factor (Pf). The maximum operating pressure for each solvent in the extraction process is 1atm, the portion of Eq. (2) involving MOP goes to zero leaving only the VP portion. Equation 3 was then used to calculate the index values for all the parameters (toxicity, vapor density, T_f, P_f) for each solvent.

Recommendation of a solvent depends on a company's goals. Safety and cost are usually high priorities within a company. There are tradeoffs that a company must make when making decisions pertaining to safety and cost. The tradeoff for selecting ethanol or methanol, which were characterized as the safest would be an increased cost. The cost penalty will be a 20% increase but the safety index will be enhanced by 60%. Although toluene is the least costly of the solvents, looking at the tradeoffs between cost and safety, the penalty for safety would be higher than the penalty for cost. Since methanol is used in the pretreatment and biodiesel steps of the process and methanol is

the one of the safest of the solvents evaluated, it may be of benefit to use methanol as the solvent and modify the process to reduce costs. Safety analysis should be done at the design stages along with analysis of other criteria to obtain a comprehensive evaluation of a process. For example, if methanol is used in the extraction step, it may be possible to eliminate some of the separation processes and send the methanol along with the fatty acid, triglycerides or both to the pretreatment process. If cost is the main deterrent to using a certain solvent, it should not be eliminated without further evaluation. In modifying or redesigning a process, a new comprehensive (including safety and cost) evaluation would be necessary to determine the benefits or drawbacks of the modified process.

5.9   Conclusions

A systematic procedure was introduced for the design, simulation, integration, screening, and analysis of sewage sludge-to-biodiesel process. Different solvent extraction alternatives were considered, and the associated process flowsheets were simulated and analyzed. In addition to techno-economic metrics, a new safety metric was introduced that is based on a combination of the solvent properties and the process conditions. A case study was solved to focus on extracting oils from sewage sludge followed by pretreatment, transestrification, and separation. The cost of utilities (such as for the extraction process for methanol or ethanol) and the price of solvents and other raw materials (such as methanol for the biodiesel processes) are key factors in the profitability of the process. Safety, as well as cost and performance, should be

considered in the evaluation and selection of process alternatives. Based on a detailed economic analysis, the process utilizing toluene is the least costly followed by hexane and methanol, with ethanol being the most expensive, especially due to the high demand of utilities for the extraction with methanol and ethanol in comparison to the extraction with hexane and toluene. On the other hand, based on the safety index calculations, ethanol and methanol are the preferred solvents followed by hexane with toluene being the least safe. The estimated cost of biodiesel for the overall process with sewage sludge provided for free is $3.39 per gallon for ethanol, $3.37 per gallon for methanol, $2.89 for hexane, and $2.79 per gallon for toluene used as the extraction solvent.

6 FLEXIBLE DESIGN STRATEGIES FOR THE MULTI-FEEDSTOCK BIOREFINERY

6.1 Summary

Numerous feedstocks are currently being explored for the production of biofuels in integrated biorefineries. Given the variation in the availability and cost of these feedstocks, it is important to include flexibility in the design to enable the use of various feedstocks in the biorefinery. In this work, the objective is to introduce a systematic procedure for incorporating flexibility in the design phase of the development of a multi-feedstock biofuel production process. A flexible design must incorporate all the evaluated feedstocks, and thus, differing demands on the design of the process. A mathematical formulation is developed for determining the optimal flexible design for a biorefinery that is to accommodate all feedstocks to be incorporated. Various objective functions can be utilized for the flexible plant depending on the purpose of the flexibility analysis. Such objectives include minimizing the retrofitting cost or maximizing production or throughput. A biodiesel production process is examined in the case study. It incorporates a base case for soy transesterification and two possible pretreatment options for waste cooking oil and free fatty acids extracted from sewage sludge.

6.2   Introduction

Biofuels and the integrated biorefinery are the subject of growing interest in the world of alternative energy. With increased concerns about greenhouse gases (GHG), the debates are inevitable on food versus fuel, the availability and evaluation of new and alternative feedstock, and the surge of multi-feedstock biorefineries. One example of the growing emergence of the multi-feedstock biorefinery is the spread of multi-feedstock biodiesel plants in the United States. An increasing number of biodiesel producers are being classified as "Multi-feedstock" producers. Of the 185 producers that are members of the National Biodiesel Board, 104 are classified as Multi-feedstock producers (National Biodiesel Board, 2010). Multi-feedstock is a term used for plants that can use a variety of feedstocks, namely vegetable oils, animal fats, and recycled cooking oil or yellow grease (National Biodiesel Board, 2010). Fifteen additional producers utilize more than one feedstock, but were not classified as Multi Feedstock producers. Biodiesel is a relevant and growing alternative fuel source that helps to ease the demand on fossil fuel resources and a biorefinery model that can be used to study the use of multiple feedstocks.

In the case of biodiesel, most vegetable oils are refined oils, meaning that free fatty acid (FFA) content is low enough that no pretreatment is needed. Refined oils, however, are more costly feedstocks than waste or recycled oils. Non-food feedstocks such as animal derived feedstocks (i.e. renderings and tallow) or waste oils or recycled oils (which can be from vegetable or animal sources) are typically less expensive than refined oils, but have a higher FFA content and require pretreatment (an added cost).

Examples of waste oils or recycled oils are restaurant cooking oil, yellow grease, and trap grease.   The use of waste cooking oil in scheduling biodiesel production was recently explored by Elms and El-Halwagi (2009). Oils from sewage sludge are yet another non-food oil source that is being used for biodiesel production.

Sewage sludge is an unwanted component of wastewater treatment facilities. There are significant lipids in the sludge that can be extracted for use in biodiesel production. These lipids include triglycerides that can be transesterified to fatty acid methyl esters (FAME) which can then be purified to obtain biodiesel. Fatty acids comprise a large portion (up to 60%) of the lipids portion of sludge. Fatty acids can be pretreated (i.e. by acid catalyzed esterification) to obtain FAME which can then be further processed to obtain biodiesel. The extraction of lipids from sewage sludge was investigated by Pokoo-Aikins et al. (2010). It is of importance to the flexibility analysis for the multifeedstock biorefinery to include a variety of feedstocks.

The flexible biorefinery is one that accommodates a variety of feedstocks with no change to the design of the overall plant. It can be described as a "super plant" that can process all pre-determined feedstocks because the flexible plant must have components (processing units, capacity, operating conditions, etc.) for processing all these feedstocks. The concept of flexibility is one that has been under investigation for many years. Flexibility analysis is useful for the design, synthesis, and analysis of chemical processes with levels of uncertainty. For example, for the multi-feedstock biorefinery, there are uncertainties about when each feedstock will be utilized and design and operating conditions are based on feedstock choices.

Pioneering works in the area of flexibility include works by Grossmann and Sargent (1978), Halemane and Grossmann (1983), Grossmann, Halemane, and Swaney (1983), Swaney and Grossmann (1985), and Grossmann and Floudas (1986) in which earlier works dealt with uncertainty in process design and the term "flexibility" increased in usage over time. More recently Pintaric and Karavanja (2008) addressed the problem of reducing the set of uncertain parameter points in flexibility problems through the approach of identifying a minimum set of critical points. These authors proposed three methods for reducing the set of uncertain parameters by identifying critical points. Al-Qahtani and Elkamel (2008) investigated multisite integration for a petroleum refinery network with different combinations of feedstock (namely various crude oil compositions). In their analysis, they developed a mixed-integer linear program with the overall objective of minimizing total annualized cost. While their study does not mention flexibility directly, conceptually it is a flexibility problem as it involves modeling and optimization of a multicomponent and multifeed process that involves varying degrees of uncertainty.

Flexibility analysis was used by Cheng and Friis (2007) to evaluate a milk treatment process. They utilized modeling tools (e.g. Pro/II) and engineering know-how to simulate a treatment process for reducing the fat content in milk. Flexibility is important in this study because a goal in the food production industry is to maximize the usefulness of an existing production line by making the production line able to handle a variety of products and production demands. The flexibility formulation used for optimization is presented in their paper. A parallel hybrid algorithm was developed by

Moon et al. (2008) for flexiblility analysis. The algorithm employs stochastic search and nearest constraint projection to solve the flexibility index problem for the global solution aside from design constraint convexity. They employ a flexibility formulation by Floudas, Gumus, and Ierapetritou (2001). Flexibility formulation involves several components. Constraints can be functions of vectors of design variables, state variables, controls, fixed parameters, and uncertain parameters. The objective function can be subject to inequality and equality constraints. Flexibility formulations found in the literature include some or all of the components mentioned above. Notwithstanding the usefulness of the previous works, it is important to develop a specific approach for the design of flexible biorefineries which focuses on the problem of utilizing multiple feedstocks. This is the primary objective of this work.

6.3   Motivation and Problem Statement

An increasing number of plants are being built as multi-feedstock facilities to accommodate for the variation in availability, economics, and environmental impact of feedstock alternatives. A base case process for a flexible plant must utilize pre-specified feedstocks to induce flexibility for biorefineries. Effective biorefineries need to be flexible in their capabilities to process a variety of feedstocks in a way that promotes sustainability and profitability. In order to do this, it is a goal to:

1 Incorporate feedstock flexibility into the process design of the biodiesel production facilities.

2 Conduct a techno-economic study for the selected feedstock options

The main aim of this work is to develop a systematic approach for the flexible design of a biofuel production process. Formally stated, the problem is as follows: Given is a biofuel production facility of with a certain base-case design handling a specific feedstock. A certain number (N_f) of alternative feedstock that can be used in conjunction with or in lieu of the current feedstock are available for consideration. It is desired to develop a systematic procedure for the design of a flexible biorefinery that accommodates all of the pre-specified feedstocks that may be utilized while maintaining a certain production level and quality constraints.

The following questions will be addressed:

• Should feedstocks be processed separately or co-fed?

• Which scenarios must be accounted for in the process design?

• What retrofitting changes are needed?

The following is a more detailed statement of the problem to be addressed.

Given a continuous process with:

- A set of pretreatment units P= {p|p= 1,2, …, N_{PT}}. Each pretreatment unit, p, has a set of input streams $INPUT_p = \{m_p \mid m_p = 1,2..., N_p^{in}\}$ and a set of output streams $OUTPUT_p = \{n_p \mid n_p = 1,2..., N_p^{out}\}$. Input stream m_p, has a flowrate, A_{m_p}, composition of component x as $Y_{m_p,x}$. Output stream n_p, has a flowrate, B_{n_p}, composition of component x as $Z_{n_p,x}$.

- A set of common process units C= {c|c= 1,2, …, N_{CP}}. Each process unit, c, has a set of input streams $INPUT_c = \{m_c \mid m_c = 1,2..., N_c^{in}\}$ and a set of output streams $OUTPUT_c = \{n_c \mid n_c = 1,2..., N_c^{out}\}$. Input stream m_c, has a flowrate, A_{m_c}, composition of component x as $Y_{m_c,x}$. Output stream n_c, has a flowrate, B_{n_c}, composition of component x as $Z_{m_c,x}$.

- A set of product discharges from the process R = {r|r= 1,2, …, N_R}.

- A set of intermediate streams I= {i|i= 1,2, …, N_I} that are redirected back into the process. Input stream m_i, has a flowrate, A_{m_i}, composition of component x as $Y_{m_i,x}$. Output stream n_c, has a flowrate, B_{n_i}, composition of component x as $Z_{m_i,x}$.

- A set of waste discharges from the process L = {l|l= 1,2, …, N_L}.

- A set of feedstocks (scenarios) SCENARIOS = {s|s = 1,2, …, N_s} . Within each scenario, s, there is a certain feedstock, pre-treatment units, processing units, production capacity, etc.

It is desired to form a systematic procedure that can be used to determine an optimal flexible process design that accommodates for a variety of feedstocks.

6.4   Approach

Process modifications to the base-case design include two options. The first option is that modifications are conducted by manipulation of certain design and operating variables for each unit within permissible ranges. The second option is the addition of new units (e.g., pretreatment systems). The task of designing a flexible plant must insure that the design is retrofitted so as to accommodate for the various scenarios. A scenario can be described by a certain flowrate of a feedstock. For each scenario, the process may have to be retrofitted to adjust plant requirements (raw materials, unit operations, equipment, operating conditions, etc.) that are needed for processing a certain feedstock. Given the multiple scenarios, it is necessary to adopt a process integration approach which addresses the various scenarios simultaneously. Fig. 6.1 shows a schematic of individual scenarios. The optimal design of the flexible plant should take into consideration the requirements of each scenario such that the selected flexible plant design can process any pre-specified feedstock without any change to the plant design. Fig. 6.1 also gives a schematic representation of the flexible plant which will simultaneously consider the two scenarios.
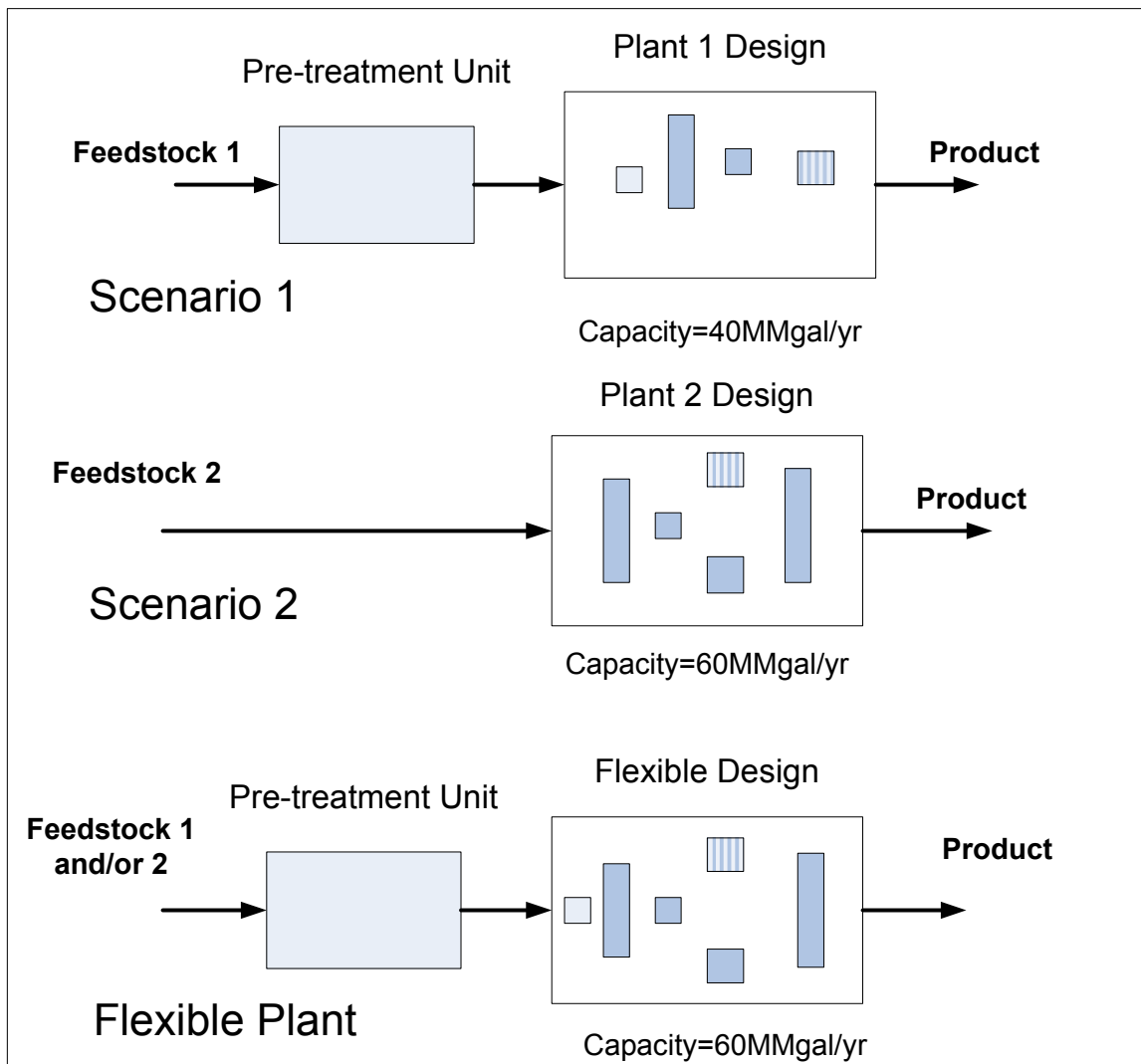
Fig. 6.1. Schematic of individual scenarios and of a flexibly designed plant for the simultaneous consideration of the two scenarios.

The first step in the approach is the development of a structural representation of the problem. A source-sink representation (Fig. 6.2) is used to connect the flow of the core processes that can occur within each scenario and to provide a superstructure to facilitate optimization. For each scenario, there are potential pre-treatment units,

common process units, input and output flows to and from these units (respectively), and waste, product, and intermediate streams. Flows from the pretreatment or common process units can split into fractions which can later mix with other streams.
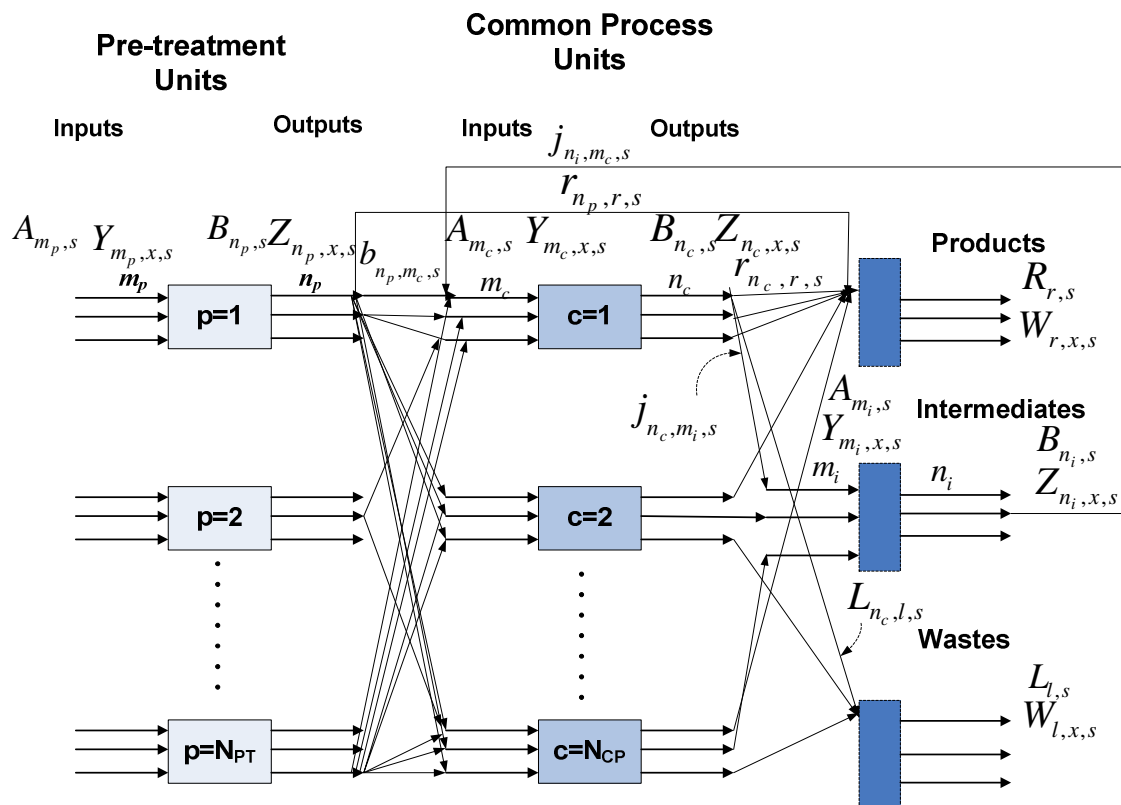
Fig. 6.2. A structural representation of the problem.

Given this structure, the following mathematical formulation is developed:

6.4.1   Pretreatment Units

The mass balance equation for the pretreatment unit p for scenario s is written as:

$$\sum_{n_p} B_{n_p,s} = \sum_{m_p} A_{m_p,s} \qquad\qquad \forall p, s \qquad\qquad (6.1)$$

and the xth component balance for unit p for scenario s is given by:

$$\sum_{n_p} B_{n_p,s} * Z_{n_p,x,s} = \sum_{m_p} \left(A_{m_p,s} * Y_{m_p,x,s} + \text{Net\_Gen}_{p,x,s} \right) \qquad \forall x, p, s \qquad (6.2)$$

where the additional index, s, in the flowrate and composition terms, corresponds to the scenario for which these flowrates and compositions are considered. Additionally, the performance model for unit p for scenario s is expressed as a set of algebraic equations represented by:

$$(B_{n_p,s}, Z_{n_p,x,s} : n_p = 1,2,..., N_p^{out}, x = 1,2,...N_{\text{components}})$$

$$= f_p(A_{m_p,s}, Y_{m_p,x,s} : m_p = 1,2,..., N_p^{in}, x = 1,2,...N_{\text{components}}, d_{p,s}, o_{p,s}) \qquad \forall p, m_p, x, s \qquad (6.3)$$

6.4.2   Common Process Units

The mass balance equation for the common process unit c for scenario s is written as:

$$\sum_{n_c} B_{n_c,s} = \sum_{m_c} A_{m_c,s} \qquad\qquad \forall c, s \qquad\qquad (6.4)$$

and the xth component balance for unit c for scenario s is given by:

$$\sum_{n_c} B_{n_c,s} * Z_{n_c,x,s} = \sum_{m_c} \left(A_{m_c,s} * Y_{m_c,x,s} + \text{Net\_Gen}_{c,x,s} \right) \qquad \forall x, c, s \qquad (6.5)$$

and the performance model for the cth common process unit is expressed as a set of algebraic equations represented by:

$$(B_{n_c,s}, Z_{n_c,x,s} : n_c = 1,2,..., N_c^{out}, x = 1,2,...N_{components})$$

$$= f_c(A_{m_c,s}, Y_{m_c,x,s} : m_c = 1,2,..., N_c^{in}, x = 1,2,...N_{components}, d_{c,s}, o_{c,s}) \qquad \forall c, m_c, x, s \qquad (6.6)$$

6.4.3   Product Streams

The flowrate of the rth product out of the process is written as:

$$R_{r,s} = R_{r,s}^{PT} + R_{r,s}^{CP} = \sum_{p} \sum_{n_p} r_{n_p,r,s} + \sum_{c} \sum_{n_c} r_{n_c,r,s} \qquad \forall r, s \qquad (6.7)$$

where

$$R_{r,s}^{PT} = \sum_{p} \sum_{n_p} r_{n_p,r,s} \qquad \forall r, s$$

is the total flowrate of the rth product from the N_{PT} pretreatment units for scenario s and

$$R_{r,s}^{CP} = \sum_{c} \sum_{n_c} r_{n_c,r,s} \qquad \forall r, s$$

is the total flowrate of the rth product from the N_{CP} common process for scenario s. The xth component material balance for the rth product stream from the process is given by:

$$R_{r,s} * W_{r,x.s} = (R_{r,s}^{PT} * W_{r,x,s}^{PT}) + (R_{r,s}^{CP} * W_{r,x.s}^{CP})$$

$$= \sum_{p} \sum_{n_p} r_{n_p,r,s} * Z_{n_p,x,s} + \sum_{c} \sum_{n_c} r_{n_c,r,s} * Z_{n_c,x,s} \qquad \forall r, x, s \tag{6.8}$$

where $r_{n_p,r,s}$ is the flowrate assigned from the n_p to the rth product stream and $W_{r,x,s}$ is the composition of component x in the product outlet stream for scenario s and

$$R_{r,s}^{PT} * W_{r,x,s}^{PT} = \sum_{p} \sum_{n_p} r_{n_p,r,s} * Z_{n_p,x,s} \qquad \forall r, x, s \tag{6.9}$$

is the xth component material balance for the rth product stream coming from the N_{PT} pretreatment units and

$$R_{r,s}^{CP} * W_{r,x,s}^{CP} = \sum_{c} \sum_{n_c} r_{n_c,r,s} * Z_{n_c,x,s} \qquad \forall r, x, s \tag{6.10}$$

is the xth component material balance for the rth product stream coming from the N_{CP} common process units.

6.4.4 Intermediate Block

The mass balance equation for the intermediate block i for scenario s is written as:

$$\sum_{n_i} B_{n_i,s} = \sum_{m_i} A_{m_i,s} \qquad \forall i, s \tag{6.11}$$

and the xth component balance for the intermediate block for scenario s is given by:

$$\sum_{n_i} B_{n_{ic},s} * Z_{n_i,x,s} = \sum_{m_i} \left(A_{m_i,s} * Y_{m_i,x,s} + Net\_Gen_{i,x,s} \right) \qquad \forall x, i, s \tag{6.12}$$

6.4.5 Waste Streams

The flowrate of the lth waste stream out of the process is given by:

$$L_{l,s} = L_{l,s}^{PT} + L_{l,s}^{CP} = \sum_{p} \sum_{n_p} l_{n_p,l,s} + \sum_{c} \sum_{n_c} l_{n_c,l,s} \qquad \forall l,s \qquad (6.13)$$

where

$$L_{l,s}^{PT} = \sum_{p} \sum_{n_p} l_{n_p,l,s} \qquad \forall l,s \qquad (6.14)$$

is the total flowrate of the lth product from the N_{PT} pretreatment units for scenario s and

$$L_{l,s}^{CP} = \sum_{c} \sum_{n_c} l_{n_c,l,s} \qquad \forall l,s \qquad (6.15)$$

is the total flowrate of the rth product from the N_{CP} common process for scenario s.

The xth component material balance for the lth waste stream from the process is given by:

$$L_{l,s} * W_{l,x.s} = (L_{l,s}^{PT} * W_{l,x,s}^{PT}) + (L_{l,s}^{CP} * W_{l,x.s}^{CP}) \qquad (6.16)$$

$$= \sum_{p} \sum_{n_p} l_{n_p,l,s} * Z_{n_p,x,s} + \sum_{c} \sum_{n_c} l_{n_c,l,s} * Z_{n_c,x,s} \qquad \forall l,x,s \qquad (6.17)$$

where $l_{n_p,l,s}$ is the flowrate assigned from the n_p to the lth product stream and $W_{l,x,s}$ is the

composition of the waste outlet stream and

$$L_{l,s}^{PT} * W_{l,x,s}^{PT} = \sum_{p} \sum_{n_p} l_{n_p,l,s} * Z_{n_p,x,s} \qquad \forall l,x,s \qquad (6.18)$$

is the xth component material balance for the lth product stream coming from the N_{PT}

pretreatment units and

$$L_{l,s}^{CP} * W_{l,x.s}^{CP} = \sum_{c} \sum_{n_c} l_{n_c,l,s} * Z_{n_c,x,s} \qquad \forall l,x,s \qquad (6.19)$$

is the xth component material balance for the lth product stream coming from the N_{CP} common process units.

6.4.6   Mixing and Splitting of Streams

6.4.6.1   Splitting of Source n_p

The term $b_{n_p,m_c,s}$ is used to represent the flowrate assigned from source n_p to destination m_c for scenario s. Output flow from the pretreatment units has four possible destinations.   Flow from source n_p can be directed to other pretreatment units, the common processing units, final product streams, and/or waste streams. The material balance for the splitting of source n_p is written as:

$$B_{n_p,s} = \sum_{p}\sum_{n_p} b_{n_p,m_p,s} + \sum_{c}\sum_{n_c} b_{n_p,m_c,s} + \sum_{r} r_{n_p,r,s} + \sum_{l} l_{n_p,l,s} \quad \forall p,n_p,s \qquad (6.20)$$

6.4.6.2   Mixing of the Split Flowrate before the m_c^{th} Input to the cth Common Process Unit

Some streams leaving the common process units join the intermediate stream and are recycled back to the common process units.   These streams along with streams leaving the pretreatment units contribute to the m_c^{th} input to the cth common process unit. The term $j_{n_i,m_c,s}$ represents the flowrate from the intermediate source n_i to destination m_c for scenario s. The material balance for the mixing of the split flowrate before the m_c^{th} input to the cth common process unit is written as:

$$A_{m_C,s} = \sum_{p} \sum_{n_p} b_{n_p,m_c,s} + \sum_{i} \sum_{n_i} j_{n_i,m_c,s} \qquad \forall c,m_c,s \qquad (6.21)$$

and the xth component balance for scenario s is expressed as:

$$A_{m_C,s} * Y_{m_c,x,s} = \sum_{p} \sum_{n_p} b_{n_p,m_c,s} * Z_{n_p,x,s} + \sum_{i} \sum_{n_i} j_{n_i,m_c,s} * Z_{n_i,x,s} \quad \forall c,m_c,x,s \qquad (6.22)$$

6.4.6.3 Splitting of the n_c^{th} Stream L:eaving c^{th} Common Process Unit

Streams leaving the N_{CP} common process units can split and are destined to one of three destinations. These output streams (n_c) are destined for waste streams, product streams and intermediate streams that are recycled back to the process. The term $l_{n_c,l,s}$ represents the flowrate assigned to the lth waste stream, the term $r_{n_c,r,s}$ represents the flowrate assigned to the rth product stream, and the term $j_{n_c,i,s}$ represents the flowrate assigned to the ith intermediate stream. The material balance for the splitting of the n_c^{th} stream is written as:

$$B_{n_c,s} = \sum_{l} l_{n_c,l,s} + \sum_{r} r_{n_c,r,s} + \sum_{i} j_{n_c,i,s} \qquad \forall c,n_c,s \qquad (6.23)$$

6.4.6.4 Intermediate Streams Recycled back into the Process

Mixing of the Split Flowrate before the n_i^{th} Input to the Intermediate Block

The flowrate of the ith intermediate stream from the N_{CP} common process units is written as:

$$J_{i,s}^{CP} = \sum_c \sum_{n_c} j_{n_c,i,s} \qquad \forall i, s \qquad\qquad (6.24)$$

and the xth component material balance for the ith intermediate stream from the N_{CP} common process units is given by:

$$J_{i,s}^{CP} * W_{i,x,s}^{CP} = \sum_c \sum_{n_c} j_{n_c,i,s} * Z_{n_c,x,s} \quad \forall i, x, s \qquad\qquad (6.25)$$

Streams leaving the common process units serve as the m_i^{th} input to the intermediate block. The term $j_{n_c,m_i,s}$ represents the flowrate from source n_c to destination m_i for scenario s. The material balance for scenario s for the mixing of the split flowrate before the m_i^{th} input to the intermediate block is written as:

$$A_{m_i,s} = \sum_{n_c} j_{n_c,m_i,s} \qquad \forall\, i, m_{\,i}, s \qquad\qquad (6.26)$$

and x^{th} component balance for scenario s is given by:

$$A_{m_c,s} * Y_{m_c,x,s} = \sum_{n_c} j_{n_c,m_c,s} * Z_{n_c,x,s} \qquad \forall i, m_i, x, s \qquad\qquad (6.27)$$

6.4.6.5   Splitting of the n_i^{th} Stream Leaving the Intermediate Block

The term $j_{n_i,m_c,s}$ refers to the flowrate from source n_i to destination m_c for scenario s. The material balance for the splitting of source n_i is written as:

$$B_{n_i,s} = \sum_c \sum_{n_c} j_{n_i,m_c,s} \qquad \forall i, n_i, s \qquad\qquad (6.28)$$

6.4.7   Constraints

The design and operating constraints for the pretreatment units are:

$$d_p^{\min} \leq d_{p,s} \leq d_p^{\max} \tag{6.29}$$

$$o_p^{\min} \leq o_{p,s} \leq o_p^{\max} \tag{6.30}$$

The design and operating constraints for the common process units are:

$$d_c^{\min} \leq d_{c,s} \leq d_c^{\max} \tag{6.31}$$

$$o_c^{\min} \leq o_{c,s} \leq o_c^{\max} \tag{6.32}$$

The product demand and composition constraints are expressed as:

$$R_{r,s} \leq R_{r,s}^{Demand} \tag{6.33}$$

$$W_{r,x}^{\min} \leq W_{r,x,s} \leq W_{r,x}^{\max} \tag{6.34}$$

The flowrate constraints for the $m_p{}^{th}$ input to the pretreatment unit and the $m_c{}^{th}$ input to the common process units are given by:

$$A_{m_p}^{\min} \leq A_{m_p,s} \leq A_{m_p}^{\max} \tag{6.35}$$

$$A_{m_c}^{\min} \leq A_{m_c,s} \leq A_{m_c}^{\max} \tag{6.36}$$

The composition constraints for $m_p{}^{th}$ input to the pretreatment unit and the $m_c{}^{th}$ input to the common process units are given by:

$$Y_{m_p}^{\min} \leq Y_{m_p,s} \leq Y_{m_p}^{\max} \tag{6.37}$$

$$Y_{m_c}^{\min} \leq Y_{m_c,s} \leq Y_{m_c}^{\max} \tag{6.38}$$

6.4.8   Objective Function

Different objective functions can be pursued depending on the goals of a flexibility study.   One objective is to maximize the plant throughput of feedstocks subject to a limitation on the retrofitting budget, i.e.:

$$\max \sum_{s} \sum_{m_c} A_{m_c,s} \tag{6.39}$$

subject to:

$$\psi_{\cos t} = h(\bar{d},\bar{o}) \leq Budget \tag{6.40}$$

and the rest of the aforementioned model.

$$g(\bar{d},\bar{o}) \leq 0 \tag{6.41}$$

Another objective is to minimize the retrofitting cost subject a certain desired throughput.   Another objective is to maximize the product flowrate subject to budget constraints, inequality constraints and constraints on the flowrate through the common process unit, i.e.:

$$\max \sum_{s} \sum_{r} R_{r,s} \tag{6.42}$$

subject to constraints (6.40) and (6.41).

The optimization problem may be one in which the objective function is to minimize the cost of retrofitting the plant for a given flowrate of each feedstock. This can be the cost of retrofitting an existing plant with a flexible design or the cost of a

grassroots flexible multi-feedstock plant. which can be expressed as a function of the design and operating variables:

$$\min\left(\sum_p \psi(\bar{d}_p,\bar{o}_p) + \sum_c \psi(\bar{d}_c,\bar{o}_c)\right) \tag{6.43}$$

6.5   Case Study

The base case is a process for producing 40 MM gal/yr of biodiesel from soy bean oil. More information on this process can be found in literature (e.g., Myint and El-Halwagi, 2009; Elms and El-Halwagi, 2009). It is desired to retrofit the plant to enable it to be flexible enough to process free fatty acids (FFAs) extracted from sewage sludge. In addition to retrofitting existing units, it is also necessary to introduce a pretreatment system to extract the lipids and render them in a state that can be processed by the trans-esterification plant.

The process model and cost data were developed by running ASPEN Plus and ICARUS for the two feedstocks at different flowrate scenarios. For each flowrate scenario, the simulation results identify the necessary extent of retrofit for each process unit, the size of the pretreatment facility, and the associated cost of retrofitting. These data were entered into the optimization formulation which was solved to maximize the product flow subject to a constraint on available budget for the total retrofitting cost (pretreatment and trans-esterification). Three values for the budget constraint were used. A plot of the product flowrates versus budget constraint, pretreatment and retrofitting cost is given in Fig. 6.3.
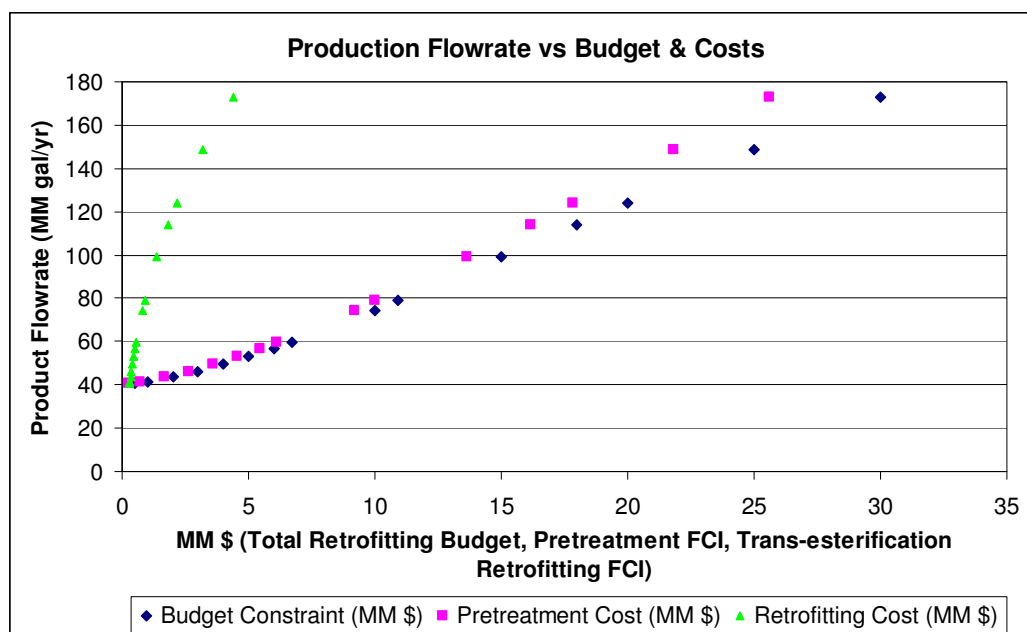
Fig. 6.3. Product flowrate versus budget constraints and pretreatment and trans-esterification FCI.

6.6   Conclusions

A systematic procedure has been introduced to design multi-feedstock flexible biorefineries. A mathematical formulation has been developed for use in representing, modeling and optimizing the flexible multi-feedstock biorefinery. By considering soy bean and sewage sludge as feedstocks, a case study has been solved to demonstrate the concepts of flexibility as applied to the multifeedstock biodiesel example. An objective function for maximizing throughput was applied. Results for the example indicate that there will be added costs for retrofitting the plant to accommodate the necessary added pretreatment units as well as increase in the flowrate. These results can be used to determine an optimum level of flexibility by comparing the cost of flexibility versus the value added by producing more biofuel.

7 SYNTHESIS OF FLEXIBLE HEAT EXCHANGER NETWORKS FOR MULTI-FEEDSTOCK BIODIESEL PRODUCTION PROCESSES

7.1 Summary

Feedstock cost is the largest contributor to the biodiesel production cost. Therefore, it is important to enable the process to handle multiple feedstocks to correspond to fluctuations in price and availability of the potential feedstocks. By designing processes that can utilize a variety of feedstocks, choices can be made to promote the use of the more sustainable and economical feedstock at a given time. One aspect of process flexibility that is being examined is the synthesis of heat exchanger networks in the flexible biodiesel production process. In this work, the objective is to develop a systematic procedure for incorporating flexibility and heat integration in the design phase of the development of a flexible feedstock production process. A two-phase biodiesel production process is examined for three feedstocks in the case study. Each feedstock incurs differing demands on the design of the process. A mathematical formulation is developed for determining the heat exchange network design for the case study. By incorporating the three feedstock scenarios into a combined mixed integer linear program formulation, a flexible heat exchange network scheme can be developed

that provides for a process that can accommodate the heating and cooling demands of the various scenarios.

7.2 Introduction

Biodiesel is now a well established renewable fuel source often used as an alternative to petroleum derived diesel since it can be used in existing engines with comparable performance (EPA, 2002). Traditionally, biodiesel is made from vegetable oils (or plant oils or plant seed oils), animal fat and tallow. Common vegetable oils used in preparing biodiesel are soy, sunflower, safflower, canola, and palm. Palm oil has numerous positive aspects for biodiesel production. Among those attributes are that it has a high production rate, a high oil content, 27 times more oil can be produced per acre than soy, and life cycle analysis (LCA) reveals that production of palm based biodiesel can reduce green house gases (GHG) more than other leading vegetable oils (Abdullah et al., 2009). Algal oil is a non-food feedstock that is growing in research, development and use for biodiesel production. Like terrestrial plants, algae grow by photosynthesis through the use of CO_2, water and sunlight. Unlike terrestrial plants, algae grow in aqueous suspensions, allowing for more efficient use of H_2O, CO_2, and other nutrients. This gives algae the potential to produce more oil per unit area than other crops currently being used for biodiesel production. Lipid content in algae has been known to increase up to 50% under the appropriate conditions. An in-depth investigation into the potential use of algae to produce biodiesel was conducted by Pokoo-Aikins et al., 2009.

The use of non-food oil sources for biodiesel production is particularly important with newer biodiesel plants that are being constructed. Some older biodiesel plants continue to use vegetable oils but many are converting to utilize a variety of feedstock, not just vegetable oils. Government incentives drive down the cost of vegetable oils and the cost of pretreating waste oils and triglycerides from waste animal fats and algal oil means that vegetable oils will continue to be used to produce biodiesel until the cost of using non-food feedstock is stable and lower than the cost of using food feedstock options. In the meantime an increasing number of biodiesel plants are being considered "Multi Feedstock" producers because they utilized a variety of feedstock namely vegetable oils, animal fats and recycled cooking oil or yellow grease (National Biodiesel Board, 2010). Use of variety of feedstock is important as biodiesel continues to be an important fuel source that is helping to reduce the demand on petroleum based fuels and shows continued promise as one of many alternative fuel sources for a more fuel-stable future. The United States biodiesel industry has seen a dramatic increase since the implementation of the Biodiesel Tax Incentive. Production has increased from 25 million gallons per year in 2004 to 450 million gallons per year in 2007 to 700 million gallons per year in 2008 (National Biodiesel Board, 2009).

Synthesis of heat exchange networks (HEN) is a topic that has gained much interest in recent decades and one in which there are still many opportunities for study, contribution and expansion of the design methods. A detailed review of the research in the area of the synthesis of HENs was reported by Furman and Sahinidis (2002). Papaoulias and Grossmann (1983) proposed an approach for designing heat recovery

networks based on the transshipment model. Integral to the HEN design problem is an understanding of heat integration and the pinch analysis method (Linnhoff and Hindmarsh, 1983).

The flexible heat exchange network problem is considered an over-design problem (i.e. over-design of process units). It generally involves considering uncertainties in relation to streams entering the process (e.g. stream number, flowrate, and temperature). A new approach to the design of flexible heat exchange networks was introduced by Chen (2005) that considers cost while incorporating disturbances in range of source-stream temperatures and flowrates. A strategy for synthesizing flexible networks that account for variations in process inlet stream flowrates, temperatures (HEN) and composition (MEN) was extended to heat and mass exchange networks (Chen and Hung, 2007). Xiangkun et al (2007) also proposed a two-stage approach for the synthesis of flexible multi-stream HENs.

Yee and Grossmann (1990) developed a mixed integer linear program for the simultaneous optimization of utility cost, exchanger areas and the selection of matches. Aaltola (2002) later applied the work of Yee and Grossmann (1990) to the multi-period problem. Zhang (2006) then extended the two works to the application of flexible heat exchange networks.

The term flexibility as it is used in current literature refers to variations in the number of streams, and the flowrates and compositions of the streams. The use of flexibility in this work is broader (i.e. plant flexibility) and which in this case must be achieved by incorporating a variety of feedstock scenarios in the design of the heat

exchange network for the plant. Formulations for the multi-period heat exchange network deal more with a scheduling problem. Multi-period HEN formulations can be modified, extended for and applied to the flexible multi-feedstock facility by considering various scenarios that are time-independent in place of the time horizon of the multi-period HEN problem.

7.3   Motivation and Problem Statement

Although and increasing number of biodiesel plants are becoming or being built as "Multi Feedstock" facilities, the primary feedstock continues to be vegetable oils such as soybean. It is important to consider traditional biodiesel feedstock as well as alternative feedstock such as algal oil in the design of grassroots production facilities or in the retrofitting of existing plants. Feedstock cost is the bulk of the operating cost for the biodiesel production process. Flexibility in feedstock choices could provide an economic and environmental advantage to the biodiesel industry. In order to promote energy conservation which results in cost savings and reduction in greenhouse gas emissions, it is important to design heat-exchange networks that are flexible enough to operate properly even when feedstocks are altered. The main aim of this work is to develop a systematic approach for the flexible heat exchange network design for a biodiesel production process. Formally stated, the problem is as follows:

A given biodiesel production facility has a known production and design process that utilizes a certain feedstock. Available for consideration are a number (N_f) of alternative feedstock that can be combined with or used instead of the current feedstock.

It is desired to develop a systematic procedure for the design of a flexible heat exchange network that accommodates for the various feedstock that may be utilized while maintaining a specified production level and quality.

Question to be addressed are:

- What are the targets for minimum heating and cooling utilities for different feedstock alternatives?

- What is the minimum number of heat exchangers that can be used under variations in types and flowrates of the feedstocks?

- Which heat exchangers should be used and with which feedstock? When?

The following is a detailed statement of the problem to be addressed.

Given a continuous biodiesel production process with:

- A set of operational scenarios: $\{s|s = 1,2, \ldots, N_s\}$. Each scenario corresponds to a given feedstock, throughput, and process operation.

- A set of common process units $C= \{c|c= 1,2, \ldots, N_{CP}\}$. Each process unit, c, has a set of input streams $INPUT_c = \{m_c \mid m_c = 1,2..., N_c^{in}\}$ and a set of output streams $OUTPUT_c = \{n_c \mid n_c = 1,2..., N_c^{out}\}$. Input stream m_c, has a flowrate, A_{m_c}, composition of component x as $Y_{m_c,x}$ and a temperature, T_{m_c}. Output stream n_c, has a flowrate, B_{n_c}, composition of component x as $Z_{m_c,x}$ and a temperature, T_{n_c}.

- For each feedstock operation, s, a set of hot streams $HS_s=\{h_s|h_s= 1,2,\ldots, N_{HS,\, s}\}$, streams that need to be cooled or external heating utilities.

- For each feedstock operation, s, a set of cold streams $CS_s = \{k_s | k_s = 1, 2, \ldots, N_{CS, s}\}$, streams that need to be heated or external cooling utilities.

It is desired to form a systematic procedure that can be used to determine an optimal process design that accounts for heat integration and used to synthesize a flexible heat exchange network (HEN) that operates for a variety of scenarios by incorporating different feedstock.

The problem is presented in a diagram illustrating the common process units, process streams, subsets of hot and cold streams and HENs (Fig. 7.1).
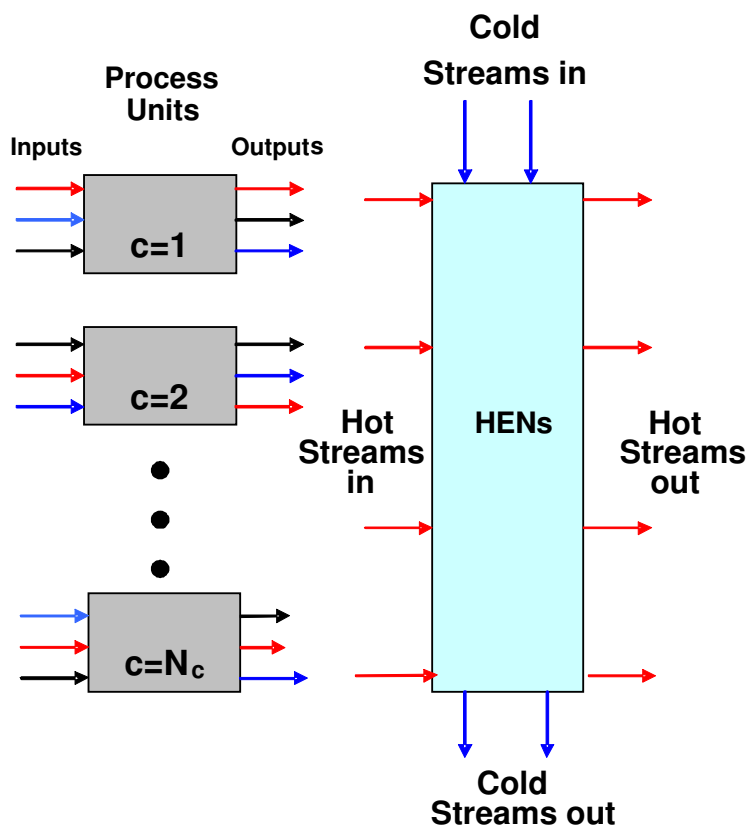
Fig. 7.1. Diagram for the process and HEN.

7.4 Approach

The HEN must be synthesized to account for various expected scenarios. The challenge is to synthesize a single configuration accommodating all expected changes. A number of expected scenarios are identified in advance. A multi-scenario HEN synthesis problem is solved to generate a single network configuration that accommodates all expected scenarios.

Simplifying assumptions were made as follows:

• The scenarios are looked at as individual processes. Each scenario is discretized into N_s components, a set of scenarios is defined as SCENARIOS = $\{s|s = 1,2, \ldots, N_s\}$. The scenarios are taken into account for each feedstock and used in determining the optimal flexible design.

• Process modifications are limited to two options. The first option is that modifications are conducted by manipulation of certain design and operating variables for each unit within permissible ranges. The second option is the addition of new heat exchangers.

The approach for synthesizing the flexible multi-scenario heat exchange network is presented in Fig. 7.2. First, the relevant input data and constraints are gathered and a number of excepted scenarios are identified. Next, the process model is developed with the proper level of detail to account for the process performance in terms of the design and operating decision variables. Then, a linear programming (LP) formulation is developed to incorporate the expected scenarios into the design. The LP formulation is generated for heat integration utilizing data about hot and cold inputs and outputs for each scenario. Next, a mixed integer linear program (MILP) formulation is developed to determine the minimum heating and cooling utility targets for the HEN. The MILP formulations for each scenario are combined to allow the simultaneous optimization of the HEN while accounting for the expected scenarios. An MILP multi-scenario HEN formulation is developed to determine the configuration of the flexible heat exchange network that can address all the variations associated with the expected scenarios.
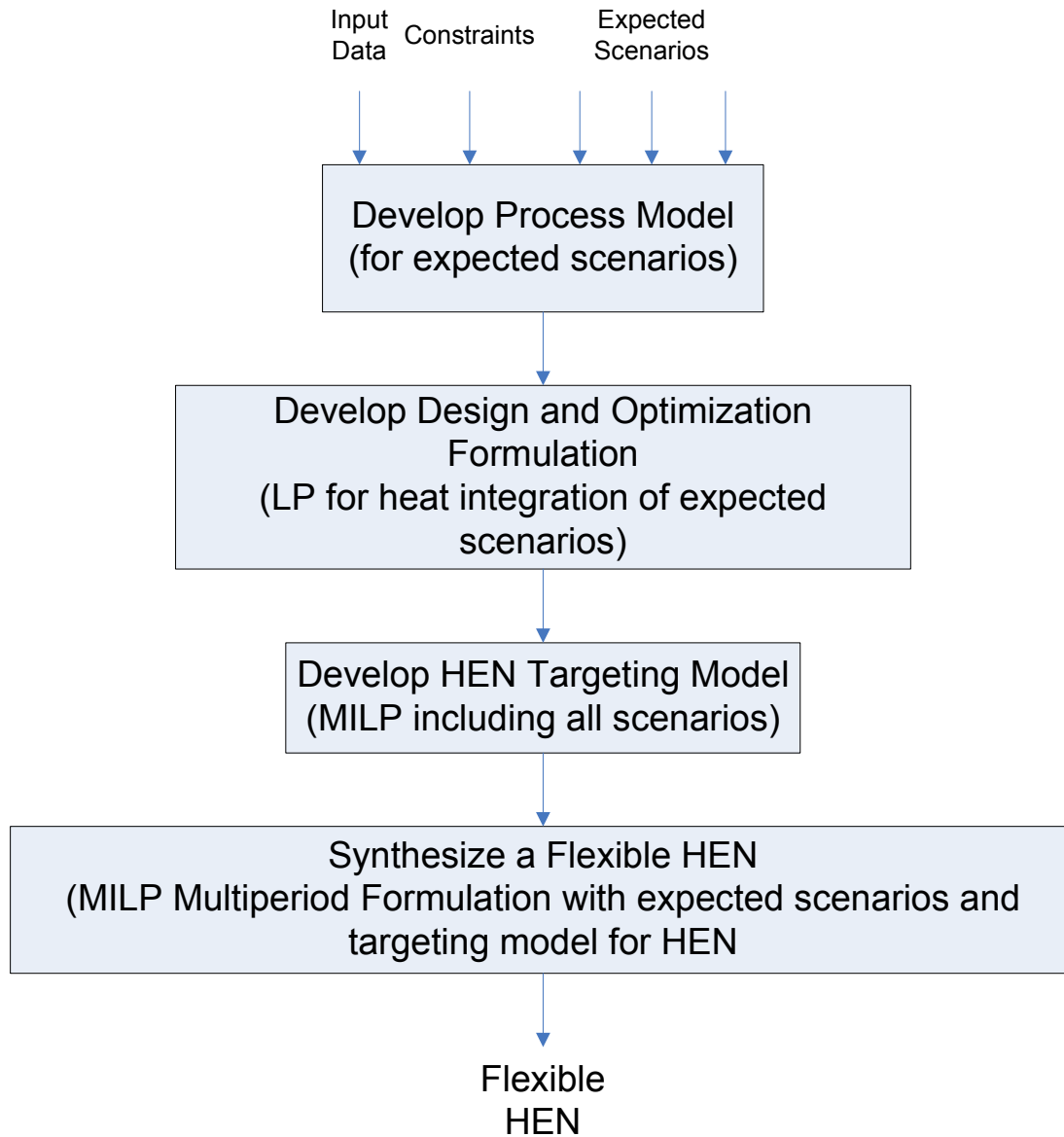
Fig. 7.2. Flowchart of heat exchange network synthesis approach.

7.5   Mathematical Formulation

7.5.1   Heat Integration

Heat integration is performed for each scenario prior to heat exchange network synthesis. Procedures for heat integration that were used are described by Kemp (2007), El-Halwagi (2006), and Smith (2005).

7.5.2   Heat Exchange Network Synthesis

A method for stream matching and HEN design was developed by Papoulias and Grossman (1986). This method was extended to address the multiple operational with modifications to allow for flexible HEN synthesis considering the different feedstock scenarios. The formulation is entered into optimization software (e.g. LINGO) for each individual scenario to confirm that the matching is working for all scenarios before combining the formulations and introducing the MILP to include all scenarios being investigated. According to the pinch rule, no heat should be passed through the pinch. This rule is incorporated into the program formulation by taken the problem as two subnetworks (SN), one above the pinch and one below the pinch. Denotation for the subnetworks will be as follows: index v is defined as *1* for above pinch and *2* for below pinch. Each interval over which heat is passed is denoted as y. The objective function is to minimize number of heat exchangers ($E_{h,k,v}$).

$$\min \sum_{v=1,2} \sum_{h \in HS} \sum_{k=CS} E_{h,k,v} \qquad\qquad (7.1)$$

s.t.

Heat balance for hot stream around the temperature intervals:

$$\delta_{h,y,s} - \delta_{h,y-1,s} + \sum_{k \in CS} Q_{h,k,y,s} = Q^{H}_{h,y,s} \qquad h \in HS, y \in SN_v, v = 1,2 \tag{7.2}$$

Heat balance for each cold stream around the temperature intervals:

$$\sum_{h \in HS} Q_{h,k,y,s} = Q^{C}_{k,y,s} \qquad k \in CS, y \in SN_v, v = 1,2 \tag{7.3}$$

Matching of loads:

$$\sum_{y \in SN_v} Q_{h,k,y,s} - U_{h,k,y,s} E_{h,k,v} \leq 0 \qquad h \in HS, k \in CS, y \in SN_v, v = 1,2 \tag{7.4}$$

Non-negative residuals:

$$\delta_{h,y,s} \geq 0 \qquad h \in HS, y \in SN_v, v = 1,2 \tag{7.5}$$

Non-negative loads:

$$Q_{h,k,y,s} \geq 0 \qquad h \in HS, k \in CS, y \in SN_v, v = 1,2 \tag{7.6}$$

Binary integer variables for matching streams:

$$E_{h,k,v} = 0/1 \qquad h \in HS, k \in CS, v = 1,2 \tag{7.7}$$

where $Q_{h,k,y,s}$ is the heat exchanged between the hth hot stream and the kth cold stream in interval y for scenario s and $Q^{H}_{h,y,s}$ is the total heat load for the hth hot stream in interval y for scenario s and $Q^{C}_{k,y,s}$ is total heat load for the kth cold stream in interval y for scenario s and $U_{h,k,y,s}$ is an upper bound on the exchangeable heat between streams h and k in SN_v.

Solving the above mathematical program will lead to matches for the minimum number of heat exchangers for the multi-scenario problem. Due to the nature of the

units and streams being investigated for the various scenarios, careful inspection of the solution will be required to ensure that the result is indeed the minimum number.

7.6   Case Study

There are three feedstocks investigated in the case study: soy, palm and algal oil. The biodiesel process is based on a base-case design as described by Pokoo-Aikins et al (2009). In the base-case design vegetable oils or algal oil can be processed to produce 44-52 MMGPY of biodiesel via transesterification (Fig. 7.3). Two reactors are used to increase throughput. An 8,000 hour work year is assumed. Reaction temperature is $60^{o}C$ in each reactor. Conversion through each reactor is assumed to be 97.7%. The alcohol to triglyceride (oil) ratio is 6:1. Oils entering the transesterification process are assumed to have a free fatty acid (FFA) content of 0.5% or less. Glycerol is separated from the resulting methyl esters and purified. Biodiesel is washed with water. Biodiesel purity for each feedstock ranges from 99.5-99.7% and glycerol purity is approximately 98% regardless of feedstock.

For each of the feedstock, heat integration was performed for the biodiesel process without any heat exchangers to determine the pinch point and minimum heating and minimum cooling utilities. Results from the heat integration are used to determine the minimum number of heat exchangers required for each process as well as to synthesize the heat exchange network.
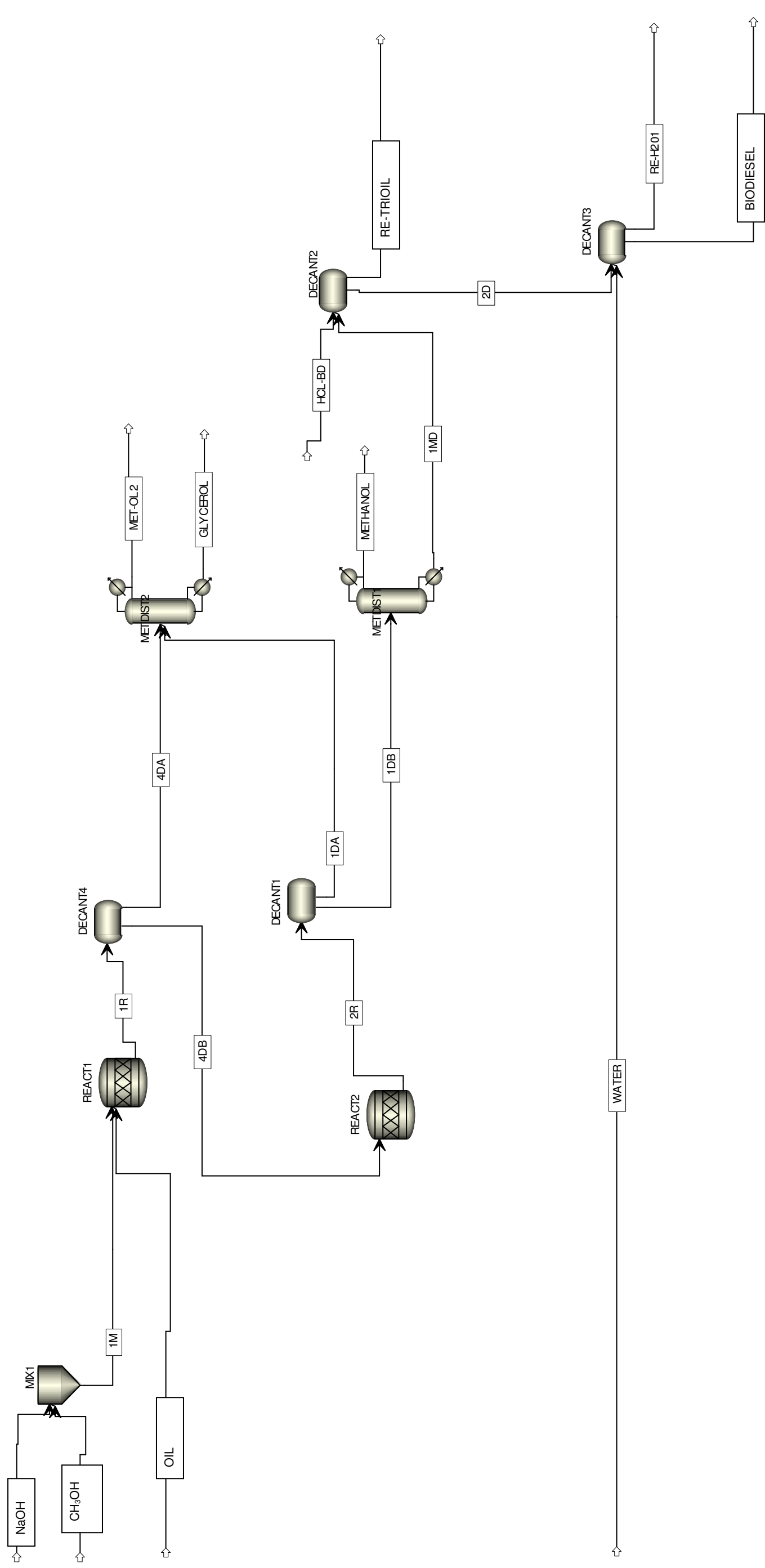
Fig. 7.3. Biodiesel production flowsheet without heat exchangers.

Table 7.1   Solution results for the common heat exchangers

Exchanger Number	From Utility or Process Unit	To Process Unit	Soy Heat Exchanger Value	Palm Heat Exchanger Value	Algae Heat Exchanger Value
E-1	Cooling Utility (CU)	MET-DIST1	E142	E142	E132
E-2	Cooling Utility (CU)	MET-DIST2	E242	E242	E232
E-3	REACT1	REACT2	E331	E332	NA
E-4	REACT1	MET-DIST1	NA	E312	E311
E-5	REACT1	MET-DIST2	E321	NA	NA
E-6	Heating Utility (HU)	MET-DIST1	E411	NA	E511
E-7	Heating Utility (HU)	MET-DIST 2	E421	E421	E521
E-8	Cooling Utility (CU)	REACT1	NA	E342	E332
E-9	Cooling Utility (CU)	REACT2	NA	NA	E432
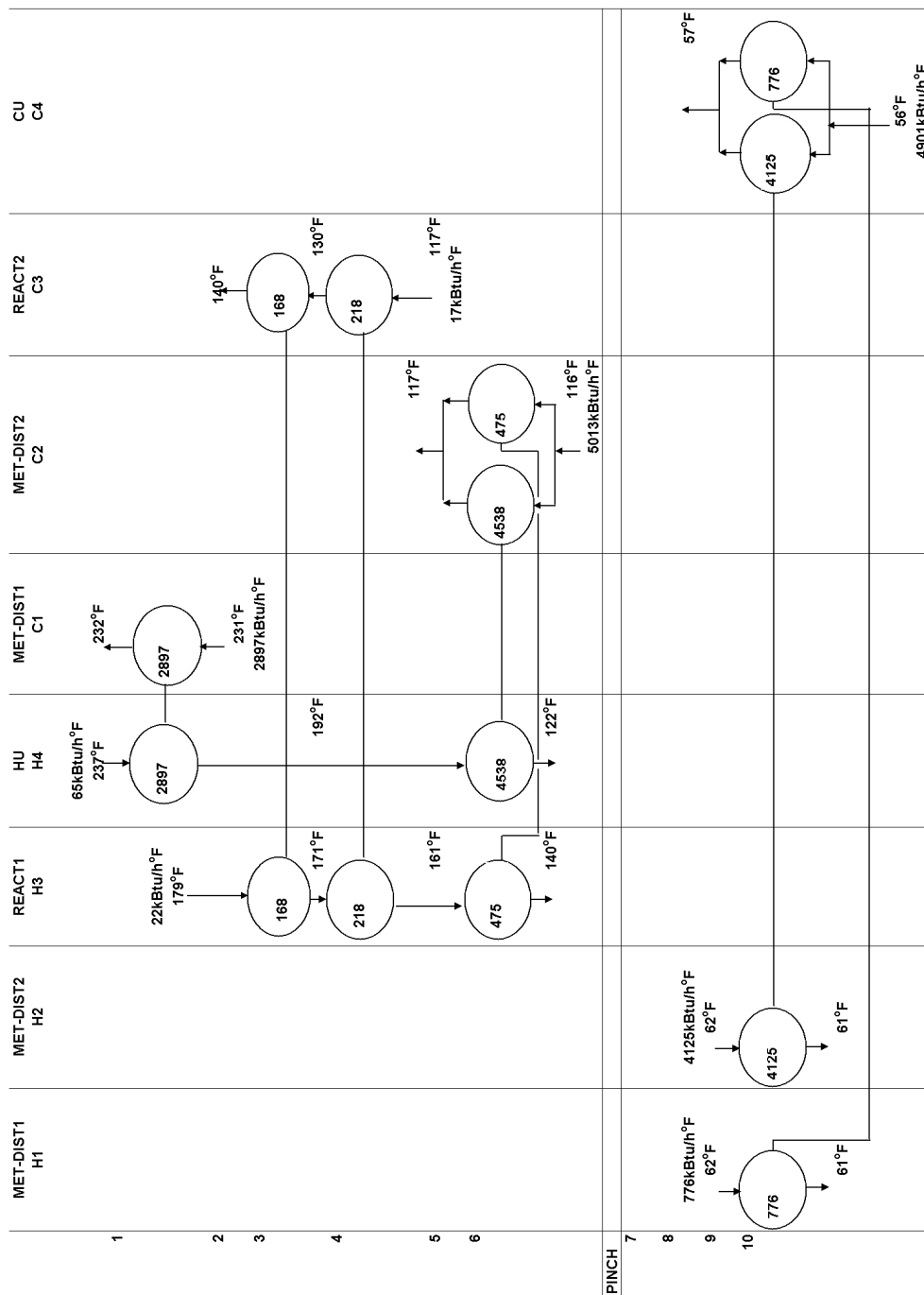
Fig. 7.4. HEN for soy oil scenario.
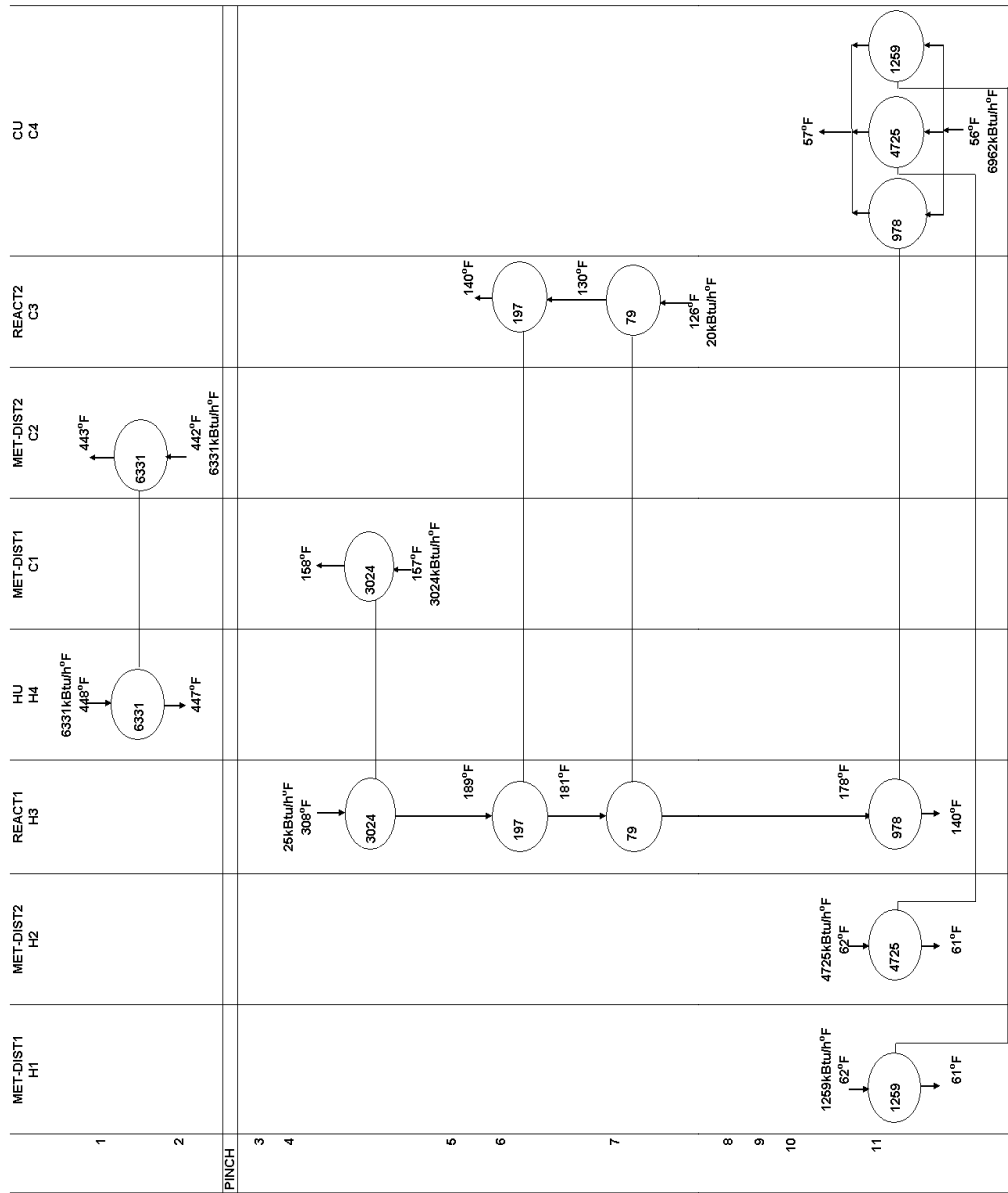
Fig. 7.5. HEN for palm oil scenario.
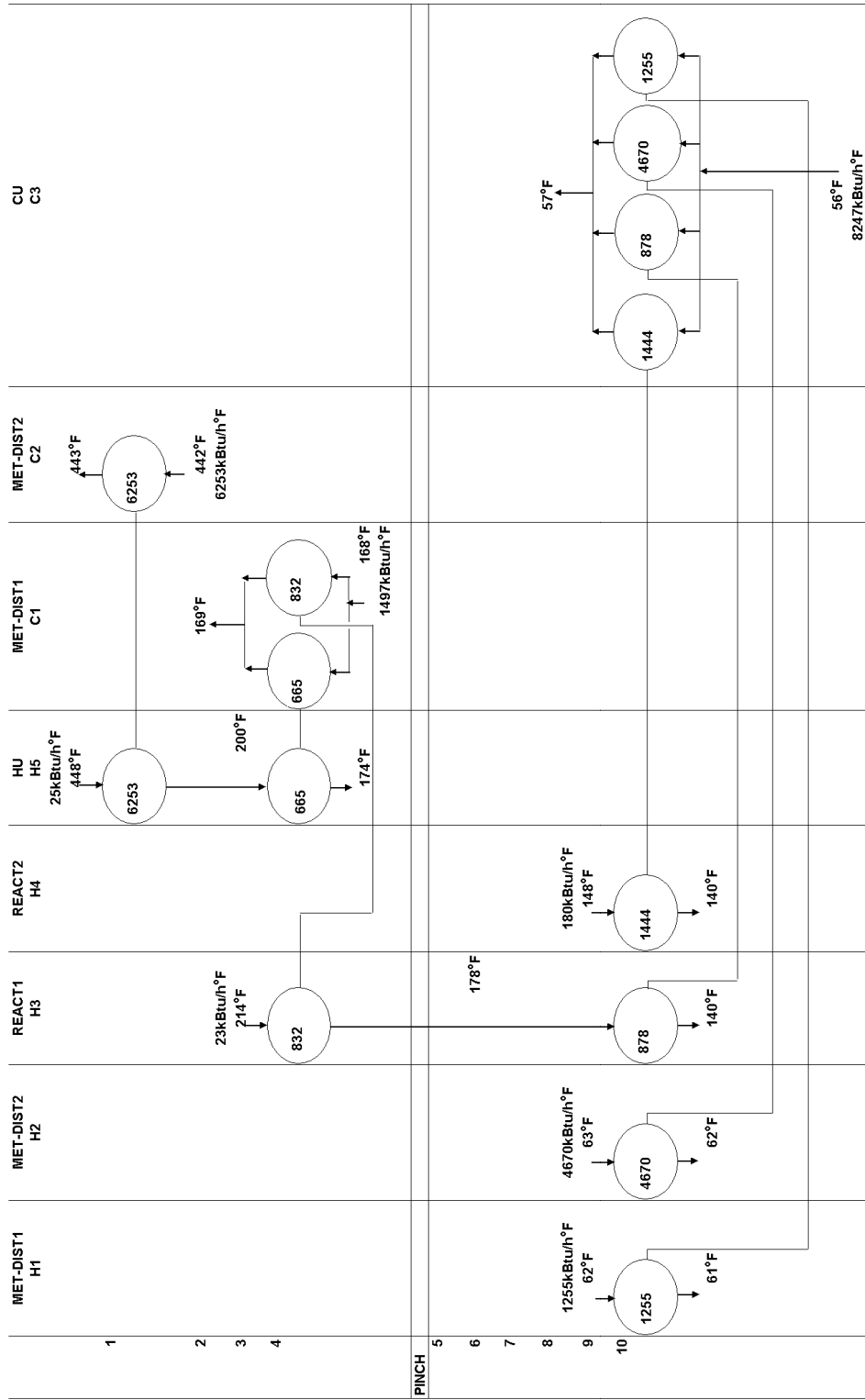
Fig. 7.6. HEN for algal oil scenario.
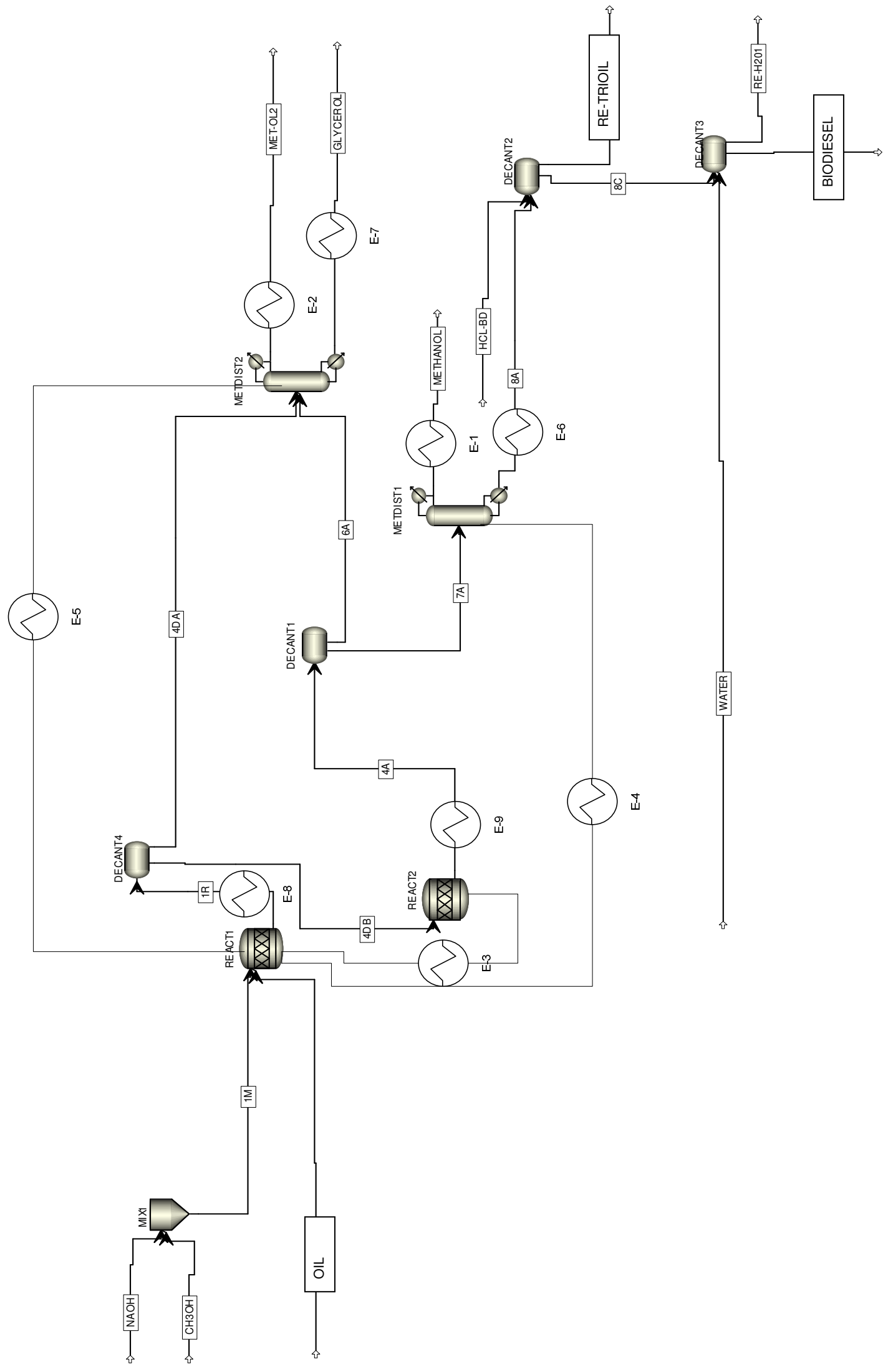
Fig. 7.7. Flexible HEN configuration that accommodates all scenarios.

Heat integration was performed for each feedstock scenario. Integration results revealed the minimum heating and cooling utilities needed for each scenario. Integration results were used to generate a MILP for determination of optimal HEN for the given scenario. The minimum number heat exchangers required for each individual scenario were 6 for soy, and 7 each for palm and algal oil. The total number of heat exchangers needed to accommodate the three scenarios is 9 units (Table 7.1). The heat exchange network designs for the individual scenarios are depicted in Figures 7.4, 7.5, and 7.6 for soy, palm and algal oil respectively. Fig. 7.7 represents the superstructure for the HEN accommodating the three scenarios. Fig. 7.7 depicts the flexible heat exchanger configuration relative to the process units involved. The process design configuration with the minimum number of heat exchangers for the flexible plant will have the nine heat exchangers positioned where needed. All nine heat exchangers must be present and associated with the necessary units in order for the flexible plant to accommodate all three of the feedstock investigated.

7.7   Conclusions

This work has addressed the problem of designing a common heat exchange network for a multi-feedstock biodiesel production facility. For each feedstock type and throughput, a detailed simulation study was carried out to determine the process performance and the heating and cooling requirements. Minimum heating and cooling utility requirements were determined for each scenario. Then, a multi-period mixed-integer linear program was developed and solved to generate the common structure for

all the scenarios that will minimize the number of heat exchangers while satisfying minimum heat and cooling utility requirements for each scenario. A case study was solved to address a three-feedstock biodiesel facility using soy bean, palm, and algal oil.

8 CONCLUSIONS AND RECOMMENDATIONS

The focus of this work has been on the development of systematic procedures for the design and analysis of flexible biodiesel processes with multiple feedstocks. Biodiesel production was used as a representative biofuel for the case studies.

First, the use of algae produced via CO_2 sequestration to produce biodiesel was analyzed. By incorporating the high and low performance scenarios as well as the assumptions for oil content, four costs for the production of algal oil, as well as two average costs for the 30% and 50% oil content cases (averages of the high and low performance cases), were obtained for later use in economic analysis of the biodiesel production from algal oil. A species of algae with the potential to produce high oil yields was selected (Chlorella species) and a two stage alkali-catalyzed transesterification reaction was simulated in ASPEN PLUS. ASPEN ICARUS was used to evaluate economics for both transesterification scenarios. Detailed sensitivity analysis for all performance cases, oil content cases, and transesterification processes stated previously, was conducted. Specifically, sensitivity analysis included the following parameters: 30% and 50% oil content, high performance and low performance cases, an average of the high and low performance cases, and the two transesterification simulations. The results of the calculations for profit, payback period, return on investment and breakeven analyses revealed that the most profitable scenarios for producing biodiesel from Chlorella species microalgal oil are those assuming 50% oil

content and incorporating heat integration. Considering the variety of scenarios evaluated, careful selection of the right parameters can and will indeed lead to the profitable production of biodiesel from microalgal oil. Biodiesel production form algal oil will be a competitive alternative to food derived plant oils under the appropriate conditions including the selection of algae with a high oil content, consideration of technology choice for algal growth and processing, selection of a high yield biodiesel process, and achieving high levels of process integration. Biodiesel and glycerol selling prices vary under normal market conditions and selling prices of product and by-product also affect the profitability of the algal oil-to-biodiesel process. In addition to algae, there are other innovative non-food oil sources for biodiesel production, including oil sources from waste.

With the possibility of obtaining raw sewage sludge with an incentive or at no cost, oils from sewage sludge were investigated as a possible alternative feedstock for biodiesel production. Using a systematic procedure for designing, simulating, integrating, screening, and analyzing the sewage sludge-to-biodiesel process, different solvent alternatives were considered for the extraction of sewage sludge, the associated process flowsheets were designed, simulated and analyzed. A new safety metric was introduced that is based on a combination of the solvent properties and the process conditions. The metric was used in conjunction with technical and economic criteria as part of a multi-criteria approach to the evaluation of the process. Extraction of oils from sewage sludge was followed by pretreatment of the extracted oils, transesterification, and separation. Utilities cost were notable higher for the extraction utilizing methanol

and ethanol although the cost of raw materials for extraction with methanol and ethanol were considerably cheaper. Utility cost contributed most to the economics of the extraction process. Heat integration provided a significant savings in utility costs. Safety was considered together with cost and performance in the evaluation of process alternatives. Use of toluene as the extraction solvent proved to be the least costly solvent choice for the process that is presented. Hexane is the next least costly followed by methanol, with ethanol being the most expensive, mainly due to the high demand of utilities for the extraction with methanol and ethanol in comparison to the extraction with hexane and toluene. Safety analysis revealed by the newly developed safety index used to evaluate the process, however, revealed that ethanol and methanol are the preferred solvents followed by hexane with toluene being the least safe. The estimated cost of biodiesel for the overall process with sewage sludge provided for free is $3.39 per gallon for ethanol, $3.37 per gallon for methanol, $2.89 for hexane, and $2.79 per gallon for toluene used as the extraction solvent. Once alternative non-food feedstock have been evaluated for technical, economic, safety and other criteria to check for potential feasibility of use of the feedstock, the feedstock can be incorporated into the multi-feedstock process assessment. As the technology for processing alternative feedstock continues to be developed, traditional feedstock may continue to be used and should also be incorporated into a flexible multi-feedstock biorefinery.

A systematic procedure and mathematical formulation were also introduced for representing, modeling and optimizing the flexible multi-feedstock biorefinery. Various objective functions can be developed and applied to the multi-feedstock biorefinery

depending on the goals of the flexibility analysis. Soybean oil and oils from sewage sludge were considered as feedstocks to demonstrate the concepts of flexibility as they apply to the multi-feedstock biodiesel example. The objective function in the example provided involved the maximization of throughput subject to cost constraints. A base case transesterification process was presented with added pretreatment processes. In increasing throughput, retrofitting of the base case process may be required. Results indicate that added costs for retrofitting the plant to accommodate the necessary added pretreatment units as well as increase in the flowrate may be required. These results can be used to determine an optimum level of flexibility by comparing the cost of flexibility versus the added values of producing more biofuel. It is important to note that the utility of the flexibility formulation is not limited to the example provided. Numerous other scenarios exist for issues pertaining to the design of a flexible multi-feedstock biorefinery (i.e. minimizing the cost of building a grassroots facility). The formulation is generalized enough for broad application. In developing a flexible multi-feedstock process, various aspects of the process design must be taken into consideration, including the design of various process units and equipment. One such important design aspect is the design of heat exchange networks within the multi-feedstock process.

With focus on energy efficiency, a systematic procedure was developed for addressing the problem of designing a common heat exchange network for a multi-feedstock biodiesel production facility. The formulation is an extension of the multi-period heat exchange network problem. To demonstrate the utility of the formulation, a detailed simulation study was carried out for each feedstock type and throughput to

determine the process performance and the heating and cooling requirements. Minimum heating and cooling utility requirements were determined for each scenario and then used to develop and solve a multi-period mixed-integer linear program. A common structure was generated that will minimize the number of heat exchangers while satisfying minimum heat and cooling utility requirements for each scenario. Soybean oil, palm oil and algal oil were simulated and incorporated into a three-feedstock biodiesel facility in order to demonstrate the use of the flexible heat exchange network formulation and methods.

8.1 Recommendations for Future Work

The following topics are recommended for future work:

• Integration of process design and operation for biorefineries

• Combing the flexible design problem with the scheduling and operating problem. The flexible design problem is more or less one that can be independent of scheduling but that would benefit from scheduling. Numerous works deal with and focus on scheduling issues for chemical processes (including the biodiesel process and the biorefinery). Fewer attempts have been made at addressing the flexible design problem. It would be of benefit to develop systematic procedure for incorporating scheduling and operating formulation into the flexible design problem.

• Development of procedures for designing combined heat and power for multi-feedstock biorefinereis. This will be an extension of the heat integration work developed

in this dissertation and will include steam systems that will serve to provide heating and turbine systems to provide power.

• Design under uncertainty: For example work investigating how to deal with design when there are fluctuations in feedstock cost and selling price of products.

• Incorporation of Life Cycle Analysis into Design: This will enable global assessment of various biofuel production pathways and impact on land and global climatic issues.

NOMENCLATURE

Description of symbols and acronyms in alphabetical order

AEGL	Measure of toxicity
$a_{i,j}$	Weighting factor for safety index equation
A_{m_c}	Flowrate of input stream m_c
A_{m_i}	Flowrate of input stream m_i
$A_{m_c}^{min}, A_{m_c}^{max}$	Minimum and maximum flowrate for the m_c^{th} input to common process unit c, respectively
A_{m_p}	Flowrate of input stream m_p
$A_{m_p}^{min}, A_{m_p}^{max}$	Minimum and maximum flowrate for the m_p^{th} input to pretreatment unit p, respectively
ASPEN	A type of simulation software for synthesizing chemical processes
ASPEN ICARUS	A type of simulation software for estimating economics of a process
ASPEN PLUS	A type of simulation software for synthesizing chemical processes (here FFA pretreatment and transesterification)
B100	Biodiesel that is 100% biodiesel and 0% petroleum diesel; essentially, non-blended biodiesel

Description of symbols and acronyms in alphabetical order (continued)

B20	Biodiesel blend that is 20% biodiesel
B5	Biodiesel blend that is 5% biodiesel
B6	Biodiesel blend that is 6% biodiesel
BE	Breakeven point
B_{n_c}	Flowrate of output stream n_c
B_{n_i}	Flowrate of output stream n_i
B_{n_p}	Flowrate of output stream n_p
$b_{n_p,m_c,s}$	Assigned from source n_p to destination m_c for scenario s
$b_{n_p,m_p,s}$	Flowrate from source n_p to destination m_p for scenario s
BP	Boiling point of chemical (in Kelvin)
BX	Notation for biodiesel blends where B represents biodiesel and X represents the percentage of biodiesel in the blend
C	A set of common process units
c	Index for common process units
CN	Cetane number; biodiesel property that is a measure of ignition quality
CP	Cloud point; a fuel property for biodiesel that is an indication of likelihood of gelling
CS	A set of cold streams

Description of symbols and acronyms in alphabetical order (continued)

$\bar{d}$	Design vector
$\bar{d}_c$	Design vector for common process units
$d_c^{\min}, d_c^{\max}$	Minimum and maximum vectors describing the design variables of unit c, respectively
$d_{c,s}$	Vectors describing the design variables of unit c for scenario s
$\bar{d}_p$	Design vector for pretreatment units
$d_p^{\min}, d_p^{\max}$	Minimum and maximum vectors describing the design variables of unit p, respectively
$d_{p,s}$	Vectors describing the design variables of unit p for scenario s
$E_{h,k,v}$	Number of heat exchangers
ERPG	Measure of toxicity
EXCEL	Microsoft brand software for creating spreadsheets
f	Index for feedstock alternatives
FAME	Fatty Acid Methyl Esters
FCI	Fixed capital cost
FFA	Free fatty acid
HYSIS	A type of simulation software for synthesizing chemical processes
g	A function designated for inequality constraints

Description of symbols and acronyms in alphabetical order (continued)

GHG	Greenhouse Gas
H	A function designated for equality constraints (section 6)
h	Index to represent hot streams (section 7)
HEN	Heat exchange network
HS	A set of hot stream loads
I	A set of intermediate streams that are redirected back into the process
i	Index for intermediate streams that are redirected back into the process (section 6)
i	Index corresponding to chemical in sludge safety analysis (section 5)
ICARUS	A type of simulation software for estimating economics of a process; software used to generate economic analysis information for ASPEN Plus simulation results
ICIS	Source for obtaining prices of chemicals
IDLH	Measure of toxicity
ΔI_j	Weighting factor for each category in sludge safety analysis
$INPUT_c$	The set of input streams for common process unit, c
$INPUT_p$	The set of input streams for pretreatment unit, p
ISIS	Software for constructing molecules for export into ASPEN

Description of symbols and acronyms in alphabetical order (continued)

j	Ranking category in sludge safety analysis (i.e. j = 1 for LC_{50}, j=2 for VD, j=3 for T_f, j=4 for P_f)
$J_{i,s}^{CP}$	Flowrate of the ith intermediate stream from the N_{CP} common process units for scenario s
$j_{n_c,i,s}$	Flowrate assigned from output stream n_c to the ith intermediate stream for scenario s
$j_{n_c,i,s}$	Flowrate assigned from source n_c to the ith intermediate stream for scenario s
$j_{n_c,m_i,s}$	Flowrate assigned from source n_c to destination m_i for scenario s
$j_{n_i,m_c,s}$	Flowrate assigned from intermediate source n_i to destination m_c for scenario s
k	Index for process step in sludge safety analysis (section 5)
k	Index to represent cold streams for CS (section 7)
L	A set of waste discharges
l	Index for waste discharges
LCA	Life cycle analysis
LC_{50}	Lethal concentration to kill 50% of population
LINGO	Optimization software program

Description of symbols and acronyms in alphabetical order (continued)

$L_{l,s}^{CP}$	Flowrate of the lth waste stream from the N_{CP} common process units for scenario s
$L_{l,s}^{PT}$	Flowrate of the lth waste stream from the N_{PT} pretreatment units for scenario s
$L_{l,s}$	Flowrate of the lth waste stream out of the process for scenario s
$l_{n_c,l,s}$	Flowrate assigned from output stream n_c to the lth waste stream for scenario s
$l_{n_p,l,s}$	Flowrate from n_p to the lth waste stream for scenario s
LP	Linear programming
m_c	Index to represent input streams for common process unit, c
m_i	Index to represent input stream for the 'intermediate block'
MILP	Mixed integer linear program
MM	Million
MMGPY	Million gallons per year
MOP	Maximum operating pressure
MOT	Maximum operating temperature (in Kelvin)
m_p	Index to represent input streams for pretreatment unit, p
MSDS	Material safety data sheet
n_c	Index to represent output streams for common process unit, c

Description of symbols and acronyms in alphabetical order (continued)

N_c^{in}	Number of input streams for common process unit, c
$N_{components}$	Number of components, x
N_c^{out}	Number of output streams for common process unit, c
N_{CP}	Number of common process units, c
N_{CS}	Number of hot streams for CS
$Net\_Gen_{c,x,s}$	Net generation of component x in common process unit c for scenario s
$Net\_Gen_{i,x,s}$	Net generation of component x in intermediate stream i for scenario s
$Net\_Gen_{p,x,s}$	Net generation of component x in pretreatment unit p for scenario s
N_f	Number of feedstock alternatives, f
N_{HS}	Number of hot streams for HS
N_I	Number of intermediate streams that are redirected back into the process
n_i	Index to represent output stream for the 'intermediate block'
N_L	Number of waste discharges
NO_X	Nitrogen oxide emissions that are greenhouse gases to the environment
n_p	Index to represent output streams for pretreatment unit, p
N_p^{in}	Number of input streams for pretreatment unit, p

Description of symbols and acronyms in alphabetical order (continued)

N_p^{out}	Number of output streams for pretreatment unit, p
N_{PT}	Number of pretreatment units, p
N_r	Number of product discharges, r
N_s	Number of scenarios, s
$\bar{o}$	Operating vector
$\bar{o}_c$	Operating vector for common process units
o_c^{min}, o_c^{max}	Minimum and maximum vectors describing the operating variables of unit c, respectively
$o_{c,s}$	Vectors describing the operating variables of unit c for scenario s
$\bar{o}_p$	Operating vector for pretreatment units
o_p^{min}, o_p^{max}	Minimum and maximum vectors describing the operating variables of unit p, respectively
$o_{p,s}$	Vectors describing the operating variables of unit p for scenario s
$OUTPUT_c$	The set of output streams for common process unit, c
$OUTPUT_p$	The set of output streams for pretreatment unit, p
P	Profit (section 4)
P	A set of pretreatment units (section 6)
p	Index for pretreatment units
P_f	Pressure factor (unit less)

Description of symbols and acronyms in alphabetical order (continued)

PFAD	Palm fatty acid distillate
PP	Payback period (section 4)
PP	Pour point; a fuel property for biodiesel that is an indication of likelihood of gelling (section 2)
$Q^C_{k,y,s}$	Total heat load for the kth cold stream in interval y for scenario s
$Q^H_{h,y,s}$	Total heat load for the hth hot stream in interval y for scenario s
$Q_{h,k,y,s}$	Heat exchanged between the hth hot stream and the kth cold stream in interval y for scenario s
R	A set of product discharges
r	Index for product discharges
RB	Retrofitting budget
$r_{n_c,r,s}$	Flowrate assigned from output stream n_c to the rth product stream for scenario s
$r_{n_p,r,s}$	Flowrate assigned from n_p to the rth product stream for scenario s
ROI	Return on investment
$R_{r,s}$	Flowrate of the rth product out of the process
$R^{CP}_{r,s}$	Total flowrate of the rth product from the N_{CP} common process units in scenario s
$R^{Demand}_{r,s}$	Demand for product r for scenario s

Description of symbols and acronyms in alphabetical order (continued)

$R_{r,s}^{PT}$	Total flowrate of the rth product from the N_{PT} pretreatment units in scenario s
s	Index for a given scenario for a certain feedstock
SCENARIOS	A set of scenarios
SI	Safety index
$SI_{i,k}$	Safety index for chemical i in process k
SN	Subnetworks; one above the pinch and one below the pinch
SN_v	Subnetwork for index v
SRE	Safety ranking equation
SRM	Safety ranking matrix
STP	Standard temperature and pressure
TDC	Ttotal direct cost
T_f	Temperature factor (unit less)
TG	Triglyceride
T_{m_c}	Temperature of process input stream m_c
T_{n_c}	Temperature of process output stream n_c
ULSD	Ultra low sulfur diesel
WCO	Waste cooking oil
$W_{i,x,s}^{CP}$	Composition of component x in the ith intermediate stream from the N_{CP} common process units for scenario s

Description of symbols and acronyms in alphabetical order (continued)

$W_{l,x,s}$	Composition of component x in the lth waste stream out of the process for scenario s
$W_{r,x,s}$	Composition of component x in the rth product stream out of the process for scenario s
$W_{r,x,s}^{CP}$	Composition of component x in the rth product stream coming from the N_{CP} common process units in scenario s
$W_{r,x,s}^{PT}$	Composition of component x in the rth product stream coming from the N_{PT} pretreatment units for scenario s
$W_{l,x,s}^{CP}$	Composition of component x in the lth waste stream coming from the N_{CP} common process units for scenario s
$W_{l,x,s}^{PT}$	Composition of component x in the lth waste stream coming from the N_{PT} pretreatment units for scenario s
$U_{h,k,y,s}$	Upper bound on the exchangeable heat between streams h and k in SN_v
v	Index for subnetworks defined as *1* for above pinch and *2* for below pinch
VD	Vapor density
VP	Vapor pressure (in atm)
VP_{MOT}	Vapor pressure at maximum operating temperature

Description of symbols and acronyms in alphabetical order (continued)

VP_{ST}	Vapor pressure at standard temperature
y	Intervals over which residual heat exchange loads are passed
$Y_{m_c,x}$	Composition of component x in input stream m_c
$Y_{m_c,x}^{min}, Y_{m_c,x}^{max}$	Minimum and maximum composition of component x for the m_c^{th} input to pretreatment unit c, respectively
$Y_{m_i,x}$	Composition of component x in input stream m_i
$Y_{m_p,x}$	Composition of component x in input stream m_p
$Y_{m_p,x}^{min}, Y_{m_p,x}^{max}$	Minimum and maximum composition of component x for the m_p^{th} input to pretreatment unit p, respectively
$Z_{n_c,x}$	Composition of component x in output stream n_c
$Z_{m_i,x}$	Composition of component x in output stream m_i
$Z_{n_p,x}$	Composition of component x in output stream n_p

Description of Greek symbols and acronyms in alphabetical order

$\delta_{h,y,s}$	Residual heat exchange loads ($\delta_{h,y,s}$) for hot streams transferred to cold streams for each scenario
$\delta_{h,y-1,s}$	Residuals from previous intervals
ψ	A variable used in the objective function; a function
ψ_{cost}	A scalar cost variable

REFERENCES

Aaltola, J., 2002. Simultaneous synthesis of flexible heat exchanger network. Applied
     Thermal Engineering 22, 907.

Abdullah, A. Z., Salamatinia, B., Mootabadi, H., and Bhatia, S., 2009. Current status and
     policies on biodiesel industry in Malaysia as the world's leading producer of
     palm oil. Energy Policy 37, 5440–5448.

Al-Qahtani. K., Elkamel, A., 2008. Multisite facility network integration design and
     coordination: an application to the refining industry. Computers and Chemical
     Engineering 32, 2189-2202.

Anslow, M., 2008. Slippery territory: biofuels created from algae aren't as clean as they
     seem. Ecologist 38 (3), 12.

Arny, W., January 18, 2005. Department of the Navy Environmental Policy
     Memorandum 05-01; Biodiesel Fuel Use in Diesel Engines, U.S. Department of
     the Navy.

Belarbi, E-H, Molina Grima, Chisti, Y., 2000. A process for high yield and scaleable
     recovery of high purity eicosapentaenoic acid esters from microalgae and fish oil.
     Enzyme and Microbial Technology, 26, 516-529.

Boocock, D., Konar, S., Leung, A., Ly, L., 1992. Fuels and chemical from sewage
     sludge: 1. The solvent extraction and composition of a lipid from a raw sewage
     sludge. Fuel 71, 1283-1289.

Canacki, M., Van Gerpen, J., 2001. Biodiesel production from oils and fats with high free fatty acids. Transactions of American Society of Agricultural Engineers 44 (6), 1429-1436.

Carraretto, C., Macor, A., Mirandola, A., Stoppato, A., Tonon, S., 2004. Biodiesel as alternative fuel: experimental analysis and energetic evaluations. Energy 29, 2195-2211.

Chen, C.L., 2005. A novel strategy for synthesis of flexible heat-exchange networks. Journal of the Chinese Institute of Chemical Engineers 36 (5), 421-432.

Chen, C.L., Hung, P., 2007. Synthesis of flexible heat exchange networks and mass exchange networks. Computers and Chemical Engineering 31, 1619–1632.

Cheng, H., Friis, A., 2007. Operability and flexibility of a milk production line. Trans IChemE. 85(C4), 372-380. DOI: 10.1205/fbp07071

Chisti, Y. 2007. Biodiesel from microalgae. Biotechnology Advances 25, 294-306.

Chisti, Y., 2008a. Biodiesel from microalgae beats bioethanol. Trends in Biotechnology 26(3), 126-131. doi:10.1016/j.tibtech.2007.12.002

Chisti, Y., 2008b. Response to Reijnders: do biofuels from microalgae beat biofuels from terrestrial plants? Trends in Biotechnology 26(7), 351-352. doi:10.1016/j.tibtech.2008.04.002

Chongkhong, S., Tongurai, C., Chetpattananondh, P., 2009. Continuous esterification for biodiesel production from palm fatty acid distillate using economical process. Renewable Energy 34, 1059-1063.

Chongkhong, S., Tongurai, C., Chetpattananondh, P., Bunyakan, C., 2007. Biodiesel production from palm fatty acid distillate. Biomass and Bioenergy 31, 563-568.

Clean Cities Alternative Fuel Price Report, Available at http://www.afdc.energy.gov/afdc/price_report.html. Alternative Fuels & Advanced Vehicles Data Center, Accessed July 14, 2008.

Clean Tech, Available at http://media.cleantech.com/node/1073. BioKing commercializes small algae bioreactors, Accessed July 10, 2008.

Demirbas, A., 2007. Recent developments in biodiesel fuels. International Journal of Green Energy 4, 15-26.

Demirbas, A., 2008. Biodiesel – A Realistic Fuel Alternative for Diesel Engines. Springer-Verlag London Limited, London.

Demirbas, A., 2009a. Progress and recent trends in biodiesel fuels. Energy Conversion and Management 50, 14-34.

Demirbas, A., Karslioglu, S., 2007. Biodiesel production facilities from vegetable oils and animal fats. Energy Sources Part A 29, 133-141. DOI 10.1007/s10098-008-0156-5.

Dufreche, S., Hernandez, R., French, T., Sparks, D., Zappi, M., Alley, E., 2007. Extraction of lipids from municipal wastewater plant microorganisms for production of biodiesel. Journal of the American Oil Chemists' Society 81, 181-187.

Dunstan, G. A., Volkman, J. K., Jeffrey, S. W., Barrett, S. M., 1992. Biochemical composition of microalgae from the green algal classes Chlorophyceae and Prasinophyceae. 2. Lipid classes and fatty acids. Journal of Experimental Marine Biology and Ecology 161, 115-134.

Edwards, D. W., Lawrence, D., 1993. Assessing the inherent safety of chemical routes: is there a relation between plant cost and inherent safety? Process Safety and Environmental Protection 71(B4), 252-258.

El-Halwagi, M.M., 1997. Pollution Prevention Through Process Integration. Academic Press, San Diego, CA.

El-Halwagi, M.M., 2006. Process Integration. Academic Press, New York.

Elms, R., El-Halwagi, M.M., 2009. Optimal scheduling and operation of biodiesel plants with multiple feedstocks. International Journal of Process Systems Engineering 1(1), 1-28.

EPA, October 2002. A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions (EPA420-P-02-001).

Fajardo, A. R., Cerdán, L. E., Medina, A. R., Frenández, F. G. A., Moreno, P. A. G., Grima, E. M., 2007. Lipid extraction from the microalga Phaeodactylum tricornutum, European Journal of Lipid Science and Technology 109, 120-126.

Fisher Ethanol MSDS, 2009. Available at <http://fscimage.fishersci.com/msds/89308.htm>. Accessed November 05, 2009.

Fisher Toluene MSDS, 2009. Available at <http://fscimage.fishersci.com/msds/23590.htm>. Accessed November 05, 2009.

Floudas, C. A., Gumus, Z. H., Ierapetritou, M. G., 2001. Global optimization in design under uncertainty: feasibility test and flexibility index problems. Industrial and Engineering Chemistry Research 40, 4267–4282.

Food Fats and Oils. 2006. Institute of Shortening and Edible Oils. Washington, DC. Ninth Edition. Available online http://www.iseo.org/foodfats.htm or http://www.iseo.org/foodfatsoils.pdf.

Foon, Cheng S., May, Choo Y., Ngan, Ma A., Hock, Chuah C., 2004. Kinetics study on transesterification of palm oil. Journal of Oil Palm Research 16(2), 19-29.

Freedman, B., Butterfield, R.O., Pryde, E., 1986. Transesterification kinetics of soybean oil. Journal of American Oil Chemist's Society 63, 1375-1380.

Freedman, B., Pryde, E., Mounts, T., 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. Journal of American Oil Chemist's Society 61(10), 1638-1643.

Frohlich, A, Rice, B., 2005. Evaluation of Camelina sativa oil as a feedstock for biodiesel production. Industrial Crops and Products 21, 25-31.

Fukuda, H., Kondo, A., Noda, H., 2001. Biodiesel fuel production by transesterification of oils. Journal of Bioscience and Bioengineering 92(5), 405-416.

Furman, K. C., Sahinidis, N. V., 2002. A critical review and annotated bibliography for heat exchanger network synthesis in the 20th century. Industrial and Engineering Chemistry Research 41, 2335.

Georgogianni, K.G., Kontominas, M.G., Pomonis, P.J., Avlonitis, D., Gergis, V., 2008. Conventional and in situ transesterification of sunflower seed oil for the production of biodiesel. Fuel Processing Technology 89, 503-509.

Gerpen, J. V., 2005. Biodiesel processing and production. Fuel Processing Technology 86, 1097-1107.

Gerpen, J. V., 2006. Biodiesel Production and Technology: A Workshop for the 2006 National Biodiesel Conference and Expo. V:2, February 2006.

Gerpen, J., Shanks, B., Pruszko, R., 2004. Biodiesel Production Technology, National Renewable Energy Laboratory. Subcontractor Report, NREL/SR-510-36244.

Ginder, R., July/August 2004. Evaluating biodiesel as a value-added opportunity. Agricultural Marketing Resource Center Action 1(9), Available at http://www.agmrc.org/media/cms/biodieselopportunity_254411A7B6DAB.pdf, Accessed October 5, 2009.

Gouveia, L., Oliveira, A.C., 2009. Microalgae as a raw material for biofuels production. Journal of Industrial Microbiololology and Biotechnology 36, 269-274. DOI 10.1007/s10295-008-0495-6.

Grima, E. M., Medina, A. R., Giménez, A. G., Pérez, J. A. S., Camacho, F. G., Sánchez, J. L. G., 1994. Comparison between extraction of lipids and fatty acids from microalgal biomass. Journal of the American Oil Chemist's Society 71(9), 955-959.

Grossmann, I. E., Floudas, C. A., 1986. Active constraint strategy for flexibility analysis in chemical processes. Computers and Chemical Engineering 11(6), 675.

Grossmann, I.E., Halemane, K.P., Swaney, R.E., 1983. Optimization strategies for flexible chemical processes. Computers and Chemical Engineering 7, 439–462.

Grossmann, I. E., Sargent, R. W. H., 1978. Optimum design of chemical plants with uncertain parameters. AIChE Journal 24(6), 1021.

Haas, M.J., McAloon, A.J., Yee, W.C., Foglia, T.A., 2006. A process model to estimate biodiesel production costs. Bioresource Technology 97, 671-678.

Halemane, K. P., Grossmann, I. E., 1983. Optimal process design under uncertainty. AIChE Journal 29(3), 425.

Hanagata, N., Takeuchi, T., Fukuju, Y., Barnes, D.J., Karube, I., 1992. Tolerance of microalgae to high CO2 and high temperature. Phytochemistry 31(10), 3345-3348.

Heikkila, A-M., Hurme, M., Jarvelainen, M., 1996. Safety consideration in process synthesis. Computers and Chemical Engineering 20, S115-S120.

Higgins, A., Kaplovsky, A., Hunder, J. V., 1982. Organic composition of aerobic, anaerobic, and compost-stabilized sludges. Journal Water Pollution Control Federation 54(5), 466-473.

Hill, J., Nelson, E., Tilman, D., Polasky, S., Tiffany, D., 2006. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. Proceedings of the National Academy of Sciences of the United States 103(30), 11206-11210.

Hope, J., 1986. Sewage sludge disposal and utilization study. Washington State
Institute for Public Policy. Document No. 86-01-4101. Available at
<http://www.wsipp.wa.gov/rptfiles/sewage.pdf> Accessed November 05, 2009.

HSDB n-Hexane. 2009. Animal Toxicity Studies. Available at
<http://toxnet.nlm.nih.gov>. Accessed November 05, 2009.

HSDB Toluene. 2009. Animal Toxicity Studies. Available at
<http://toxnet.nlm.nih.gov>. Accessed November 05, 2009.

Hu, Q., Sommerfeld, M., Jarvis, E., Ghirardi, M., Posewitz, M., Seibert, M., Darzins, A.,
2008. Microalgal triacylglycerols as feedstocks for biofuel production:
perspectives and advances. The Plant Journal 54, 621-639.

ICIS Pricing. 2008. Available at http://www.icispricing.com. Accessed July 14, 2008.

ICIS Pricing Ethanol. 2009. Available at
<http://www.icispricing.com/il_shared/Samples/SubPage173.asp>. Accessed
November 05, 2009.

ICIS Pricing Hexane. 2009. Available at
<http://www.icispricing.com/il_shared/Samples/SubPage90.asp>. Accessed
November 05, 2009.

ICIS Pricing Methanol. 2009. Available at
<http://www.icispricing.com/il_shared/Samples/SubPage135.asp>. Accessed
November 05, 2009.

ICIS Pricing Sodium Hydroxide. 2009. Available at <http://www.icis.com/StaticPages/a-
e.htm>. Accessed November 05, 2009.

ICIS Pricing Toluene. 2009. Available at

      <http://www.icispricing.com/il_shared/Samples/SubPage138.asp>. Accessed

      November 05, 2009.

The Innovation Group. 2009. Available at <http://www.the-innovation

      group.com/ChemProfiles/Sulfuric%20Acid%20(smelter).htm> Accessed

      November 05, 2009.

Israel21c. 2009. Available at

      <http://www.israel21c.org/bin/en.jsp?enScript=PrintVersion.jsp&enDispWho=A

      rticles^l1492> Accessed November 05, 2009.

Kalam, M.A., Masjuki, H.H., 2002. Biodiesel from palmoil – an analysis of its

      properties and potential. Biomass and Bioenergy 23, 471-479.

Kemp, I.C., 2007. Pinch analysis and process integration. Second edition. Oxford:

      Butterworth-Heinemann.

Knothe, G., 2001. Historical perspectives on vegetable oil-based diesel fuels. Inform 12,

      1103-1107.

Knothe, G., Dunn, R. O., Bagby, M.O., 1997. Biodiesel: The use of vegetable oils and

      their derivatives as alternative diesel fuels. Fuels and Chemicals from Biomass.

      Washington, D.C.: American Chemical Society.

Leevijit, T., Tongurai, C., Prateepchaikul, G., Wisutmethangoon, W., 2008.

      Performance test of a 6-stage continuous reactor for palm methyl ester

      production. Bioresource Technology 99, 214-221.

Lepper, H., Friesenhagen, L., August 26, 1986. Process for the production of fatty acid esters of short-chain aliphatic alcohols from fats and/or oils containing free fatty acids. US Patent No. 4,608,202.

Lepper, H., Friesenhagen, L., March 24, 1987. Process for the production of fatty acid alkyl esters. US Patent No. 4,652,406.

Leung, D. Y. C., Guo, Y., 2006. Transesterification of neat and used frying oil: optimization for biodiesel production. Fuel Processing Technology 87, 883-890.

Lin, K-L., 2006. Minerology and microstructures of sintered sewage sludge ash as lightweight aggregates. Journal of Industrial and Engineering Chemistry 12(3), 425-429.

Linnhoff, B., Hindmarsh, E., 1983. The pinch design method for heat exchanger networks. Chemical Engineering Science 38(5), 745.

Lotero, E., Liu, Y., Lopez, D.E., Suwannakarn, K., Bruce, D.A., Goodwin, J.G., 2005. Synthesis of biodiesel via acid catalysis. Industrial and Engineering Chemistry Research 44, 5353-5363.

Ma, F., Hanna, M. A., 1999. Biodiesel production: a review. Bioresource Technology 70, 1-15.

Mara, D., Horan, N. J., 2003. The Handbook of Water and Wastewater Microbiology. San Diego: Academic Press.

Marchetti, J. M., Errazu, A. F., 2008. Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides. Biomass and Bioenergy 32, 892-895.

Marchetti, J.M., Miguel, V.U., Errazu, A.F., 2007. Possible methods for biodiesel production. Renewable and Sustainable Energy Reviews 11, 1300-1311.

Meher, L.C., Sagar, D.V., Naik, S.N., 2006. Technical aspects of biodiesel production by tranesterification – a review. Renewable and Sustainable Energy Reviews 10, 248-268.

Meka, P. K., Tripathi, V., Singh, R. P., 2007. Synthesis of biodiesel fuel from safflower oil using various reaction parameters. Journal of Oleo Science 56(1), 9-12.

Miao, X., Wu, Q., 2006. Biodiesel production from heterotrophic microalgal oil. Bioresource Technology 97, 841-846.

Mondala, A., Liang, K., Toghiani, H., Hernandez, R., French, T., 2009. Biodiesel production by in situ transesterification of municipal primary and secondary sludges. Bioresource Technology 100, 1203-1210.

Moon, J., Kulkarni, K. Zhang, L., Linninger, A.A., 2008. Parallel hybrid algorithm for process flexibility analysis. Industrial and Engineering Chemistry Research 47, 8324-8336.

Myint, L. L., El-Halwagi, M.M., 2009. Process analysis and optimization of biodiesel production from soybean oil. Journal of Clean Technology and Environmental Policy 11(3), 263-276. ISSN 1618-954X (Print), DOI 10.1007/s10098-008-0156-5.

Myint, Lay L. May 2007. Process Analysis and Optimization of Biodiesel Production from Vegetable Oils. Masters Thesis. Texas A&M University.

National Biodiesel Board, 2008. Available at

   http://www.biodiesel.org/pdf_files/fuelfactsheets/production.pdf Accessed on

   April 18, 2008.

National Biodiesel Board, 2009. Available at

   www.biodiesel.org/pdf_files/fuelfactsheets/Production_Graph_Slide.pdf,

   Accessed September 25, 2009 and December 22, 2009.

National Biodiesel Board, 2010. Available at http://www.biodiesel.org/, Accessed

   February 18, 2010.

Nebel, B.A., Mittelbach, M., 2006. Biodiesel from extracted fat out of meat and bone

   meal. European Journal of Lipid Science and Technology 108, 398-403.

Nelson, L.A., Foglia, T.A., Marmer, W.N., 1996. Lipase-catalyzed production of

   biodiesel. Journal of American Oil Chemist's Society 73(8), 1191-1195.

Noureddini, H., Zhu, D., 1997. Kinetics of transesterification of soybean oil. Journal of

   the American Oil Chemists' Society (JAOCS) 74, 1457-1463.

Otsuka, H., 1961. Changes of lipid and carbohydrate contents of Chlorella cells during

   the sulfur starvation, as studied by the technique of synchronous culture. Journal

   of General and Applied Microbiology 7, 72-77.

Papoulias, S.A., Grossmann, I. E., 1983. A structural optimization approach in process

   synthesis—II: heat recovery networks. Computers and Chemical Engineering

   7(6), 707-721.

Peters, M. S., Timmerhaus, K. D., West, R. E., 2003. Plant design and economics for

   chemical engineers (5th ed.). New York: McGraw-Hill. 242-243.

Peterson, G.R., Scarrah, W.P., 1984. Rapeseed oil transesterification by heterogeneous catalysis. Journal of American Oil Chemist's Society 61(10), 1593-1597.

Pintaric, Z.N., Kravanja, Z., 2008. Identification of critical points for the design and synthesis of flexible processes. Computers and Chemical Engineering 32, 1603-1624.

Plant Oils. 2007. Available at http://www.plantoils.in/chem/chem.html Accessed October 05, 2007.

Pokoo-Aikins, G., Heath, A, Mentzer, R.A., Mannan, M.S., Rogers, W.J., El-Halwagi, M.M., 2010. A multi-criteria approach to screening alternatives for converting sewage sludge to biodiesel. Journal of Loss Prevention in the Process Industries, doi:10.1016/j.jlp.2010.01.0051061 (in press).

Pokoo-Aikins, G., Nadim, A., El-Halwagi, M. M., Mahalec, V., 2009. Design and analysis of biodiesel production from algae grown through carbon sequestration. Journal of Clean Technology and Environmental Policy, ISSN 1618-954X (Print), 1618-9558 (Online), DOI 10.1007/s10098-009-0215-6.

Rahman, M., Heikkila, A-M., Hurme, M., 2005. Comparison of inherent safety indices in process concept evaluation. Journal of Loss Prevention in the Process Industries 18, 327-334.

Rashid, U., Anwar, F., 2008. Production of biodiesel through base-catalyzed transesterification of safflower oil using an optimized protocol. Energy & Fuels 22, 1306-1312.

Rashid, U., Anwar, F., Moser, B. R., Ashraf, S., 2008. Production of sunflower oil

    methyl esters by optimized alkali-catalyzed methanolysis. Biomass and

    Bioenergy, doi:10.1016/j.biombioe.2008.03.001.

Reijnder, L., 2008. Do biofuels from microalgae beat biofuels from terrestrial plants?,

    Trends in Biotechnology, doi:10.1016/j.tibtech.2008.04.001

Richardson, M., 1996. Environmental Xenobiotics. CRC Press, Taylor and Frances.

Schmidt, C.W., 2007. Biodiesel: cultivating Alternative Fuels. Environmental Health

    Perspectives 115(2), A86-A91.

Sharma, Y.C., Singh, B., 2009. Development of biodiesel: current scenario. Renewable

    and Sustainable Energy Reviews 13, 1646-1651.

Sheehan, J., Camobreco, V., Duffield, J., Graboski, M.mShapouri, H., May 1998. Life

    Cycle Inventory of Biodiesel and Petroleum Diesel for Use in an Urban Bus -

    NREL Final Report (NREL/SR-580-24089 UC Category 1503), U.S. National

    Renewable Energy Laboratory.

Siler-Marinkovic, A., Tomasevic, A., 1998. Transesterification of sunflower oil in situ.

    Fuel 77(12), 1389-1391.

Smith, R., 2005. Process integration: Current status and future potential. Proceedings of

    ECOS 2005 (1-3), 35-42.

Suardin, J., Mannan, M. S., El-Halwagi, M. 2007. The integration of Dow's fire and

    explosion index (F&EI) into process design and optimization to achieve

    inherently safer design. Journal of Loss Prevention in the Process Industries

    20(1), 79-90.

Swaney, R. E., Grossmann, I. E., 1985. An index for operational flexibility in chemical process design, Parts I and II. AIChE Journal 31(4), 621.

Sweeney, D., 2008. Algae biofuel mania. http://www.stockhouse.com/Columnists/2008/June/11/Algae-biofuel-mania Accessed June 12, 2008.

Sung, K.D., Lee, J.S., Shin, C.S., Park, S.C., Choi, M.J., 1999. CO_2 fixation by Chlorella sp. KR-1 and its cultural characteristics. Bioresource Technology 68(3), 269-273.

Sysmex MSDS, 2009. Available at <http://www.sysmex.com/usa/lab/files/Stromatolyser%20-%204DS%20Dye%20(FFS-800)%20Final%20121304.pdf> Accessed November 05, 2009.

Tanaka, Y., Okabe, A., Ando, S., 1981. Method for the preparation of a lower alkyl ester of fatty acids. Patent number: 4303590.

Tapasvi, D., Wiesenborn, D., Gustafson, C., 2005. Process model for biodiesel production from various feedstocks. Transactions of the American Society of Agricultural Engineers 48(6), 2215-2221.

Tyson, K.S., Bozell, J., Wallace, R., Petersen, E., Moens, L., June 2004. Biomass Oil Analysis: Research Needs and Recommendations - NREL Technical Report (NREL/TP-510-34796),U.S. National Renewable Energy Laboratory.

U.S. Congress. Senate. August 6, 2009. Biodiesel Tax Incentive Reform and Extension Act of 2009. S. 1589. 111th Cong., 1st session.

Van Gerpen, J., 2005. Biodiesel processing and production. Fuel Processing and Technology 86, 1097-1107.

Van Gerpen, J., Shanks, B., Pruszko, R., Clements, D., Knothe, G., 2004. Biodiesel Production Technology. NREL/SR-510-36244.

Vegetable Fats and Oils. 2007. Available at http://en.wikipedia.org/wiki/Vegetable_fats_and_oils Accessed October 05, 2007.

Wang, Y., Ou, S., Liu, P., Xue, F., Tang, S., 2006. Comparison of two different processes to synthesize biodiesel by waste cooking oil. Journal of Molecular Catalysis A: Chemical 252, 107-112.

Wang, Y., Ou, S., Liu, P., Zhang, Z., 2007. Preparation of biodiesel from waste cooking oil via two-step catalyzed process. Energy Conversion and Management 48, 184-188.

WDEL News. 2009. Available at <http://www.wdel.com/story.php?id=489122876079>. Accessed November 05, 2009.

Wimmer, T., 1995. Process for the production of fatty acid esters of lower alcohols. Patent number: 5399731.

Xiangkun, M., Pingjing, Y., Xing, L., Wilfried, R., 2007. Synthesis of flexible multi-stream heat exchanger networks based on stream pseudo-temperature with genetic/simulated annealing algorithms. Journal of the Chinese Institute of Chemical Engineers 38, 321–331.

Yaws, C. L., Narasimhan, P. K., Gabbula, C., 2005. Yaws' Handbook of Antoine Coefficients for Vapor Pressure (2nd ed.). Knovel, Norwich, NY Accessed electronically through Knovel on September 14, 2009.

Yee, T. F., Grossmann, I. E., 1990. Simultaneous optimization models for heat integration-II. Heat exchanger network synthesis. Computers and Chemical Engineering 14, 1165.

You, Y., Shie, J. Chang, C., Huang, S., Pai, C., Yu, Y., Chang, C. H., 2008. Economic cost analysis of biodiesel production: case in soybean oil. Energy & Fuels 22, 182-189.

Zhang, W.V., 2006. Design of flexible heat exchanger network for multi-period operation. Chemical Engineering Science 61(23), 7730-7753.

Zhang, Y., Dubé, M., McLean, D., Kates, M., 2003a. Biodiesel from waste cooking oil: 1. Process design and technological assessment. Bioresource Technology 89, 1-16.

Zhang, Y., Dubé, M., McLean, D., Kates, M., 2003b. Biodiesel from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresource Technology 90, 229-240.

APPENDIX A

Potential Biodiesel Feedstocks

Virgin Plant-based
   1.) soy
   2.) canola
   3.) palm
   4.) rapeseed
   5.) corn
   6.) sunflower
   7.) peanut
   8.) olive
   9.) castor oil
   10.) cottonseed
   11.) jatropha
   12.) camelina
   13.) tallow
   14.) safflower
   15.) sesame
   16.) babassu
   17.) coconut
   18.) jojoba
   19.) kola nut
   20.) linseed
   21.) mustard
   22.) tung
   23.) algae
   24.) vegetable oil soapstock
   25.) partially hydrogenated methyl esters of soybean oil (PHSME)
Virgin Animal-based
   26.) virgin animal renderings
   27.) fat from meat and bone meal (MBM)
Recycled Feedstocks
   28.) Waste cooking oil (yellow and brown grease)
   29.) Tall oil (Turkey – by-product of paper pulp manufacturing)

APPENDIX B

Stoichiometry

Excess Methanol

In practice, an excess of alcohol in needed to ensure that the reaction goes to completion.   As a result of numerous experiments, many sources agree on the alcohol:triglyceride ratio of 6:1, which relates to 100% excess.

Oil   + 6 MeOH → Glycerol + 3 Biodiesel + 3 MeOH

1 mol + 6 mol   → 1mol   + 3 mol   + 3 mol
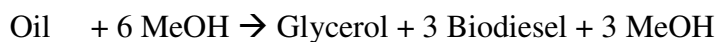
Oil: MW_{oil} g/mol

MeOH: 32.04 g/mol

Glycerol: 92.10g/mol

Biodiesel: $MW_{biodiesel}$ g/mol

Excess MeOH: 32.04g/mol

The molecular weights of methanol and glycerol are fixed. It is necessary to calculate the molecular weight of each oil and the molecular weight of the biodiesel produced.

Once the molecular weights of the oil and biodiesel are calculated, the mass of each component can be calculated.

In order to calculate the molecular weights of oil and biodiesel, the fatty acid composition of the oils must be known. Fatty acid composition of oils is readily available in literature. For the calculation of the molecular weights, it is assumed that the triglycerides are in the same proportion as the fatty acids. To calculate the molecular weight of the oil, multiply the molecular weight of each component triglyceride by the weight fraction of the corresponding fatty acids, take the sum and divide by the sum of the weight fractions. This equation is written below.

$$MW_{oil} = \frac{\sum_{i=1}^{n}(MW_{triglyceride,i} * WF_{FA,i})}{\sum_{i=1}^{n}WF_{FA,i}}, \tag{A.1}$$

where $WF_{FA,i}$ is the weight fraction of each individual fatty acid in the appropriate oil, MW_{oil} is the molecular weight of oil, $MW_{triglyceride,i}$ is the molecular weight of a given triglyceride in the oil.

Similarly, to calculate the molecular weight of the biodiesel, multiply the molecular weight of each component methyl ester by the weight fraction, take the sum and divide by the sum of the weight fractions. The resulting equation is written below.

$$MW_{biodeisel} = \frac{\sum_{i=1}^{n}(MW_{methylesters,i} * WF_{FA,i})}{\sum_{i=1}^{n}WF_{FA,i}}, \qquad\qquad (A.2)$$

where $WF_{FA,i}$ is the weight fraction of each individual fatty acid in the appropriate oil, $MW_{biodiesel}$ is the molecular weight of biodiesel, $MW_{methyl\ esters,i}$ is the molecular weight of a given methyl ester in the biodiesel.

If:

M_O= the mass of the oil

M_{Me} = the mass of the methanol

M_G = the mass of the glycerol

M_{BD} = the mass of the biodiesel

M_{EM} = the mass of the excess methanol,

then a mass calculation for the transesterification reaction with excess methanol would look like,

Oil   + 6 MeOH $\rightarrow$ Glycerol   + 3 Biodiesel   + 3 MeOH

1mol* MW_{oil} g/mol+6mol*32.04g/mol$\rightarrow$1mol*92.10g/mol+ 3mol* $MW_{biodiesel}$g/mol + 3mol*32.04g/mol

MW_{oil} = molecular weight of oil

$MW_{biodiesel}$ = molecular weight of biodiesel

Mass:

M_O g oil + M_{Me} g methanol → M_G g glycerol + M_{BD} g biodiesel + M_{EM} g excess methanol

M_O = 1mol* MW_{oil} g/mol oil = MW_{oil} g oil

M_{Me} = 6mol*32.04g/mol =192.24 g methanol

M_G = 1mol*92.10g/mol = 92.10 g glycerol

M_{BD} = 3mol* $MW_{biodiesel}$ g/mol biodiesel = 3* $MW_{biodiesel}$ g biodiesel

M_{EM} = 3mol*32.04g/mol = 96.12 g excess oil

Another way to calculate the molecular weight of the biodiesel for validation of the Equation A.2 was:

$$MW_{biodiesel} = \frac{[M_O + M_{Me} - M_G - M_{EM}]}{3} \frac{g}{mol} \qquad (A.3)$$

VITA

Grace Amarachukwu Pokoo-Aikins was born in Benin City, Nigeria but was raised in Dallas, TX where she attended Talented and Gifted Magnet High School (in Townview Magnet Center). She received a Bachelor of Arts in biology from Austin College, Sherman, TX in May 2002. She joined the graduate program at the Department of Chemical Engineering in Texas A&M University in August 2003 and completed her Master's degree in August 2006 and her Ph.D. in August of 2010. During her time at Texas A&M University she was a Graduate Diversity Fellow, and a Texas Space Grant Consortium (TSGC) Fellow. While at Texas A&M University, she was involved with process systems related projects with NASA and Tuskegee University, biofuels related projects and research pertaining to the development of the integrated biorefinery, namely biodiesel processes involving alternative feedstock, research related to chemical safety and safety metrics, and research pertaining to process optimization and integration.

Her permanent contact details are:

Grace A. Pokoo-Aikins

3122 TAMU, Jack E. Brown Chemical Engineering Building

Department of Chemical Engineering, Texas A&M University

College Station, TX 77843

Grace_ChemE_Ag_2006@AggieNetwork.com