Optimal Control of Batch Production of Biodiesel Fuel under Uncertainty

BY

PAHOLA THATHIANA BENAVIDES GALLEGO
B.S. National University of Colombia,Manizales, Colombia, 2007

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Industrial Engineering and Operations Research
in the Graduate College of the
University of Illinois at Chicago, 2013

Chicago, Illinois

Defense Committee:

David He,Chair
Urmila Diwekar, Advisor
Houshang Darabi
Michael Scott
Heriberto Cabezas, U.S.E.P.A
Ignasi Palou-Rivera, Lanzatech

ACKNOWLEDGMENT

First of all, I would like to thank my advisor, Dr. Urmila Diwekar for her confidence in me and for providing me academic guidance and strong support in every moment of my graduate studies. Her counsel and assistance has encouraged me to accomplish my research goals.

I would like to thank my committee members: Dr. David He, Dr. Michael Scott, Dr. Houshang Darabi, Dr. Heriberto Cabezas and Dr. Ignasi Palou-Rivera, for their valuable suggestions, comments and for their time and interest in this work.

This work would not have been completed without the financial support that I received from Vishwamitra Research Institute (VRI-Custom).

My thanks are also extended to past and present members of our research group: Dr. Prakash Kotecha, Dr. Yogendra Shastri, and Dr. Adrian lee, Sheraz Abbasi, and Amy David. Specially, my friends Kirti Yenkie, Dr. Nantaporn Ratisoontorn and Dr. Juan Salazar for the appreciable comments, help, unwavering support not only on my research work but also in my personal life. In addition, I would also like to thank all my professors, instructors, my classmates and friends at UIC and the helpful staff in both the Industrial and Bioengineering Department.

ACKNOWLEDGMENT (Continued)

My special thanks to my family: Martha Lucia Gallego, Segundo Leon Benavides, Carlos Albertho Benavides and also Ted Anderson for their unconditional love and support. They have always been an inspiration and a source of strength for me. I am very grateful for having them in my life.

Last, but certainly not the least, I would like to thank my God for helping achieve all my goals in life.

PTB

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

x

LIST OF ABBREVIATIONS

MCP	Maximum Concentration Problem
MTP	Minimum Time Problem
MPP	Maximum Profit Problem
FFA	Free Fatty Acids
FAME	Free Acid Methyl Ester
BGY	Billion Gallons per Year
ASEA	American Society of Agriculture Engineering
ASTM	American Society of Testing and Materials
NPW	Net Present Worth
COM	Cost of Manufacturing
FCI	Fixed Capital Investment
DMC	Direct Manufacturing Cost
COL	Cost of operating Labor
CWT	Cost of Waste Treatment
CUT	Cost of Utilities
CRM	Cost of Raw Material
GE	General Expenses

LIST OF ABBREVIATIONS (Continued)

MPOB	Malaysia Palm Oil Board
SQP	Successive Quadratic Programming
DMP	Discrete Maximum Principle
IDP	Iterative Dynamic Programming
ODE	Ordinary Differential Equation
SMCP	Stochastic Maximum Concentration Problem
SMPP	Stochastic Maximum Profit Problem
NLP	Nonlinear Programming
HSS	Hammersley Sequence Sampling
MCS	Monte Carlo Sampling
RKF	Runge Kutta Fehlberg

SUMMARY

In recent years, diminishing fossil fuel, global warming, and environmental pollution have become important global issues. The use of bio-based fuels is one of the alternatives to help resolve these issues. Amongst all the biofuels, biodiesel is considered one of the best biofuel candidates. Biodiesel is superior to diesel oil in terms of sulfur and aromatic content, and it is environmentally safe, non-toxic, and biodegradable (1). One of the most common pathways for producing biodiesel is the transesterification method, which is the formation of triglycerides from vegetable oils with short-chain alcohols. Two operating modes can be used to produce biodiesel: continuous or batch. For a batch process, a batch reactor can be employed whereas for a continuous process, continuous stirred tank reactors (i.e. CSTR reactors) can be used. In the first part of this research, a comparison between these operating modes is carried out. This comparison is based on performance and economics. Although available literature and existing computer tools mostly deal with optimal design of continuous processes, in this research it is found that batch processes can be a good alternative over continuous processes since it can handle the seasonal variability of feedstock. However, modeling and controlling batch processes is complex due to their dynamic nature.

In the second part of this research, batch production of biodiesel is improved through dynamic optimization- also known as optimal control. This strategy consists of finding a control policy that can change with time and maximize or minimize a performance index. Due to

SUMMARY (Continued)

the time dependent nature of these processes, optimal designs and control problems involve differential and algebraic equations that can be difficult to solve. Optimal control problems encountered in biodiesel production can be formulated using various performance indices, namely, maximum concentration, minimum time, and maximum profit. These problems involve determining optimal temperature profile (as the control policy) so as to optimize these indices. Such problems become even more complicated when uncertainties are taken into account. In this thesis, a novel approach to solve optimal control of a batch reactor under uncertainties in biodiesel production is presented. Feed stock variability is the commonly encountered uncertainty in biodiesel production. These uncertainties can be characterized using probability distributions as they are static uncertainties. However, they result in dynamic uncertainties due to their dynamic nature. In this research, the time-dependent uncertainties are modeled using Ito processes, which are also used in finance theory. The problem then becomes a stochastic optimal control problem which is difficult to solve. A new approach is presented to solve stochastic optimal control problems in which the stochastic dynamic programming formulation is converted into a stochastic maximum principle. The main characteristic of this approach is that the solution to the partial differential equations involved in the dynamic programming formulation is avoided. Moreover, an efficient algorithm that combines the maximum principle and Non-Linear Programming (NLP) techniques is also proposed to solve the maximum profit problem. A brief chapter related to implementation of these temperature control profiles in a jacketed batch reactor is also presented.

CHAPTER 1

INTRODUCTION

The best of all things is to learn. Money can be lost or stolen, health and strength may fail,

but what you have committed to your mind is yours forever

-Louis L'Amour,1908-1988

1.1   Motivation

The need for energy is ubiquitous for development. As the population increases, the energy requirements also increase thus becoming one of the most important issues in modern life. This growing demand for energy has made a significant impact on our social and economic development resulting in the depletion of fossil fuel reserves, rising petroleum prices, and the alarming environmental concerns due to the climate change. Although it is projected that around 85% to 90% of world primary energy consumption (projected until 2030) will continue to be based on fossil fuels (2), the development of new technologies for renewable energy provides an excellent opportunity for reduction of greenhouse gas emissions and mitigation of global warming through substituting conventional energy sources. In this sense, the production of energy from renewable sources has received wide attention among politicians, scientist and engineers. For instance, the U.S congress has established in the Energy Independence and Security Act of 2007 that mandates by 2022 the U.S. economy should be using 36 BGY (billion gallons per year) of renewable transportation fuel which represents and enormous growth over

the current production level of 13 BGY (3). On the other hand, researchers have been exploring different alternatives such as plant-based fuels, plant oils, and fats as promising biofuel sources that can secure the future energy supplies. Among those sources, biodiesel has been considered one of the best alternatives to replace the conventional diesel fuel. As a result, in the last decade a large expansion in biodiesel production along with research and innovation of production techniques can be found. Figure 1 presents U.S. biodiesel production from 1999 to 2012. In 1999 biodiesel production was only 0.5 million gallons while in 2012 this value reached 2127 million gallons. Note: The values from 1999 to 2011 were obtained from (4) while the values of 2012 were obtained from (5)

.

A biodiesel production plant involves a series of unit operations which can be operated in continuous or batch mode. According to the ASEA (American Society of Agriculture Engineering), biodiesel production technology consists of a crude oil degumming section, refining section,transesterification reaction section, water washing, glycerol refining section, and methanol recovery (6). Most of the studies of biodiesel production have been done with continuous models since the existing computer software is built for continuous processes. However, in this work it is argued that batch production provides a better alternative due to the flexibility of the operation. Therefore, in the first part of this study, a comparison of batch versus continuous production of biodiesel from soybean oil is proposed.
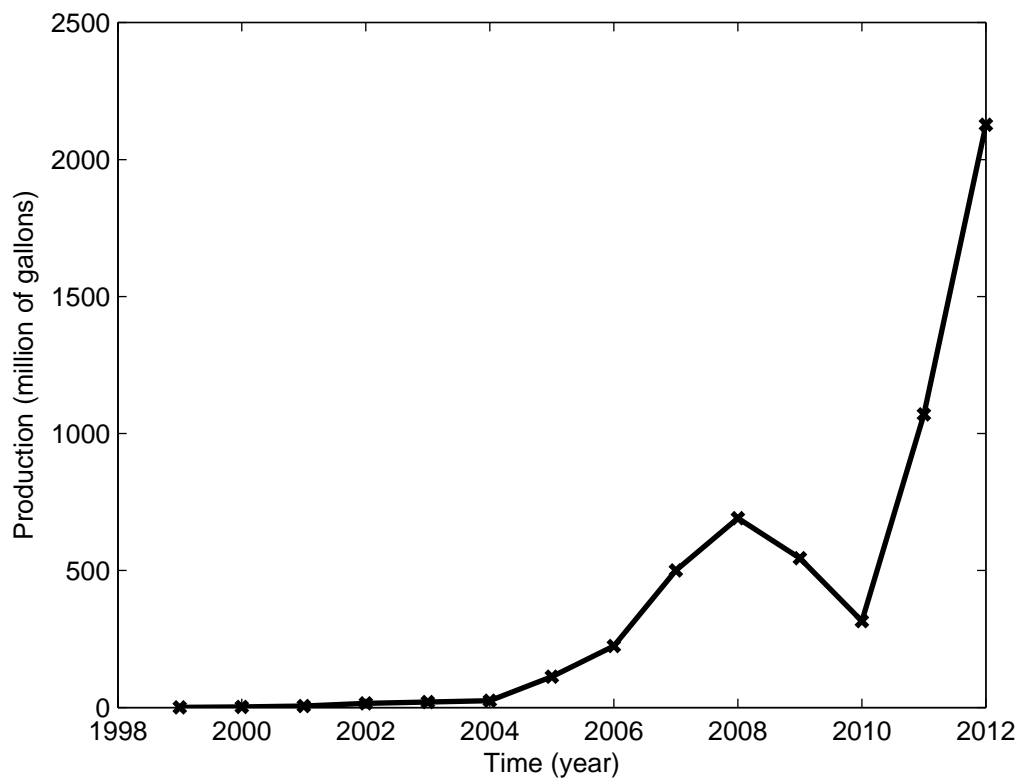
Figure 1. U.S. Biodiesel production from 1999 to 2012

The biodiesel transesterification reactor resembles the heart of any biodiesel manufacturing plant. The design of this reactor provides challenging problems with respect to basic functionality, safety product quality, and yield related issues (7). In addition, any drift that occurs in a batch reactor under standard conditions will lead to significant changes in the process variables and production quality specifications. In general, these types of reactors are excellent at handling complicated materials which represent a helpful solution for many types of reac-

tions, and they are versatile for different applications that range from specialty chemical and pharmaceutical manufacturing to agricultural, food and consumer products, and most recently the constantly growing spectrum of biotechnology enabled products (8). Therefore, this thesis concentrates on optimizing the reaction section of the batch biodiesel production. Since batch reactors are inherently dynamic, their optimization results in dynamic optimization problems, also known as optimal control problems. Optimal control problems encountered in biodiesel production can be formulated using various performance indices, such as maximum concentration of biodiesel, minimum reaction time, and maximum profit. To maximize or minimize these performance indices, it is necessary to determine the optimal control policy, e.g. optimal temperature profile. Depending on the downstream process requirement (i.e. plant schedule, quality, quantity, etc.), any of these performance indices can be used. For example, for a fixed batch time the Maximum Concentration Problem (MCP) maximizes the product, whereas if the quality (or conversion) of the product becomes the main constraint in the process, the desired product is achieved by solving the Minimum Time Problem (MTP). In this thesis, three optimal control problems in biodiesel production are studied (i.e. Maximum concentration, minimum time, and maximum profit problems (MPP). These problems become more challenging when variability and uncertainty in any parameter is included. In biodiesel production, there are inherent uncertainties arising due to variation in the initial composition, operating parameters, and mechanical equipment design that can have a significant impact on the product quantity, quality and process economics. One of the most influential uncertainties is the uncertainty due to feed composition variability since the percentage and type of triglycerides in biodiesel com-

position varies considerably. These uncertainties result in dynamic uncertainties which imply the solution of stochastic optimal control problems. These problems are solved using a new and efficient approach. In addition, deterministic versus stochastic results are compared and practical implementation strategies are discussed.

1.2   Structure of the thesis

The first part of this work addresses the following research question: *Is biofuel production better in continuous or batch processes?* Batch processes are dynamic processes that arise from the requirement of generating high quality, and low volume products with great flexibility. Although, in our opinion there are clear advantages to batch production of biodiesel, most of the work and commercial facilities are moving towards continuous production thinking that will provide cost advantages. Hence, Chapter 2 presents a detailed comparison of batch and continuous production of biodiesel considering performance and economics. The economic feasibility of biodiesel production and the plant configuration not only depends on technical design aspects but also on other important factors such as seasonal variation of feedstock, transportation costs, and storage costs of material. Therefore, the comparison presented here involves size of the market, transportation distance from supplier to producer facility, and feedstock availability of soybean oil by allocation of raw material supply. It is found that batch production is favored over continuous production in most of the cases. This chapter appears in Environmental Progress and Sustainable Energy as an invited paper (9).

Once batch processes are selected as an attractive option for biodiesel production, Chapter 3 answers the second research question: ***Can we come up with better operating policies that can optimize this production?*** Although, batch processes offer the most attractive and challenging problems, modeling and controlling these processes is complex due to their dynamic nature. Therefore, in this chapter dynamic optimization is studied to improve biodiesel production in a batch reactor. This Chapter presents the deterministic optimal control problem in biodiesel production where the three optimal control problems, namely, maximum concentration, minimum time, and maximum profit are introduced. These problems are formulated for the deterministic case, that is, no uncertainty is considered in the process. To solve these problems, methods such as maximum principle and non-linear programming are employed. The content of this Chapter appears as two papers in the journal of Fuel (10) and (11).

As stated earlier, biodiesel production is inherently uncertain. Therefore, Chapter 4 and 5 answers the question regarding uncertainties: ***Why is important to consider uncertainties in biofuel production?*** Chapter 4 introduces Ito processes. Ito processes, also used in financial theories, deal with time-dependent uncertainties in bio-processing. This chapter presents methods and tools for characterizing, quantifying, and propagating time dependent uncertainties. Following that,Chapter 5 presents various optimal control problems in the face of feed composition uncertainties. These static uncertainties result in dynamic uncertainties making the problem difficult to solve. New approaches are used to solve these problems. The results of the stochastic optimal control problems are compared with deterministic results. This

work appears in two papers in the journal of Fuel (11) and (12). The second paper recently received a national award from American Institute of Chemical Engineering (AIChE) sustainability engineering forum.

Chapter 6 describes some aspects regarding the implementation of the optimal temperature control such as the reactor cooling/heating configuration, and energy balance. It has been found that to control the temperature of the reaction in industrial batch reactors, a control system manipulates the jacket reactor temperature through the coolant/heating fluid temperature depending on the nature of the reaction (i.e. endothermic or exothermic). The cooling and temperature profile for reactor jacket is presented here for the different optimal control problems studied earlier.
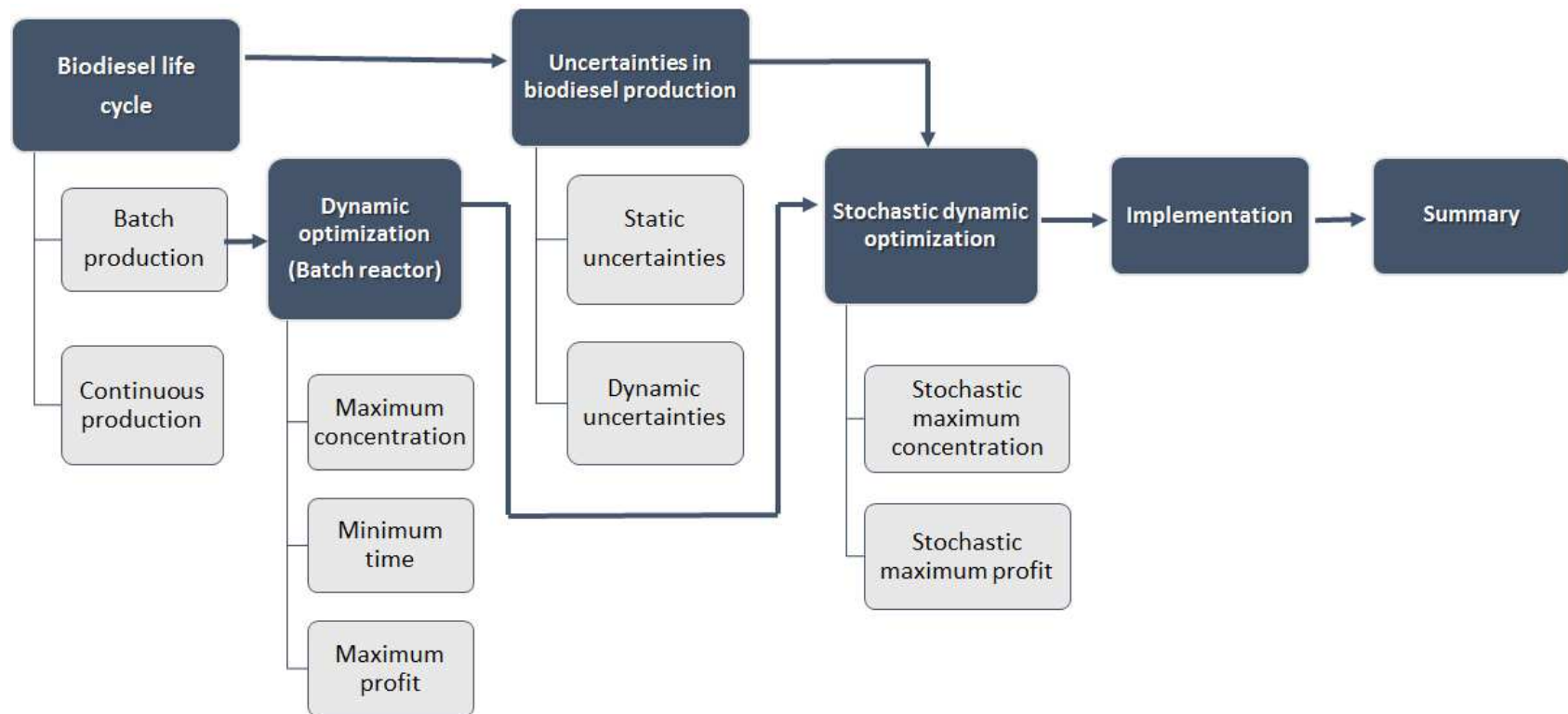
Figure 2. Overview of the thesis

Finally, the last part of the thesis provides the summary and contributions of this study, along with recommendations for future research. According to the research questions and objectives described above, the structure of the thesis is summarized in Figure 2. This Figure shows the important points discussed in this thesis from Chapters 2 to Chapter 7.

1.3   Biodiesel background

During 1930s and 1940s, vegetable oils were used as emergency fuels (13). However, the use of these oils and their blends were generally considered to be unsatisfactory because of their high viscosity and low volatility properties that caused problems such as engine deposit, injector coking, piston ring sticking, and thickening of lubricating oil (14). All these problems were eliminated through the transesterification reaction of these vegetable oils with an alcohol to form fatty acid methyl esters also known as biodiesel. The full exploration of biodiesel only came into light in the 1980s after the oil crisis in 1970s. This situation revived the interest in renewable (energy) sources for reducing greenhouse gas (GHG) emissions, and alleviating the depletion of fossil fuel reserves. This made biodiesel as a good alternative for the replacement of petroleum-based diesel. The most commonly used vegetable oil is soybean oil, and methanol is widely considered the most cost-effective and readily available alcohol. This clean renewable fuel is superior to diesel oil in terms of sulfur and aromatic content that allows biodiesel to burn much cleaner than conventional diesel. Although the burning of biodiesel is a combustion process that releases carbon dioxide (i.e.CO_2) to the atmosphere, biodiesel consumption does not add CO_2 to the atmosphere because it is derived from plant sources which trap CO_2 during

photosynthesis (15). Several studies have compared the difference between biodiesel and diesel fuel. For instance, Wu et al. (16) compared the performance of five methyl ester biodiesel samples (i.e. palm oil, soybean, rapeseed, cottonseed, and waste cooking oil methyl esters). These samples were run on a direct injection engine, and tested the emissions. Their studies have shown that the reductions in particulate matter range from 53% to 69% dry soot ranges from 79% to 83% hydrocarbons ranges from 45% to 67% and carbon dioxide ranges from 4% to 16% compared with petroleum diesel. However, nitric oxides (NOx) showed slight increase from 10% to 23%. The reasons for variations of the emission performance of each methyl ester are associated with the oxygen content and viscosity of the methyl ester which further depend on the properties of the feedstock. On the other hand, biodiesel can be used in any compression ignition engine without the need of any modifications (17). The lubricant properties of biodiesel are better than diesel, which can help to increase the engine life and improve their operations even if it is used in very low concentrations of 1%. Biodiesel also raises the cetane number of fuels which is the measurement of the combustion quality of diesel fuel during compression ignition.

Some properties of biodiesel and diesel fuels are compared in Table I. As it can be seen, biodiesel produced from various vegetables oils has viscosity values close to diesel. Moreover, the volumetric heating values are a little lower, but they have high cetane numbers and flash points.

TABLE I

PHYSICAL AND CHEMICAL PROPERTIES OF BIODIESEL

Vegetable oil	Kinematic viscosity(mm2/s)	Cetane number	Lower heating value(MJ/L)	Flash point(^{0}C)	Density (g/l)
Soybean[a]	4.5(37.8^{0}C)	45	33.5	178	0.885
Soybean[b]	4.0(40^{0}C)	45.7-56	32.7	-	0.880(15^{0}C)
Peanut[a]	4.9(37.8^{0}C)	54	33.6	176	0.883)
Palm[b]	4.3-4.5(40^{0}C)	64.3-70	32.4	-	0.872-0.877(15^{0}C)
Rapeseed[b]	4.2(40^{0}C)	51-59.7	32.8	-	0.882(15^{0}C)
Diesel	12-3.5(40^{0}C)	51	35.5	-	0.830-0.84(15^{0}C)
JIS[c]-2D(Gas oil)	2.8(30^{0}C)	58	42.7	59	0.833

a(19);b(20);c(21)

Therefore, due to these similarities to diesel fuel, biodiesel is a strong candidate for replacement (18).

Although in this work the focus is on biodiesel production through transesterification of soybean oil with methanol, there are other routes that have been adopted for it production. Four primary ways are shown in Table II (22) direct use and blending, micro-emulsions, thermal cracking, and transesterification. These methods are available to minimize the viscosity of vegetable oils, making them practical for use in internal combustion engines. As the name indicates, the direct use and blending methods mix the raw oils directly into the existing diesel fuel. Micro-emulsification disperses the vegetable oils into a solvent such as alcohol (e.g. methanol, ethanol, or butanol), surfactant, and cetane improver in suitable proportions.

TABLE II

DIFFERENT METHODS OF BIODIESEL PRODUCTION

Method	Advantage	Disadvantage	Problems of using in engines
Direct use and blending	Liquid nature-portability, heat content(80% of diesel fuel),readily available, renewability	Higher viscosity, lower volatility, reactivity of unsaturated hydrocarbon chains	Coking and trumpet formation, carbon deposits,oils ring sticking, thickening and gelling of the lubricating oil
Micro-emulsion	Better spray patterns during combustion, Lower fuel viscosities	Lower cetane number, Lower energy content	Irregular injector needle sticking,incomplete combustion heavy carbon deposits increase lubricant oil viscosity
Thermal cracking (pyrolysis)	Chemical similar to petroleum-derived gasoline and diesel fuel	Energy intensive and hence cost	-
Transesterification	Renewability, higher cetane number, lower emissions, higher combustion efficiency	Disposal of byproduct (glycerol and waste water)	-

Thermal cracking or pyrolysis involves heating the oil with catalyst in the absence of air or oxygen. And finally, the transesterification reaction that involves heating the oil with a catalyst and an alcohol to change its chemical structure.

The transesterification reaction can occur with the use of acid, alkali, or enzyme as catalysts, or in a supercritical fluid system without catalyst. The most common technology used to produce biodiesel is alkaline homogeneous transesterification, with conversion efficiency of more than 98%. However, the homogeneous transesterification has a disadvantage as it consumes

large amount of water for wet washing to remove the salt produce from the neutralization process, and the residual acid or base catalyst. On the other hand, heterogeneous biodiesel production processes have less number of unit operations, with simpler separation and purification steps of products as there is no neutralization process required. The effectiveness of this technology depends on the effectiveness of the solid catalyst used. Table III summarizes the different transesterification methods that can be used to produce biodiesel.

TABLE III

DIFFERENT TRANSESTERIFICATION TECHNOLOGIES

Technology	Classification	Advantages/Disadvantages	Reference
Homogeneous catalyst mediated process	Homogeneous alkali-catalyzed reaction	Special control for water content and free fatty acids (FFA) contained in raw materials is required	(23);(24)
	Homogeneous acid-catalyzed reaction	Cheap and abundant since concentrated sulfuric acid is used, however, it leads to serious issues such as severe corrosion of the equipment and environmental concerns	(25)
	Two step catalytic process with acid and alkali	Pre-esterification with an acid catalyst is conducted prior to alkali catalyst-mediated transesterification. It can be used with different oil feedstock. The economic and environmental benefits are reduced due to the complexity of the procedure.	(26);(27);(28)
Heterogeneous catalyst mediated process	Heterogeneous solid-alkali catalyst reaction	It can be reusable and easy to separate from the reaction products. The performance is generally poorer than that of the commonly used homogeneous catalysts	(29);(30)
	Heterogeneous solid-acid catalyzed reaction	This technology adapts well to feedstocks with high FFA content, and has the advantage of easy separation, but, the disadvantages are low activity, slow reaction rate, high temperature, and poor yields.	(31);(32); (33)
Lipase mediated process	Immobilized lipase mediated transformation	Need of use organic solvent systems to overcome the negative effects on the lipase activity and operational stability due to the poor solubility of methanol in oil feedstocks. For this reason is a complicated method for large-scale continuous biodiesel production. Moderate reaction conditions, low alcohol to oil ratio, easy product recovery, and environmentally friendly	(34);(35)
	Whole-cell mediated alcoholysis	Avoid complex procedures of lipase fermentation, purification and immobilization, therefore it is potential way of reducing the cost of the biocatalyst. Many challenges such as scaling up and process optimization need to be investigated further	(36)
	Liquid lipase mediated alcoholysis	Faster reaction rate and lower cost compared with immobilized lipase biodiesel yield of over 90% could be obtained after 8 h reaction. The recovery of lipase and the enzymes performance during continuous running need to be evaluated further.	(37)
Biodiesel production in a supercritical fluid system	-	Fast reaction rate and high conversion yield. Methanol is hydrophobic in supercritical conditions, and triglyceride dissolves well in supercritical methanol. This method is sensitive to operating temperature and pressure variations	(38);(39);(40)
Algae-based biodiesel production	-	Algae-based oil is non-edible oil that can avoid the competition with food source. This biomass provides higher yield production such as superior yield per hectare over conventional oil crops, and more oil content. The higher cost performance compared with traditional biodiesel-soybean based production.	(41);(42)

CHAPTER 2

COMPARING CONTINUOUS AND BATCH PROCESS PERFORMANCE FOR BIODIESEL PRODUCTION

2.1 Introduction

One of the most important decisions that an engineer has to face when designing a chemical plant is the operational mode. This decision seeks to find the process which minimizes the costs or maximizes the yield. Making this decision will affect the product quality and the viability of the process. Therefore, several aspects must be considered, such as production rates, operational process, recycle options, hazardousness of chemicals, possibilities of energy integration, and economic analysis (43). Many paths may be available to produce the same material, but the remaining question is which one would be the best and under which conditions. This chapter presents the biodiesel production and proposes performance and economic comparison between continuous and batch processes. Recently, investigations on commercial biodiesel production have focused on process technology and economical assessment. Available literature and existing computer tools mostly deal with optimal design of continuous processes. However, given the variability of feedstock and seasonal variation batch processes can be a good alternative over continuous processing because of their higher flexibility. Although very few people have given attention to batch processing of biodiesel, these processes allow engineers

to manipulate variations in feedstock and product specifications, making the process more adjustable to the requirements of a specific design.

Comparisons between batch and continuous operation have received little attention in the process engineering literature. Only some cases are available but they refer to specific chemical process. For instance, Wagialla et al. (44) presented a comparison of some technical aspects regarding batch vs. continuous refining of crude cottonseed oil. In this article, researchers evaluated the percentage of refining loss, refined oil color, caustic soda consumption based on the initial crude oil FFA content, and showed that continuous refining of cottonseed oil is more efficient in each of these performance criteria, particularly the percentage of refining loss. In Gorsek and Glavic (45), the objective was to highlight the important factors which govern the selection of a simplified operation mode (i.e. batch vs. continuous) using a single-purpose equipment. Such factors were production capacity, recycling and energy integration with heat storage. As a result, it was shown that the most profitable operation mode, in terms of net present worth (NPW) was the continuous model with recycle loops and energy integration. However, in a second part of the paper (46), the study was focused on the advantage of a batch model with multi-purpose equipment. The same example was used to produce a specialty chemical, and the results showed that batch process with multi-purpose equipment was more profitable than a batch process with single-purpose equipment and even more profitable than the continuous one. Finally, Fonseca et al. (47) compared the behavior of batch and continuous processes using the reaction rate constants found in the open literature for transesterification

of vegetable oils. In their study, they presented that a series of CSTRs can be an industrially feasible choice for replacing batch transesterification reactors in large scale biodiesel plants; however, the loss in productivity caused by changing from batch to continuous process was compensated by using higher catalyst concentrations. Literature concerning only the estimation of biodiesel production cost has been presented separately for continuous models by Myint and El Halwagi (48), Zhang et al. (28) and Haas et al. (49), and for batch models by Sakai and Kawashima (50). These works were based on capacity plant and different process technology, such as energy integration, variation in catalytic processes or availability of raw material. As an example, (50) showed a manufacturing cost comparison between continuous processes with the production of biodiesel in a batch model. This comparison was based on the type of catalyst (homogeneous and heterogeneous alkali) and method of purification of biodiesel. As a result, it was shown that their batch processes were relatively expensive compared with the continuous process shown by West et al. (51), but they were competitive when the glycerol credits were considered.

As it can be seen, the literature of economic comparisons between batch and continuous process for the production of biodiesel (especially from soybean oil) is limited. On the other hand, previous literature, related to batch and continuous production, agreed that raw material is the largest contributor to the production cost (49) and (48). This issue becomes more challenging when considering the market availability of soybean oil and distance to the biodiesel

production facility.

Therefore, the comparison proposed here is based on the supply chain management of biodiesel, having as the decision criteria: the size of the market, its distance, and feedstock availability.

2.2 Biodiesel life cycle

The life cycle of biodiesel production is related to supply chain management which assesses the challenges existing for bringing biodiesel production up to scale ((52); (53); (54)). Its objective is to include the production and transportation of the feedstock from a farm to a refinery in the most cost efficient manner. The life cycle of biodiesel is described graphically in Figure 3.
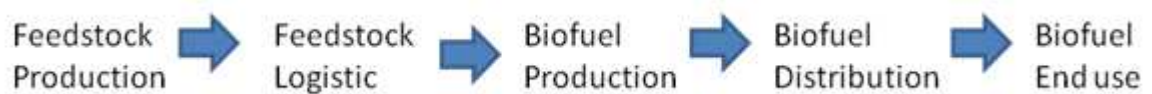
Figure 3. Biodiesel life cycle

In the first part of the life cycle, the feedstock production is considered. This section comprises issues such as land availability, seeding, growing, yield and environmental impact of growing the feedstock. Following to this section, there is the feedstock logistic. This stage has four smaller steps which are harvesting, storing, preprocessing and transportation of the feedstock from the cropland to refineries (53). Then biofuel production is the third step. Here the feedstock (e.g. soybean) is converted through transesterification reaction into biofuel (e.g. biodiesel). The last two stages are related to the transportation and end use of the biofuel that focuses on how the consumers access the biofuel. The life cycle of biodiesel production can affect significantly the economic assessment of biofuel production. For instance, the cost incurred in the feedstock logistic stage is one of the major costs drivers, and it has received minimal attention (52). This could also be one of the causes that the cost of raw material contributes in 88% of the total estimate production cost. Banariee and Noguer (54) consider three aspects regarding the economic evaluation of the feedstock logistic stage:

- Transportation vs. economy of scale: the cost of feedstock transportation and risk of supply instability can be affected due to the inherent scale economics that encourage the construction of large biomass refineries.

- Storage location: this aspect depends on the feedstock, the planted, and harvest season. For example, most of the U.S. soybeans are planted in May and early June and harvested in late September and October (55). The resulting biomass needs to be stored the rest of

the year and this can be done either in the fields where feedstock is harvested or in the refinery.

- Capital cost of inventories: the storing location of inventories is one of the key decisions in the design of a supply chain for biofuels. This aspect evaluates convenient way to store the inventories.

2.2.1   Soybean market

There are different types of oils and fats that may be used to produce biodiesel. Figure 4 includes various oils such as canola, cottonseed, coconut, edible tallow, lard, and others (corn, palm, palm kernel, peanut, sunflower, and safflower). As it is shown in this figure, soybean has been the most widely used in the U.S., contributing to 68% of the fats and oils consumption of 2010. Besides, in 2010 soybeans represented 58% of world oilseed production and 35% of those soybeans were produced in the U.S. (4). Finally, Soybeans are about 90% of U.S. total oilseed production. Among other characteristics, soybean has expandable harvest areas, cheapest feedstock among other vegetables oils and high quality due to its low FFA and high purity. Therefore, in this work soybean is chosen as the feedstock for the production of biodiesel.

Three types of soybean oil can be encountered for the production of biodiesel: crude oil, refined, and bleached. Although, high conversion can be achieved through conventional technology, it is only suitable when refined oils are employed (56). Therefore, refined oil is used in

Feedstock	Million Metric Tons
Soybean	6.52
Rapeseed	0.72
Cottonseed	0.29
Coconut	0.17
Edible Tallow	0.12
Lard	0.08
Others	1.76
Total	9.64
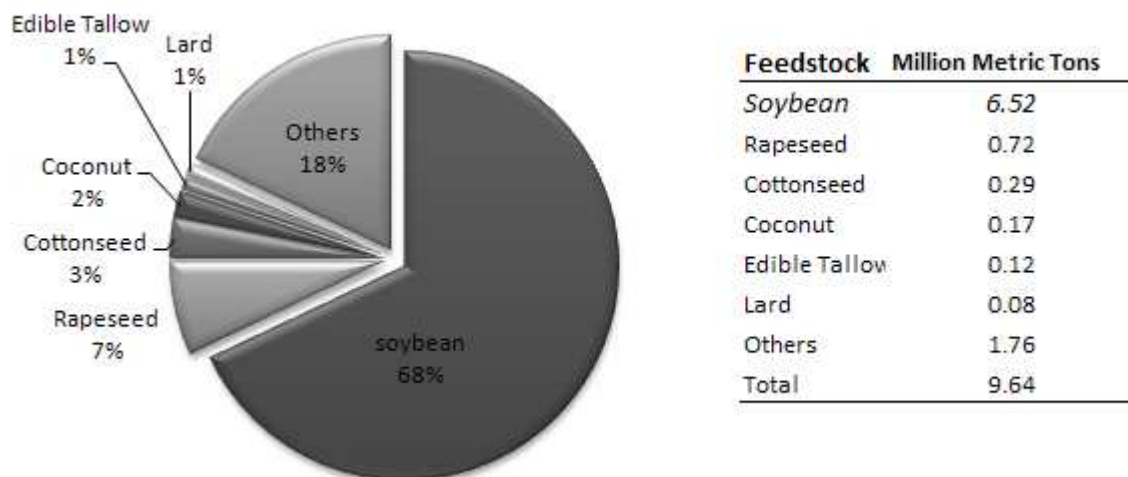
Figure 4. U.S. fats and oils consumption 2010

this work; besides, the kinetic model was obtained from refined and bleached soybean oil by (57). Refined oil refers to the amount of Free Fatty Acid (FFA) which should be lower than 0.5% in order to avoid saponification, and to make the downstream processes of biodiesel after the reaction section less complicated. The drawback of using refined oils is its price, around 1000 to 1234 U.S. $ per ton, while for crude oil, waste oil, or cooking oil, the price ranges can be around 110 to 320 U.S. $ per ton but the amount of FFA is considerable high (56).

Soybean production cost may vary for each region in the U.S. For instance, the Midwest soybean producers generally have higher yield and lower cost per acre than Southern and Easter producers (55). Figure 5 (left side) shows the soybean production and price by state in 2010. It can be seen that Iowa and Illinois have the highest production with 13.51 million tons and

12.68 million tons, respectively; while West Virginia and Florida have the lowest production both with 0.02 million tons. On the other hand, Figure 5 (right side) shows the price to farmers by state, as it can be seen Illinois and North Carolina have the highest price with 457\$/ton and 452\$/ton, respectively, while New York and Louisiana have the lowest price with 404\$/ton and 401\$/ton, respectively. This is important information that can provide the investors with criteria to find promising locations of biodiesel production plants.

Figure 5. Soybean production and price by state 2010
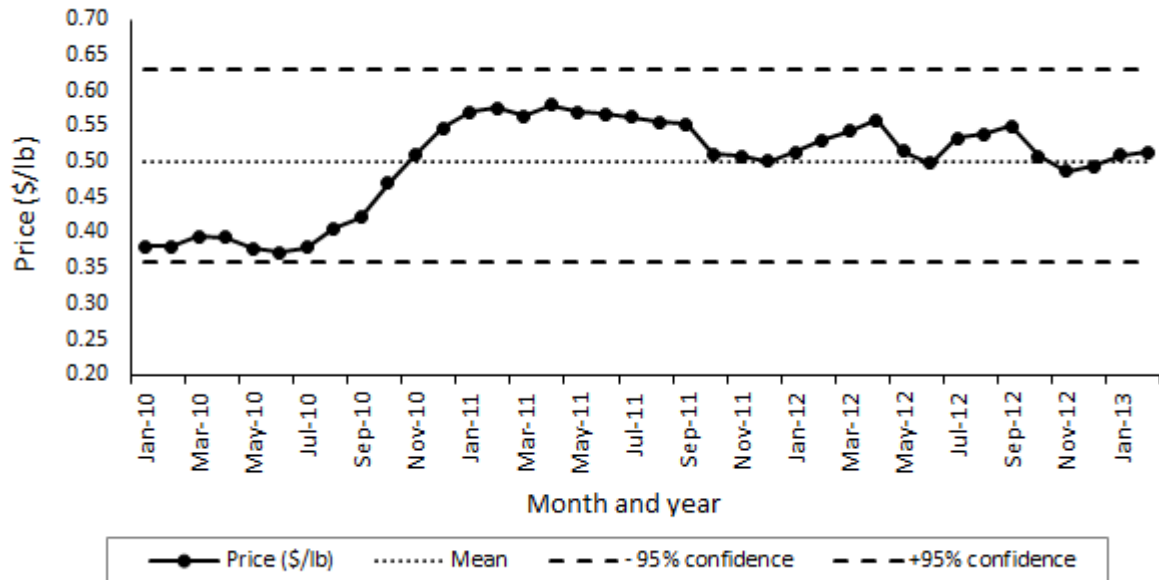
Figure 6. Soybean oil monthly prices in the U.S.

Figure 6 shows the monthly price of soybean oil. This data was reported by indexmundi.com (58) which contains detailed country statistics and information of their agricultural commodities. The information presented in this figure involves average prices of soybean oil all around the U.S. As it can be seen from this figure, the price of soybean oil has increased over the last couple years from 0.38$/lb. in January of 2010 to 0.51$/lb. in February of 2013. Some of the reason of this increase resulted from the increased worldwide demand, the global economic recession, the fluctuating value of the dollar, and the increase edible oil competition from other fats and oils (59).
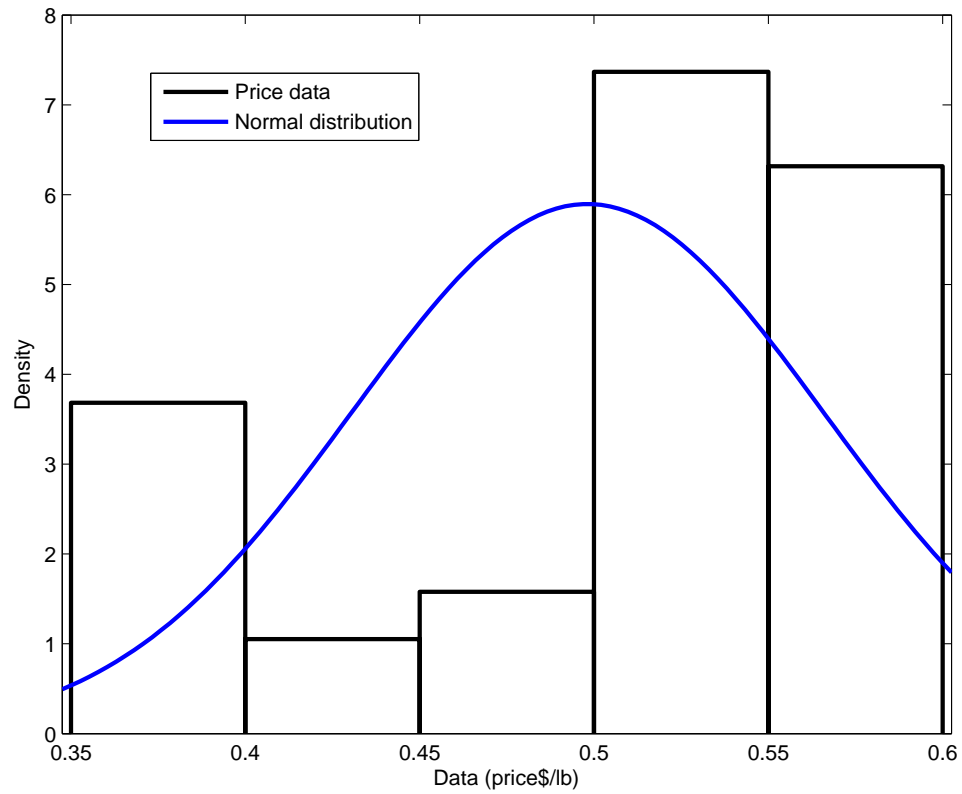
Figure 7. Normal distribution of soybean oil monthly prices in the U.S.

A statistical analysis is also shown in Figure 7. This figure shows the data of the monthly prices of soybean oil which were fitted to a normal distribution with mean 0.50 and standard deviation of 0.07.

2.2.2   <u>Soybean transportation</u>

Transportation cost of feedstock plays an important role in the supply chain management, especially in the feedstock logistics, because it influences economically the location of a biodiesel facility. Generally, this cost is a function of the method of transportation used. The selection of transportation depends on the availability of infrastructure, quality and distance. For instance, trucks, rail, or barges may be used to move the feedstock along the supply chain, each with a different cost per ton per distance. U.S. has an efficient rail system, extensive highway and barge infrastructure that make the average cost of moving U.S. crops from farm to vessel the lowest of any major grain and oilseed exporting country (57). Usually farmers move their production by truck over farm to market roads. Many farmers own trucks capable to carry up to 30 metric tons and their most common practice is to truck soybeans by a grain elevator where the soybeans are unloaded, combined with soybeans from other farms. The second transportation mode is rail. Most soybeans and grains are moved in upwards of large hopper cars that carry 80 to 90 metric tons each.

Finally, barges moves over inland waterways. The U.S. has a widespread system of waterways that stretch from the Upper Mississippi River and its tributaries in Minnesota all the way to the Gulf of Mexico. In this work, the transportation cost was determined based on the study proposed by English et al.(60) where a comparison of transportation costs for various locations is shown. Therefore, Figure 8 presents transportation costs for soybean oil vs. distance. A linear regression model was used to represents this information in to linear equations that relates
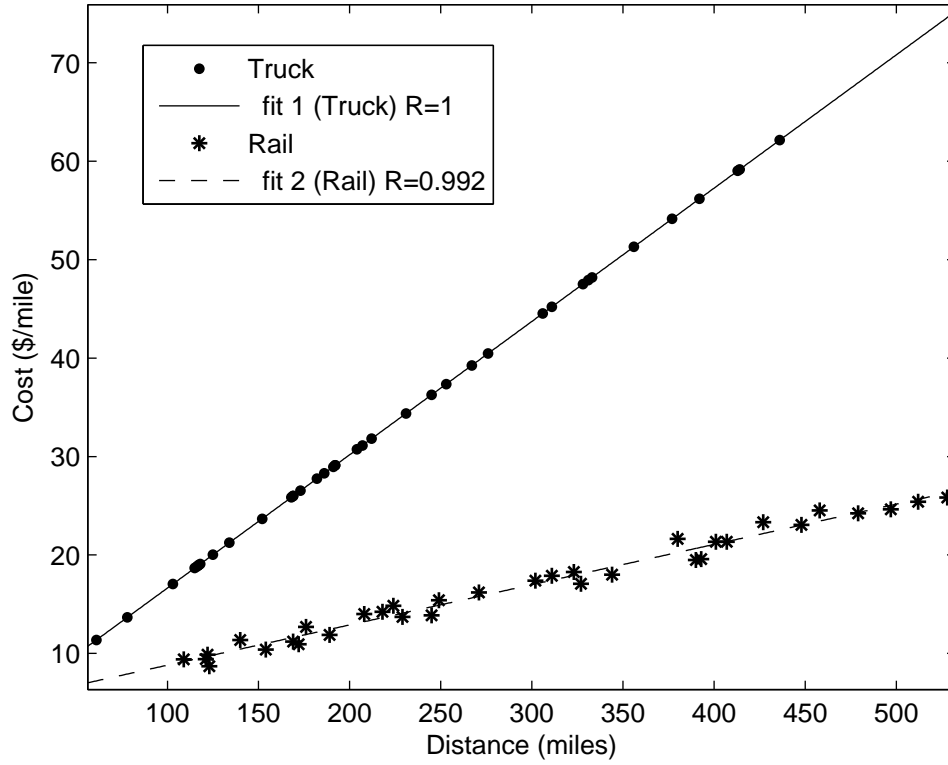
Figure 8. Transportation cost for soybean and regression analysis

the transportation cost with distance depending on the method of shipping (i.e. truck or rail). In order to obtain the transportation cost in units of $/mile, the distance d must be expressed in terms of miles. In this work, the truck method was used as the transportation method which is represented by the first equation shown in Table IV.

TABLE IV

TRANSPORTATION COST FOR SOYBEAN REGARDING THE DISTANCE D

Method	Unit ($/mile)
Truck	0.14d+3.10
Rail	0.04d+4.64

2.2.3   Biodiesel reaction

Fatty acid methyl esters, well known as biodiesel, are product of the transesterification process. This process is achieved by the reaction of triglycerides which are contained in the soybean oil, with an excess of alcohol (i.e. methanol) in the presence of an acid and alkaline catalyst (i.e. Sodium hydroxide). The intermediate steps in biodiesel transesterification are shown in Figure 9 (61).

The reaction consists of three stepwise and reversible reactions where in the first step the triglycerides with one molecule of methanol are converted into diglycerides, then, the diglycerides are converted into monoglycerides and this last one into one molecule of glycerol. In addition, in each step a methyl ester (i.e. $RiCOOCH_3$) is produced resulting in three molecules of methyl ester from one molecule of triglycerides. Figure 10 shows the overall reaction which summarizes the reaction scheme (48).

Step 1:

$$CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_1$$
$$|$$
$$CH-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2 \quad + \quad CH_3-OH \quad \underset{\longleftarrow}{\longrightarrow} \quad CH-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2 \quad + \quad CH_3-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_1$$
$$|$$
$$CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_3$$

CH$_2$-OH
CH$_2$-O-C-R$_3$

Triglycerides   Methanol   Diglyceride   Fatty Acid Methyl Ester

Step 2:

CH$_2$-OH

$$CH-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2 \quad + \quad CH_3-OH \quad \underset{\longleftarrow}{\longrightarrow} \quad CH-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2 \quad + \quad CH_3-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_3$$

CH$_2$-O-C-R$_3$ CH$_2$-OH
CH$_2$-OH

Diglyceride   Methanol   Monoglyceride Fatty Acid Methyl Ester

Step 3:

CH$_2$-OH   CH$_2$-OH

$$CH-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2 \quad + \quad CH_3-OH \quad \underset{\longleftarrow}{\longrightarrow} \quad CH-OH \quad + \quad CH_3-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2$$

CH$_2$-OH   CH$_2$-OH

Monoglyceride   Methanol   Glycerol   Fatty Acid Methyl Ester
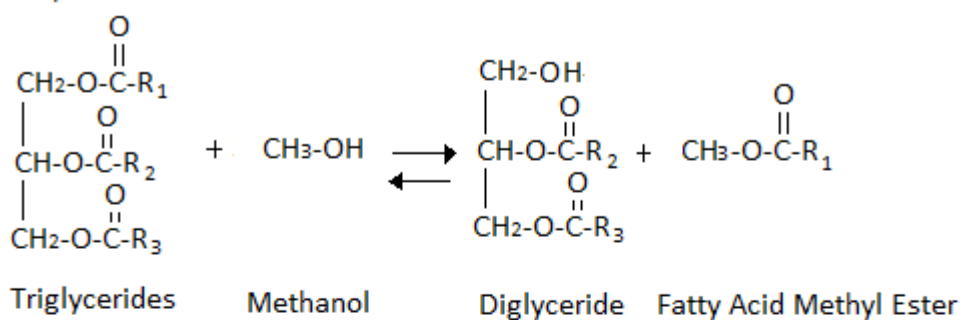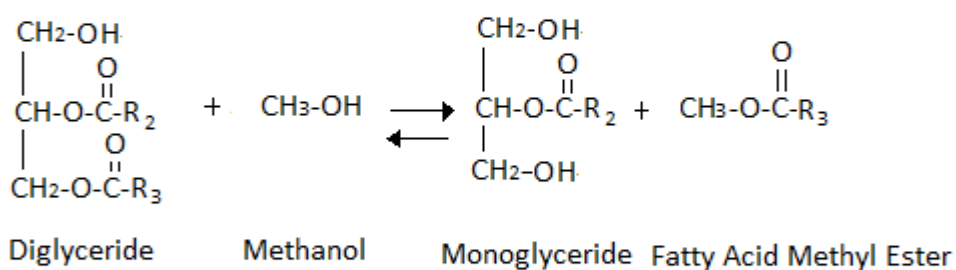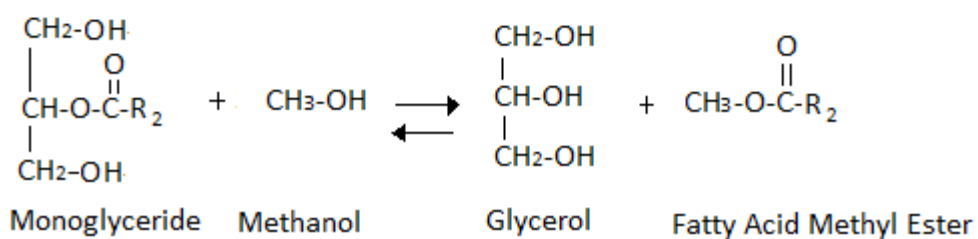
Figure 9. Intermediate step in biodiesel transesterification
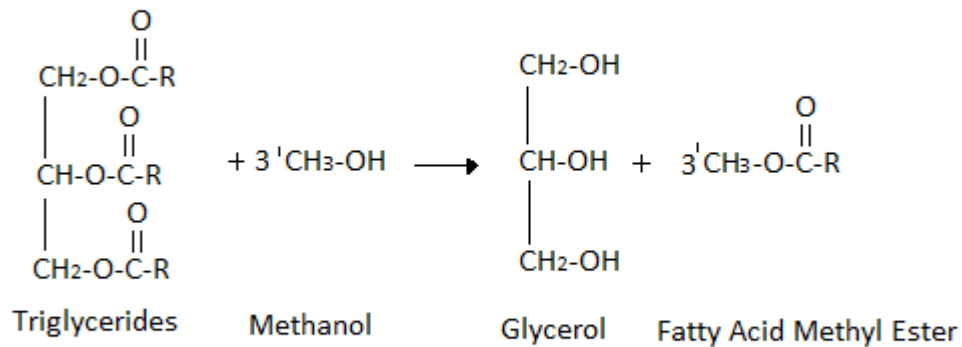
Figure 10. Overall transesterification reaction

In the biodiesel reaction, the yield is affected by different parameters; however, researchers have considered four main factors: molar ratio between alcohol and triglycerides, reaction time, catalyst, and reaction temperature. For instance, an excess of alcohol can guarantee the complete conversion of fats or oils to esters in a short time. Usually, the molar ratio employed is 6:1 in a presence of alkali catalyst. On the other hand, the conversion rate of fatty acids esters increases with time and it has been found that the yield reaches a maximum at the reaction time of less than 90 minutes (62). An excess of reaction time will decrease the yield due to the backward reactions and it will cause more fatty acids to form soap (62). The catalyst also plays an important role since its concentration increases the conversion of triglyceride, which increases the yield of biodiesel. The most commonly used catalyst is sodium hydroxide. Fi-

nally, a higher reaction temperature can decrease the viscosities of oil resulting in an increased reaction rate and a shortened reaction time. Moreover, it is possible that the yield of biodiesel decreases when the reaction temperature rises beyond the optimal level since it accelerates the saponification reaction of triglycerides (22).

2.3   Batch vs. Continuous

As mentioned before, one of the most significant decisions an engineer has to do make is regarding whether the process will be batch or continues process. A batch process is one in which a finite quantity of product is made during a period of a few hours or days. In contrast, in a continuous process, the feed is sent continuously to a series of equipment, with each piece usually performing a single unit operation (43). In the literature, it has been found that one of the most relevant differences between continuous and batch process is the size of operation; although it is not the only aspect, it noticeably influences in the selection of the mode. Other aspects have been found in comparison studies, such as seasonal demand, storage facilities, life time of the product, hazard operation, and operation labor. One advantage of batch process over continuous is its flexibility. For instances, in batch processes the same equipment can be used for multiple operations and depending on the seasonal demand and, batch processes can operate for only part of the year. On the other hand, the continuous processes to be profitable, their plants need to be large and operate throughout the year, and the storage facilities can be considered to overcome the feedstock availability and seasonal demand but the production cost

TABLE V

DIFFERENCE BETWEEN BATCH AND CONTINUOUS MODELS

Factor	Batch process	Continuous process
Size	Plant Capacity less than 500ton/yr	Plant capacity great than 5000 ton/yr
Flexibility	Often the same equipment can be used for multiple operations. Some reactions are so slow that batch processes are the only reasonable alternative.	It is possible to build in to continuous processes but often leads to inefficient use of capital. This type of processes are designed to produce a fixed suite of product from well-defined feed material
Feedstock availability	Batch processes are often preferred for products with seasonal demand or the feedstock availability is limited, which make the plant to operate for only part of the year.	In order to be profitable, continuous plants need to be large and operate throughout the year. Storage facilities can be considered to overcome this issue but the production cost will be increased.
Maintenance and operating labor	Higher operating labor costs due to equipment cleaning, preparation time and operation.	For the same process, operating labor will be lower for continuous processes.
Processing efficiency	Batch processes require strict scheduling and control. Changes in the schedule can cause serious problems with product availability for costumers. Besides, if the same equipment is used to produce different products, then the equipment cannot be optimized. Energy integration, separation and reuse of raw material are more difficult to do.	Generally, as the size increases, continuous processes become more efficient. In addition, recycle of unusual reactants and the energy integration of energy, within the process are standard practices and relative easy to achieve.

will increase. Table V presents some considerable distinctions between these two type models.

2.4   Process description

In general, the biodiesel production involves four important steps and one extra step for the treatment of the byproduct, glycerol. The first step involves the reaction, where the transes-

terification of triglycerides results in the formation of methyl ester (i.e. biodiesel) in presence of an alkalis catalyst (e.g. sodium hydroxide). After the reaction process, the following step (second step) is the separation of biodiesel from the rest of the products such as glycerol and the remaining catalyst. This step is performed in a decanter resulting in two streams, one directed to the glycerol separator (extra step) and the other stream directed to the methanol separator (third step). Finally biodiesel purification by washing with water is the final step (fourth step). For the purpose of this study, the biodiesel production flow sheet was based on one of the separation configurations presented in (48). This configuration consisted on the separation of biodiesel and glycerol first, and then water washing after removal the methanol. This scheme is shown in Figure 11.
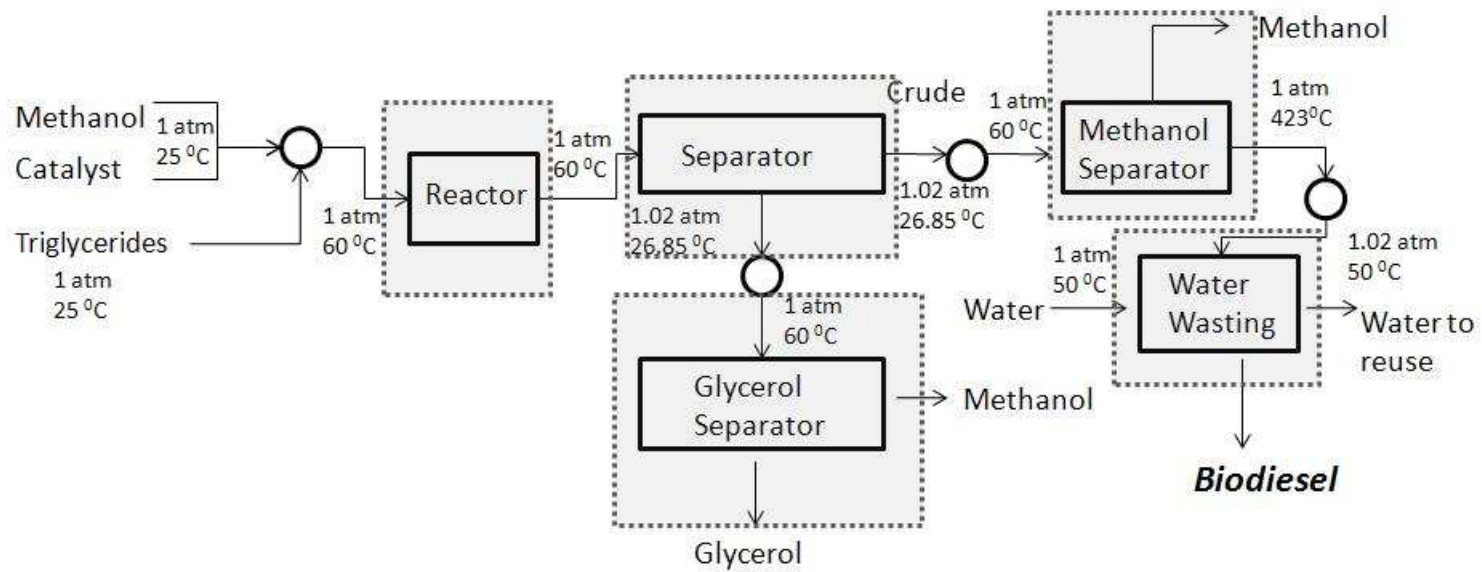
Figure 11. Process flow schematic for biodiesel production

2.4.1 Continuous model

The configuration for continuous production of biodiesel was simulated using (63). First, the catalyst (i.e. NaOH) is mixed with methanol before it is charged into the reactor at 60^0C and 1 atm. A CSTR type was used. It is important to highlight that the thermal decomposition temperature for FAME and glycerol are 250^0C and 150^0C, respectively, so during the process the temperature was remained below these levels. After the reaction process, the outlet stream is sent to the heat exchanger at 1atm and 25^0C, the stream is then sent to the first decanter (DECT1) for glycerol and biodiesel separation. The exit of glycerol stream has only 44 weight percentage concentration; therefore, this stream is sent to the heat exchanger (HEX3) before sending it to the glycerol distillation column (GLYDIs) in order to remove the glycerol. On the other hand, the biodiesel stream (DEOIL1) from decanter (DECT1) is sent first to the heat exchange (HEX4), then to the methanol distillation (METDIS) for removal of methanol. Then bottom biodiesel stream from (METDIS) is cooled down in a heat exchanger (HEX5) and then sent it to decanter (DEC2) where all the triglycerides (TRIOLR) remained from the reaction is removed. Finally, the biodiesel stream is sent to the third decanter (DECT3) where water washing take place. The resulting biodiesel stream has 99.67% purification which fulfills the ASTM (American Society for Testing and Materials) standard requirements. This production scheme can be seen in Figure 12.

Figure 12. Continuous model for biodiesel production
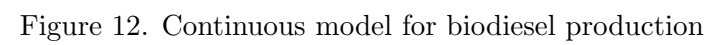
2.4.2   Batch model

The batch model for production of biodiesel follows the same idea presented in the process description. However, this model uses batch reactor and batch distillation columns for separation of glycerol and methanol, and for purification of methyl ester. A general view of this model is presented in Figure 13. The reaction part was simulated using FORTRAN for the solution of differential equations resulted from the mass balance (10) while MultiBatchDS software was employed to simulate batch distillation. MultibatchDS is a unique professional batch distillation system that offers multiple levels of models for batch column configurations, operating modes, fractions, and products (64). MultibatchDS includes various configurations of batch distillation columns and examines the challenge involved in their dynamics. Some of the configurations presented in MultiBatchDS are the rectifier (conventional column), middle vessel and stripping column. In this work, the first configuration is employed to design the glycerol-methanol separation as well as the methanol-methyl ester separation column. Table VI shows the design conditions used for the purpose of this work.

2.4.3   Batch scheduling

The production of batch processes requires to be scheduled due to short life cycles of the products and the multiproduct facilities in which the various products share the same equipment (65). The manufacturing process of biodiesel follows a recipe specified by a set of processing tasks with fixed operating condition and fixed processing times. These tasks can be represented in a chart, usually known as Gantt chart, where the time activities are also involved at each
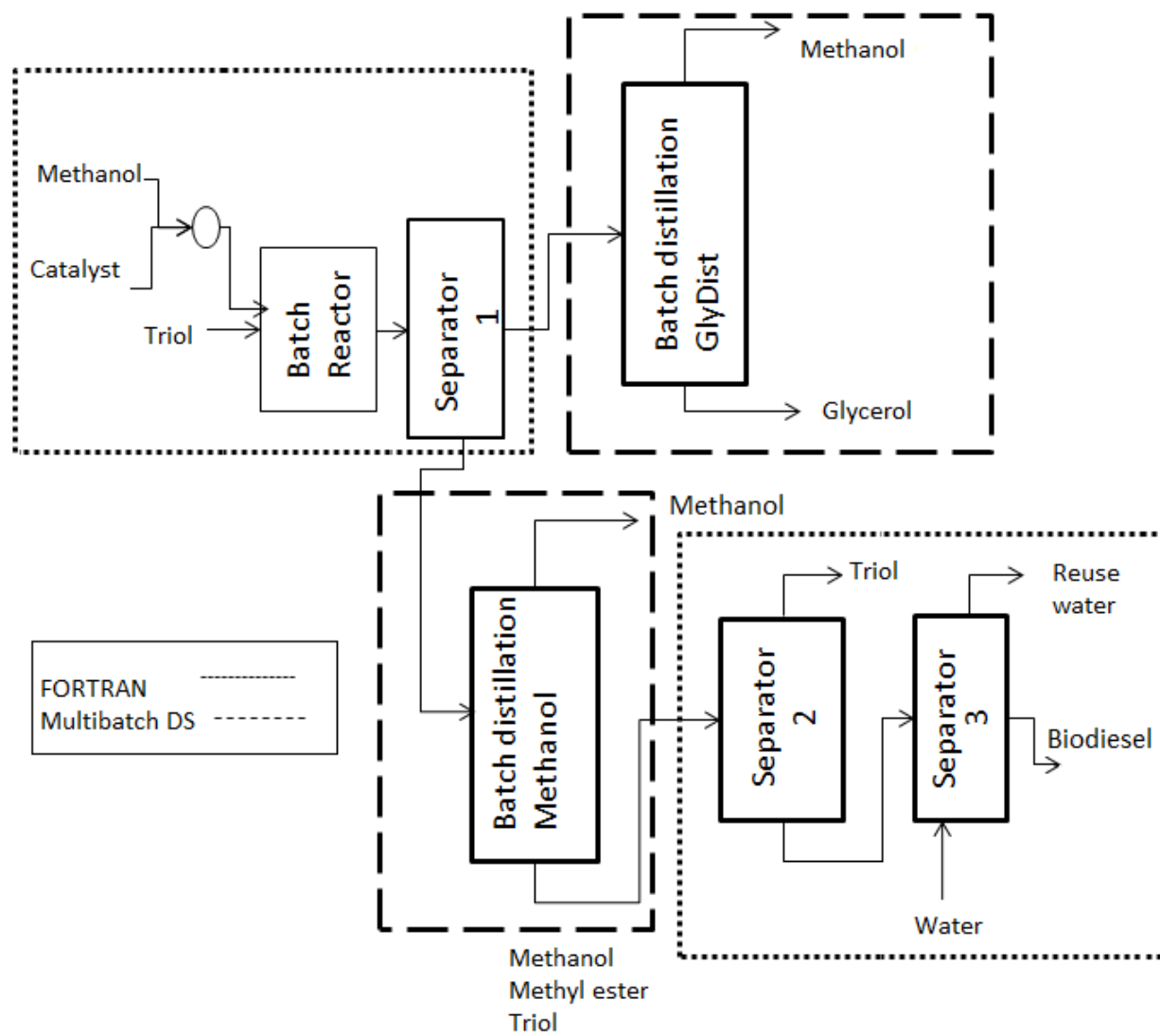
Figure 13. Batch model for biodiesel production

TABLE VI

MULTIBATCHDS CONDITIONS PROCESS

Process	Policy options	Task Specification	Model options	Design Conditions
Glycerol-Methanol separation	Constant reflux ratio	Simulation	Semi rigorous	Column: rectifier reflux ratio: 1.05
Methanol - Methyl ester separation	Constant reflux ratio	Simulation	Semi rigorous	Column: Rectifier reflux ratio: 1.5

stage of the process. Two kinds of operation can be found, non-overlapping in which each batch is processed until the proceeding one is complete or overlapping operation in which the idle times are removed in order to make batch production simultaneous. Figure 14 shows the Gantt chart for biodiesel production and compares the two modes mentioned before. (Note: In Figure 14: R represents the batch reactor, S1, S2, S2 are the Separator units, and METD is the column distillation process for the methanol recovery).

Based on the processing time at each stage presented in Table VII, it can be seen in Figure 14 that with overlapping operation more batches per day can be performed which makes this operation more efficient. Therefore, the over lapping operation is chosen. For simplicity, it is assumed that the transfer times are negligible. The process time was developed on the basis of a biodiesel production capacity of 2404.33kg/batch cycle, were the cycle time for the overlapping operation is 1.67hr. The reaction and the distillation time processing were given to the solution of mathematical models while the separator times were determined by heuristic knowledge (66).
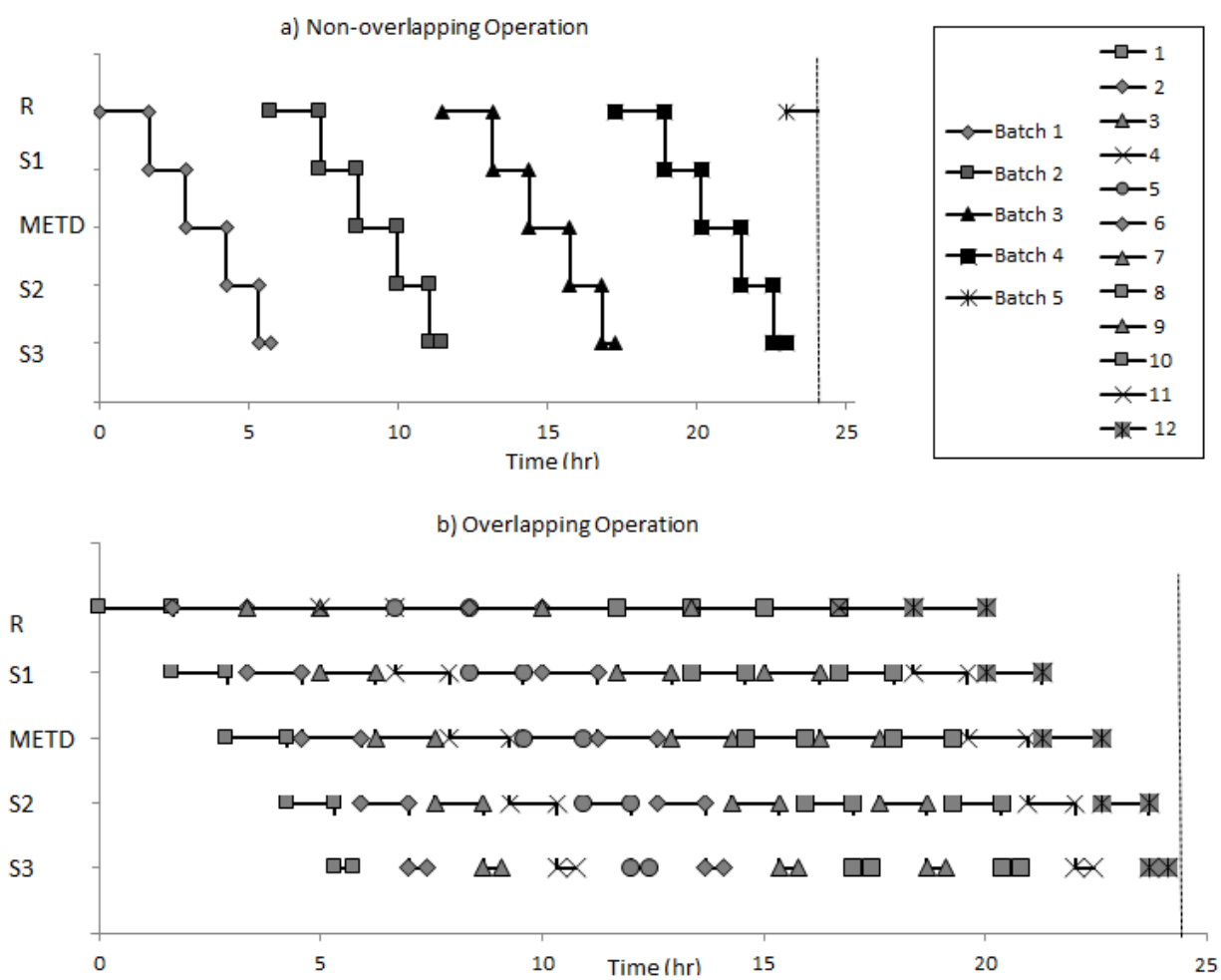
Figure 14. Gantt chart for biodiesel production

TABLE VII

PROCESSING TIMES

Stage	Batch time (h)
Reactor	1.67
Separator	1.23
Column distillation METD	1.35
Separator 2	1.1
Separator 3	0.42
Total time for 1 batch cycle	5.75

2.5   Economic assessment

Once again, the purpose of this work is to compare continuous with batch processes for biodiesel production in terms of operation, capacity, transportation costs, and feedstock availability. Therefore, in this section we present an economic assessment which refers to the evaluation of fixed capital cost, and total manufacturing cost to produce biodiesel. Initially, the plant capacity is determined based on the designs of these two operation modes (showed in Section 2.4), for instance, in the continuous plant the production capacity is 20868.40ton/yr while in one batch plant is 2404.33kg/batch. It was decided to distribute the capacity of the continuous plant in three batch plants located in different states with different percentage of distribution. The continuous plant will be located in the middle of these batch plants and the soybean oil facilities. As a result, Iowa-OI- (Batch P1), Illinois-IL- (Batch P2), and Missouri-MO- (Batch P3) are the three states for the batch plants, and at the same time, the location where the feedstock will be provided for all plants. The selection of the batch plant locations was based

Figure 15. Distribution of the production plants

on the availability of the soybean production in the U.S. As mentioned before, Illinois and Iowa are the two states with the highest production. Figure 15 shows the possible locations of the four biodiesel production plants in the Midwest. Point A represents the location of the continuous plant, while points B, C, and D are the locations Batch P1, Batch P2 and Batch P3, respectively. The darker points are some crushing facilities located in the area. (Note: Information of soybean facilities can be found at (60).

On the other hand, Figure 16 summarizes the raw material distribution for the continuous plant as well as the production capacity of each batch plant. As it can be seen in the left side of this figure, 30% of the soybean oil will come from Missouri while 35% from Illinois and Iowa, respectively. Illinois and Iowa have the highest percentage since they have the highest
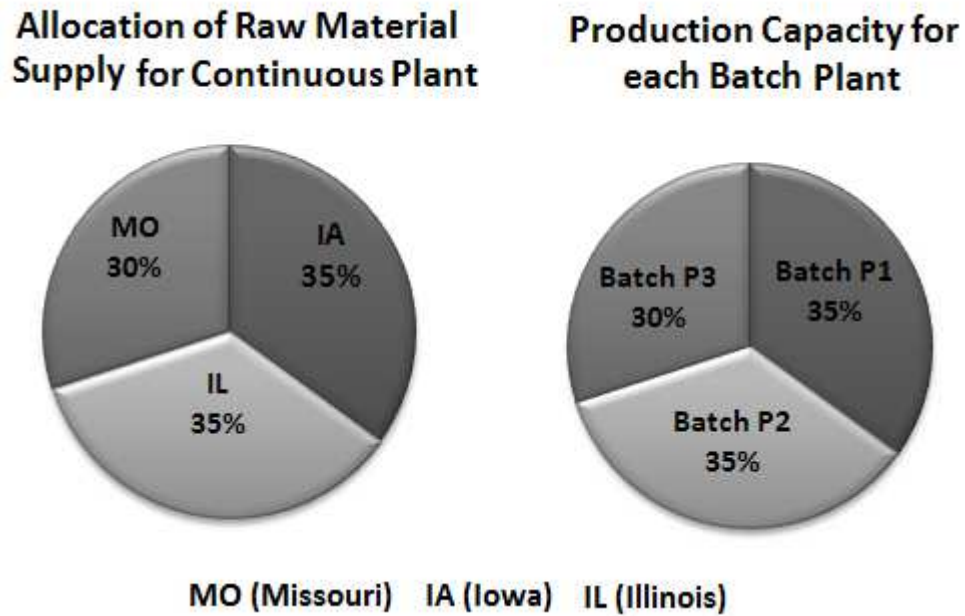
Figure 16. Raw material and capacity distribution

production of soybean oil. In the right side, it can be observed that the same percentage is distributed for the production capacity of each batch plants.

The total cost of soybean in the continuous plant includes the transportation and its production costs. This information is shown in Table VIII where the distances (miles) from each soybean oil facility to the continuous plant and their respective cost are presented. As it can be seen, the soybean oil prices for each state are within the 95% confidence interval (see Section2.2.1). Recalling Table VIII, it can be seen that transportation cost only represents the 4.4% of the total cost of soybean oil. This small percentage is the result of the high production

TABLE VIII

TOTAL COST OF SOYBEAN

Origin	Price ($/lb)	Distance (miles)	Production cost (millions$/yr)	Transportation cost (millions $/yr)	Total cost (millions $/ton)	% Transportation cost
Iowa (IA)	0.50[a]	447	9.07	0.52	9.59	5.5
Illinois (IL)	0.56[b]	296	10.06	0.35	10.42	3.4
Missouri (MO)	0.50[a]	336	7.77	0.34	8.12	4.2
Total			26.91	1.22	28.13	4.4

[a]AGP corporate
[b]ADM company

cost of the soybean (i.e. 95.6%). Therefore, the effect of feedstock transportation in biodiesel production is not significant in its cost.

In Addition to the feedstock costs for biodiesel production, other costs such as waste treatment to protect the environment, cost of personnel, administrative, utilities, and equipment costs can influence the manufacturing costs. These costs are included in the Direct Manufacturing Cost (DMC), Fixed Manufacturing Costs (FMC), and General Expenses (GE). The DMC represents operating expenses that vary with production. Table IX shows the chemical cost including raw material, catalyst, solvents, labor, and utilities costs for this economic assessment. The utilities involve the cost electricity, steam and cooling tower water consumption. On the other hand, the FMC comprise property taxes, insurances and depreciation along with equipment costs and they are independent of changes of production rate. The third category (GE) includes managements, sales, finances, and research founding. The sum of these three

categories results in the total cost of manufacturing Equation 2.1.

$$COM = DMC + FMC + GE \tag{2.1}$$

where each category can be computed as (see Table X):

$$DMC = C_{RM} + C_{WT} + C_{UT} + 1.33\ C_{OL} + 0.03\ COM + 0.069\ FCI \tag{2.2}$$

$$FMC = 0.708\ C_{OL} + 0.068\ FCI + depreciation \tag{2.3}$$

$$GE = 0.177\ C_{OL} + 0.009\ FCI + 0.16\ COM \tag{2.4}$$

Therefore, Equation 2.1 can be rewritten as:

$$COM = 0.180\ FCI + 2.73\ C_{OL} + 1.23\ (C_{RM} + C_{WT} + C_{UT}) \tag{2.5}$$

where COL is the cost of operating labor, CWT is the cost of waste treatment, CUT is the cost of utilities, CRM the cost of raw material, and FCI is the fixed capital investment. This latter value represents the cost of construction of a new plant, and involves the total direct plant cost (e.g. purchase equipment, piping, electrical systems, building) and total indirect plants cost (e.g. engineering and supervision, construction expenses, legal expenses). The complete information of the annual costs of raw material, operating labor, utilities along with estimations of the equipment costs and FCI are summarized in the Appendix A. Among the assumptions

TABLE IX

OPERATING COST

Item	Cost (U.S.$)
Raw material[a]	
Soybean oil (Triol)	See Table VIII
Methanol	$0.320/Kg
Hydrochloric acid (HCl)	$0.176/kg
Sodium hydroxide (NaOH)	$0.617/kg
Water	$0.067/1000Kg
Utilities[b]	
Electricity	$0.06/kWh
Steam (10barg, 184^0 C)	$14.19/GJ
Cooling tower water (80F to 100F)	$0.354/GJ
Additional operating cost	
Plant operators base rate	$12.50/h
Wastewater treatment[c]	$2.64e-3/kg

[a](1,2),[b](2),[c](3)

used for the calculation of total manufacturing costs are: (I) the most economical available option was chosen, for instance, the material of storage tank and reactors were specified to be constructed of carbon steel. (II) The continuous process operating hours for biodiesel plant were assumed to be 350days/yr. (III) The depreciation is assumed to be 10 percent of the *FCI*. (IV) For equipment prices the Chemical Engineering Plant Index was $I_{2010} = 552.5$ (67).

2.5.1   Result and discussion

Table X shows details about data and equations used to estimate total manufacturing costs and compares the two processes studied in this work: continuous and batch. As it can be seen, the total *DMC* is 2.45% higher in the continuous process than batch processes due to higher costs of feedstock, waste treatment, and utilities. For instance, the total cost of feedstock in

continuous process represents 73% of the total manufacturing cost while in batch processes is 71%. On the other hand, it was found that the waste water stream in the continuous process contains 85.97% more of methanol compared to the stream in batch process resulting in higher waste treatment cost. The energy consumption was found higher in continuous process since batch distillation is more effective in the separation process (i.e. requires lower value of distillate X reflux ratio). In contrast, the operation labor cost was 65.66% higher in the batch plants due to equipment cleaning, preparation time and operation of each unit. Figure 17 summarizes this comparison.

Figure 18 shows percentage values of components of total manufacturing discussed in Table X (e.g. *DMC, FMC and GE*). It can be seen that the total *DMC* shows to dominate the total manufacturing costs, for example, in continuous process this value represents 81.80% of its total manufacturing cost while in batch processes is 80.65%. As mentioned before, this difference corresponds to higher costs of feedstock, waste treatment, and utilities in the continuous process. On the other hand, the *FMC* in batch process represents 2.93% of its total manufacturing cost while in continuous model is 2.05%. The reason why this category is higher in batch processes is because this group includes the depreciation, local taxes and insurances and the plant overhead costs that depend mostly on cost of operation labor which is higher in these processes (see Table XI).

TABLE X. MULTIPLICATION FACTORS FOR ESTIMATING MANUFACTURING COST

Factor	Description	Continuous	Batch	% Difference
Direct Manufacturing Costs				
Raw material	C_{RM}	29.93	28.66	4.44
Soybean oil	-	28.14	26.87	4.5
Waste treatment	C_{WT}	0.02	0.01	38.48
Utilities	C_{UT}	0.39	0.14	184.24
Operating labor	C_{OL}	0.32	0.96	-65.66
Direct supervisory	$0.18C_{OL}$	0.06	0.17	-65.66
Maintenance and repairs	0.06FCI	0.21	0.17	20.19
Operation supplies	0.009FCI	0.03	0.03	20.19
Laboratory charges	$0.15C_{OL}$	0.05	0.14	-65.66
Patents and royalties	0.03COM	1.17	1.17	-0.97
total direct manufacturing	$C_{RM}+C_{WT}+C_{UT}+1.33C_{OL}+0.03COM+0.069FCI$	32.17	31.45	2.45
Fixed Manufacturing Cost	FMC			
Depreciation	0.1FCI	0.35	0.29	20.19
Local taxes and insurance	0.032FCI	0.11	0.09	20.19
Plant overhead costs	$0.708C_{OL}+0.036FCI$	0.35	0.78	-53.99
Total Fixed Manufacturing costs	$0.708C_{OL} + 0.068FCI + depreciation$	0.81	1.16	-29.31
General Manufacturing Expenses	GE			
Administration costs	$0.177C_{OL}+0.009FCI$	0.09	0.20	-53.99
Distribution and selling costs	0.11COM	4.31	4.27	0.97
Research and development	0.05COM	1.96	1.94	0.97
Total General Manufacturing Costs	$0.177C_{OL} + 0.009FCI + 0.16COM$	6.35	6.41	-0.66
Fixed Capital investment	FCI	3.45	2.87	20.19
Startup cost		0.35	0.29	20.19

Finally, the GE do not vary significantly since this category includes the administrative, distribution and selling costs along with research and development that is calculated based on the COM of each process.

The total capital investment was calculated using equipment and fixed capital costs (see Appendix A Tables XXV and XXVI). Figure 19 compares the total capital investment of continuous and batch processes. Although three batch plants were needed to have the equivalent production capacity to one continuous plant, it can be seen that the total capital investment is still higher in the continuous plant. The dominated factor to estimate this parameter was the purchased equipment costs where continuous process played an important role. For instance, the storage for oil in the continuous plant represents 28.8% of the total purchased equipment cost increases its fixed capital cost. This cost is consistent with results of storage facilities costs shown in (49). In contrast, the storage facilities were not considered for soybean in the batch plants since it was assumed that these plants were located in the same place where the feedstock facility was located.

As it was mentioned before, the previous information was needed to compute the value of COM. Therefore, once this information was defined and calculated, the annualized total manufacturing cost of biodiesel was obtained. The results are summarized in Table XI. This table compares the COM values in two forms: millions \$/ton and millions \$/yr between continuous and batch processes. It can be observed that the manufacturing cost of the continuous
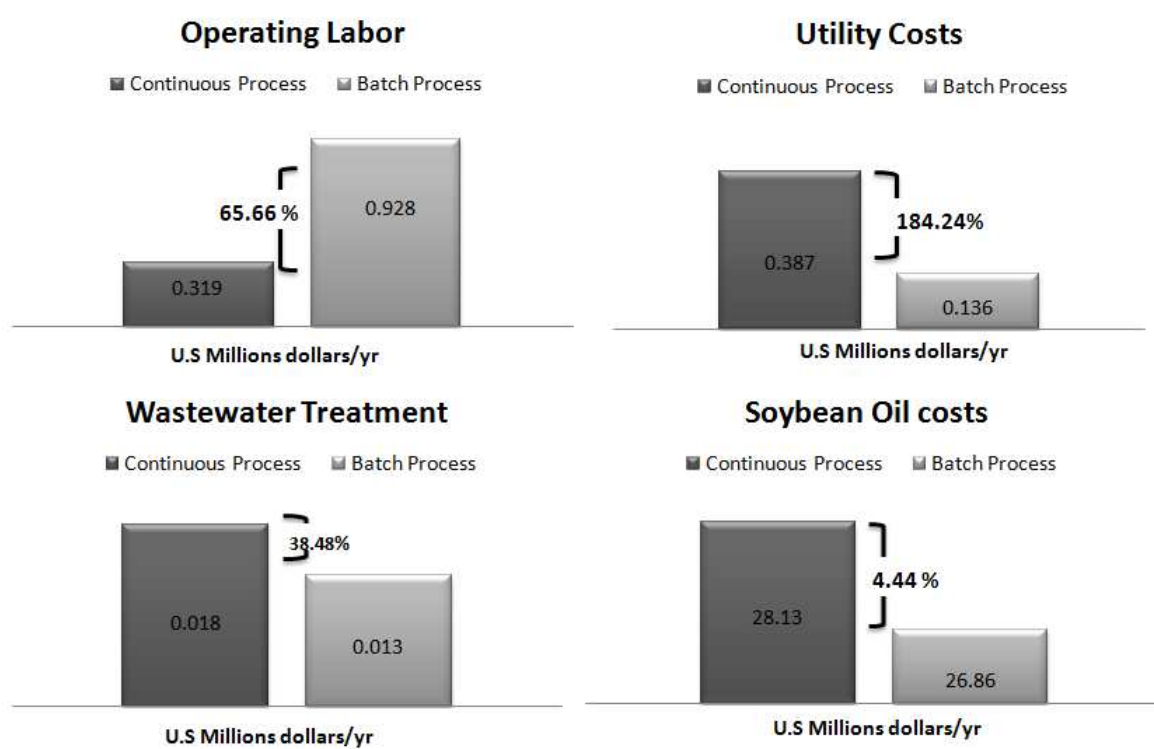
Figure 17. DMC Comparison
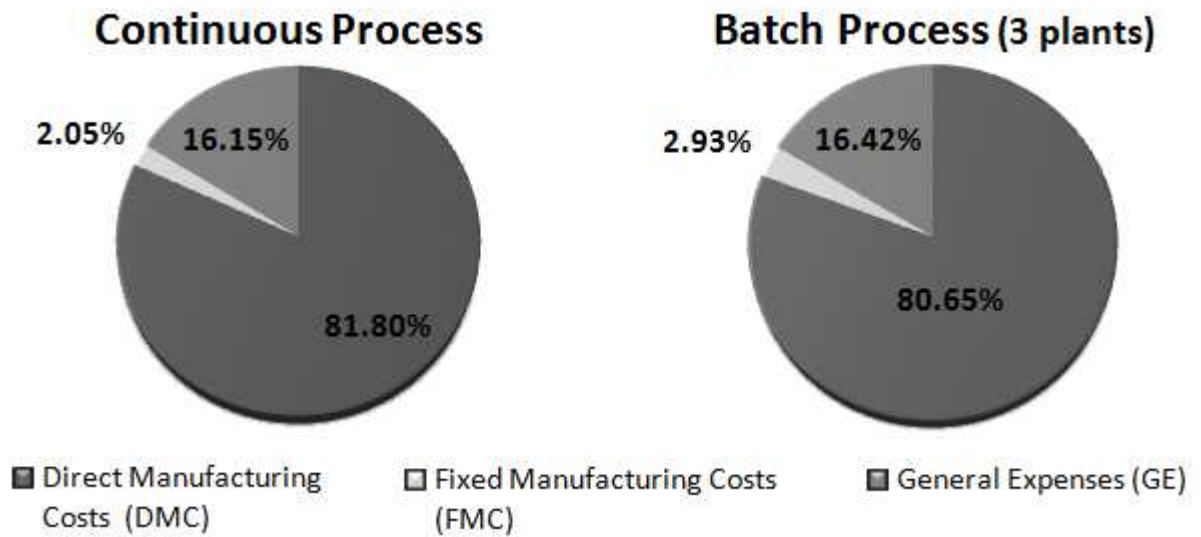
Figure 18. Comparison of the total manufacturing costs between continuous and batch processes

plant is very close to the case when three batch plants are used. In other words, to produce around 21000ton of biodiesel per year, continuous process needs $0.38 millions of dollars more than having three batch plants. Although this difference represents a marginal increase (i.e. 0.98%), it favors the batch process showing potential consideration for the industry of biodiesel.

2.5.2   Sensitivity analysis

A sensitivity analysis was carried out in order to explore more possible scenarios where the percentage of production capacity and raw material supply were more highlighted. This analysis consisted on five scenarios where the fifth scenario is the base case (Figure 16). Thus,
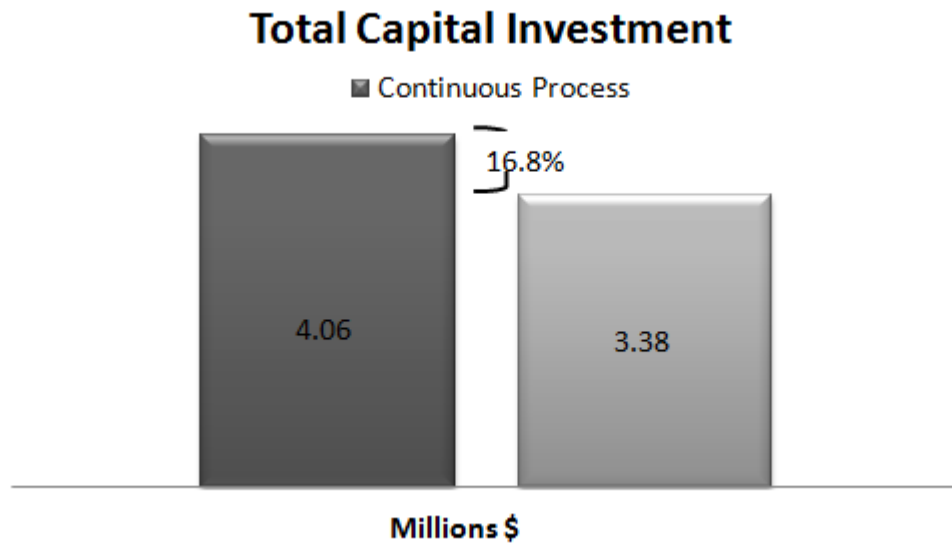
Figure 19. Comparison of the total capital investment

TABLE XI

COST OF MANUFACTURING (COM)

Total manufacturing cost (COM)	U.S. Millions ($/Ton)	U.S. Millions ($/yr)
CONTINUOUS	1.88e-3	39.15
BATCH P1	1.78e-3	14.04
BATCH P2	1.96e-3	13.68
BATCH P3	1.80e-3	11.03
TOTAL BATCH	1.84e-3	38.77

to perform this analysis, the percentage of allocation of raw material supply for the continuous plant and production capacity of each batch plants were changed. A summary of these results is shown in Table XII. Before analyzing the detailed information of this assessment, five scenarios were compared (Figure 20) based on its difference on the COM value. For instance, scenario 1 assumes that half of the biodiesel production is manufactured by Batch P2 and 50% of the supply of soybean oil comes from Illinois, meaning that Illinois dominates the production of biodiesel and supply of soybean. The remaining 50% is distributed equally between Iowa (Batch P1) and Missouri (Batch P3) for production of each batch plant and supply of raw material. It can be observe from Figure 20 that having half of the biodiesel production in Illinois and half of the feedstock supply coming from the same state, the continuous plant requires 0.26 millions of dollars more than three batch plants in order to produce around 21000ton of biodiesel per year (see Table XII). On the other hand, if Missouri dominates production and supply, meaning that half of feedstock supply comes from Missouri and half of production of biodiesel is manufactured in Batch P3 (scenario 4), the continuous plant would require 0.44 millions of dollars more to produce the same among of biodiesel per year. Although both scenarios favor the batch production, the latter one results more attractive. The reason why these scenarios favor batch production more in one case than in the other is due to the cost of feedstock and distance to the market (e.g. biodiesel plant). It is observed in scenario 1, that the cost of soybean oil is higher in Illinois (see Table VIII) but the production facility is situated in same state where the supply comes from, which means that the feedstock would travel less distance, while in scenario 4, the feedstock facility is located 336 miles away from the production facility although the
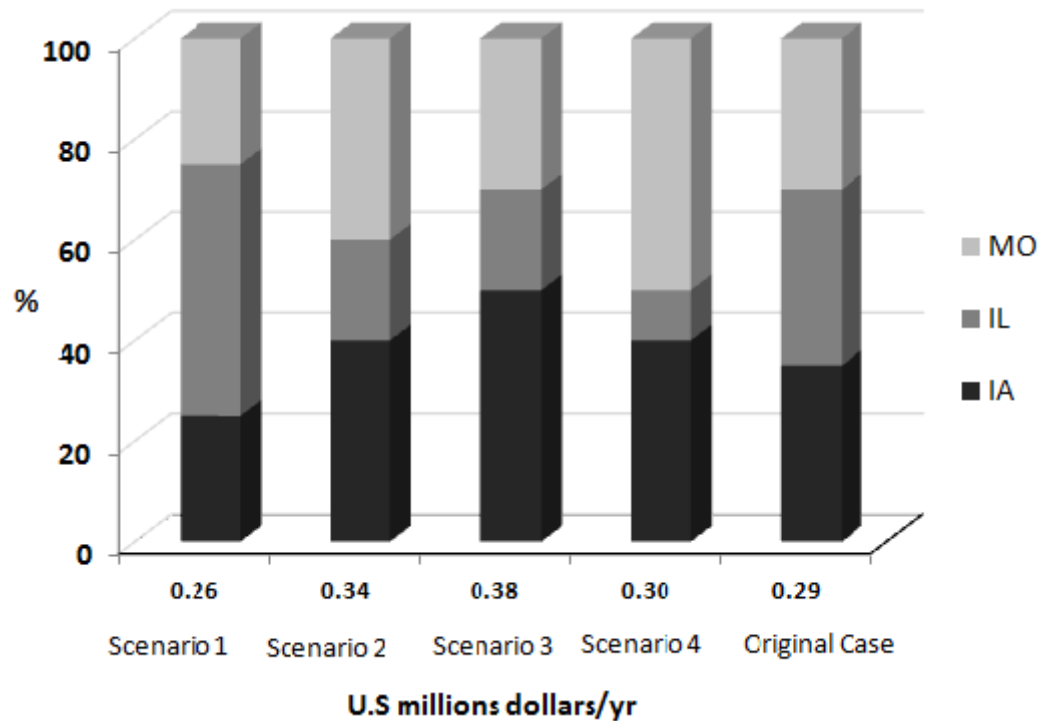
Figure 20. Comparison of the distribution capacity and raw material supply among different scenarios

price of soybean oil is lower in Missouri. Same analyses were made for the remaining scenarios obtaining favorability for batch process in all of them. As a result, it was observed that when the traveling distance from the facility to the market is high and the cost of feedstock is low, batch processes become more attractive to produce biodiesel. This is a positive feature of batch processing, especially when the feedstock supply is limited or variable due to, for example, seasonal production.

Moreover, Table XII shows the percentage of difference between continuous and batch processes of other costs, such as soybean cost, utility costs, and so on (Note: positive values mean that there is an increase favoring batch process while negative values mean the opposite situation). As expected, in terms of soybean oil cost, scenario 4 has the higher difference, that is, the cost of soybean represents 4.8% more in continuous process than batch processes. It can also be seen that in all scenarios the difference in utility cost as well as operating labor cost does not have significant variation. In contrast, waste treatment varies from 14.42% to 38.48%. This outcome shows the high influence that the scheduling of batch processes have in the calculation of the waste treatment cost. It was observed when the percentages of production capacity and supply of raw material were high; more batches per day were needed in a specific batch plant. For instance, in scenario 1, batch plant P2 had the highest production so 12 batches per day were needed, while batch plant P1 and P3 only 6 batches per day each (see Appendix A Table XXVII). Therefore, delegating more production in the batch plant results in more water consumption, meaning more water to be treated. However, this observation comes along with the distribution of those percentages. Analyzing the base case scenario, the percentage of difference of waste treatment is the highest since the distribution of capacity and supply is relatively equal. Therefore, having better distribution in those percentages along the different batch plants will favor the batch production. This conclusion adds another positive feedback to batch processing giving the engineers more flexibility to set up the scheduling so the waste treatment can be minimized.

TABLE XII

PERCENTAGE OF DIFFERENCE AMONG DIFFERENT SCENARIOS

Case	State	% raw material supply / production capacity	% Soybean cost	% Utilities	% Waste treatment	% Operating labor
1	AI	25				
	IL	50	4.1	184.67	27.79	-65.58
	MO	25				
2	AI	40				
	IL	20	4.3	184.25	32.3	-65.66
	MO	40				
3	AI	50				
	IL	20	4.6	184.67	26.86	-65.58
	MO	30				
3	AI	40				
	IL	10	4.8	184	14.42	-65.58
	MO	50				
Base	AI	35				
	IL	35	4.5	184.24	38.38	-65.66
	MO	30				

TABLE XIII

QUALITATIVE COMPARISON BETWEEN CONTINUOUS AND BATCH SCENARIOS

Scenarios	Soybean cost	Utility	Waste treatment	Operating labor	Overall cost
1	Batch	Batch	Batch	Continuous	Batch
2	Batch	Batch	Batch	Continuous	Batch
3	Batch	Batch	Batch	Continuous	Batch
4	Batch	Batch	Batch	Continuous	Batch
base case	Batch	Batch	Batch	Continuous	Batch

Table XIII summarizes the results of this comparison in terms of qualitative outcome of the four different costs showed in Table XII and the overall cost. As it can be seen in most of the cases, batch processes is the best process for biodiesel production.

TABLE XIV

SCENARIOS FOR DIFFERENT PRICE OF SOYBEAN ($/YR)

Samples	Iowa (AI)	Illinois (IL)	Missouri (MO)
1	0.51	0.56	0.86
2	0.62	0.50	0.39
3	0.65	0.58	0.40
4	0.65	0.39	0.62
5	0.51	0.62	0.46
6	0.60	0.40	0.49
7	0.58	0.45	0.63
8	0.59	0.42	0.58
9	0.45	0.50	0.60
10	0.42	0.50	0.38
Base case	0.50	0.56	0.50

2.5.3 Variability in the soybean oil price

In this last section, the variability in the soybean oil prices is also considered. As it was
showed in Section 2.2.1, price of soybean oil for the last three years has been fluctuating due to
its increasing demand and oil competition. Some statistical information such as average price
(0.50$/Lb) and standard deviation (0.07) was also presented (see Figure 7). Based on this
information, 10 random samples of soybean oil prices were generated for the three states (i.e.
IA, IL, and MO). This information is illustrated in Table XIV. The prices presented here vary
within 95% of the confidence interval showed in Figure 6.

Having these samples, costs of manufacturing (COM) for the scenarios (including base case)
presented in Section 2.5.2 were computed, and once again the difference in the COM between

TABLE XV

DIFFERENCE OF COM BETWEEN CONTINUOUS AND BATCH PROCESS BASED ON
THE VARIABILITY OF SOYBEAN PRICES

Scenario	Difference of COM (Millions $/yr)Deterministic	Difference of COM (Millions $/yr) Average	% difference
1	0.26	0.26	0
2	0.34	0.33	2.94
3	0.38	0.38	0
4	0.44	0.45	2.22
Base case	0.37	0.39	5.40

continuous and batch production was compared. These results are showed in Table XV. In this Table, Average column refers to the mean value of COM when the price of soybean oils varies based on Table XIV whereas deterministic column refers to the results showed in Figure 20, that is, when no variability is taken into account. As it can be observed, similar results were obtained under instability of the soybean oil price, confirming the previous results: batch plants are the best option to production of biodiesel. The last column shows the percentage of difference between deterministic and the average case, it can be observed that under this uncertainty of soybean oil price batch processes are even more favorable than continuous processes.

2.5.4   Conclusion

In this chapter, continuous and batch processing of biodiesel production from soybean oil were compared. The aspects for this comparison were based on the supply chain management for biofuels along with technical information concerning process utilities, waste treatment and operating labor. Modeling and simulation of continuous process were performed using ASPEN

plus while for batch processes, numerical methods and MultiBatchDS software were employed for solution of batch reactor and batch distillation models. From the results obtained in this chapter, it was found that batch processes favor biodiesel production over continuous processes when the size of the market, distance, cost of feedstock, and its availability are taken into account. The first results showed that the effects of feedstock transportation - which is taken into account only in the continuous plant - represented 4.5% of total cost of soybean oil. Although this effect is not significant in the calculation of raw material costs, it is considerable in the total manufacturing cost, since soybean cost represents 73% in a continuous plant while in batch plants is 71%. On the other hand, the flexibility of batch processes allows us to have three batch plants located in the feedstock facilities and they were scheduled depending on the feedstock supply and production capacity. Consequently, this scheme allows avoiding storage costs for soybean and obtaining interesting results that favor batch processes. For instances, it was found that the waste treatment and utility costs were lower in batch processes due to fewer impurities in the waste water stream and less energy requirements due to lower distillate rate in batch distillation. Therefore, based on the different scenarios studied in this chapter, production of 21000ton of biodiesel per year with a continuous process involves higher costs than doing it with three batch plants. Batch processing is therefore an attractive option to produce biodiesel.

CHAPTER 3

DETERMINISTIC OPTIMAL CONTROL IN BATCH PRODUCTION OF BIODIESEL

3.1 Introduction

Optimal control problems are mostly defined in the time domain and their solutions require establishing an optimal operation policy that maximizes or minimizes a performance index. This optimal operation policy is obtained using dynamic optimization techniques, and is commonly used to optimize the performance of batch reactors. Due to the dynamic nature of the decision variables in batch processes, optimal control problems are much more difficult to solve compared to normal optimization where the decision variables are scalars.

Optimization in batch processes can lead to different types of problems depending on the objective of the process. The literature in this field has paid attention mostly on the solution of maximum conversion or minimum time problems. Different approaches of optimal control have been studied. For instances, one of the earliest works that considered the study of optimal control in batch reactor was presented by (68). In this paper, the aim was to increase the yield of the reaction by determining the optimum temperature profiles for cases where there are competing side reactions. In (69), they considered the problem of finding an optimal time-varying control policy for a fed-batch penicillin reactor. They applied a solution strategy based

on successive quadratic programming (SQP) and orthogonal collocation on finite elements. In (70), the optimal temperature in a completely mixed batch reactor was computed. In this model, the approach was based on the adaptation of the Discrete Maximum Principle (DMP) for the optimal control of non-linear continuous dynamics systems. Logsdon J. (71) presented the maximization of the conversion for a desired product in a consecutive reaction. The objective was to find an optimal temperature profile using the two-point collocation method. In contrast, Longsdon and Bliegler (72) solved the same optimization problem, but their solutions were faster due to the use of a relaxed simultaneous approach. Luus (73) examined the viability of using Iterative Dynamic Programming (IDP) for highly nonlinear system in four batch reactor systems. His calculations showed that IDP was a very useful method for establishing the optimal control policy of difficult problems and were also straightforward to execute since no derivatives were required. Finally, Srinivasan, B. et al. (74) illustrated a general point of view of batch processes from the characteristic of planning, production, and optimization of the industrial perspective. Besides, he provided a unified view of the methods available to solve dynamic optimization problems and presenting the major direction in which the field has developed. However, most of these works in the area of batch reactors deal with deterministic optimal control problems, but their applications are based on a general batch reactor and do not consider biodiesel kinetics. In contrast, some research works such as (75); (76); (77), and (78) have highlighted the best operating conditions that can affect the yield of the transesterification reaction through the optimization of the process, but their results depended on the feedstock used. This Chapter presents three optimal control problems in a batch reactor for

biodiesel production: maximum concentration of methyl ester (MCP), the minimum reaction time (MTP), and the maximum profit problem (MPP). The purpose is to find a temperature control policy that can change with time using the dynamic optimization. These problems are addressed using the deterministic system of dynamic equations to calculate the optimal temperature profile that achieves the desired objective.

As mention in Chapter 2, biodiesel is the result of the transesterification reaction that can be carried out in a batch reactor. The control design of the biodiesel reaction is different from plant to plant and basically depends on the production technology adopted. Some of the most common control variables in chemical processes are temperature (e.g. temperatures of flow rates of cooling water in the coil or heating fluid in the jacket), pressure, flow, and level. For instances, in the Malaysia Palm Oil Board (MPOB) the reactant feed temperature and the reaction pressure is used as the manipulated variables. The pressure is operated at pressure higher than the atmospheric pressure and it is controlled in order to keep the methanol in the liquid phase. On the other hand, the ASAE operates the transesterification reactor at atmospheric pressure and the reactor temperature is the control variable (79). Papers like (80) and (81) present typical optimization variables, control variables and performance index for optimal control problems in batch operations. As it can be seen, temperature is most commonly use as the control variable since this variable provides critical conditions for different processes such and chemical reaction, and distillation. Therefore, the optimal control problems presented here

are expressed so the reactor temperature will maximize or minimize a performance index.

3.2   Batch reactor

A Batch reactor is an essential unit operation in almost all batch-processing industries. It can be used for small-scale operation, for testing new processes that have not been fully developed, for manufacture of expensive products, and for processes that are difficult to convert to continuous operations (82). In a batch reactor, there is no inflow or outflow of reactants or products while the reactor is being carried out. The reactants are initially charged into the vessel, are well mixed, and are left to react for a certain period or reaction time. Once the reaction time is reached, the resultant mixture is then discharged. This process is an inherently unsteady-state operation where the composition and the temperature change with time. However, the common assumption is that at any instant these parameters remain uniform throughout the reactor (83), also known as the perfect mixing conditions. Figure 21 shows a general scheme of a batch reactor for biodiesel production. Initially, the reactor is charged with triglycerides and methanol, then the reactants are left to react for about 100 minutes, and finally, the product which is biodiesel and the by-product glycerol are discharged. Some common operation conditions for biodiesel production are 1atm of pressure, 60 to 90 minutes of reaction time, and constant temperature of 323K (48).
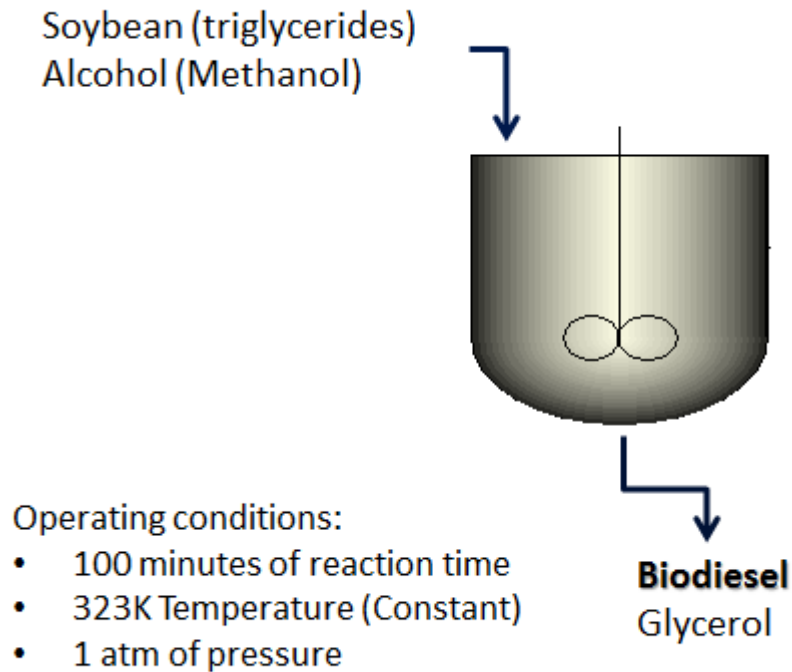
Figure 21. Batch reactor scheme for biodiesel production

3.2.1 Biodiesel model

In this section, the mathematical model is presented based on the mechanism of transesterification for biodiesel reaction shown in Chapter 2 (Section 2.2.3). The reaction steps are given by Equation 3.1 where k1 to k6 are the reaction constants which can be calculated by Equation 3.3. The values of activation energy (a_i) and frequency factors (b_i) are shown in Table XVI. The values of a_i and b_i are calculated from the Arrhenius Equation (Equation 3.3) and the energy activation along with the values of k_i are reported in (61) at constant temperature

(323 K). The fourth equation (i.e Equation 3.2) represents the overall reaction. All reactions are carried out at atmospheric pressure (61).

$$TG + CH_3OH \quad \underset{\longleftrightarrow}{k1, k2} \quad DG + R_1COOCH_3$$

$$DG + CH_3OH \quad \underset{\longleftrightarrow}{k3, k4} \quad MG + R_1COOCH_3$$

$$MG + CH_3OH \quad \underset{\longleftrightarrow}{k5, k6} \quad GL + R_1COOCH_3 \qquad (3.1)$$

Overall reaction:

$$TG + 3\,CH_3OH \quad \longleftrightarrow \quad GL + 3\,R_1COOCH_3 \qquad (3.2)$$
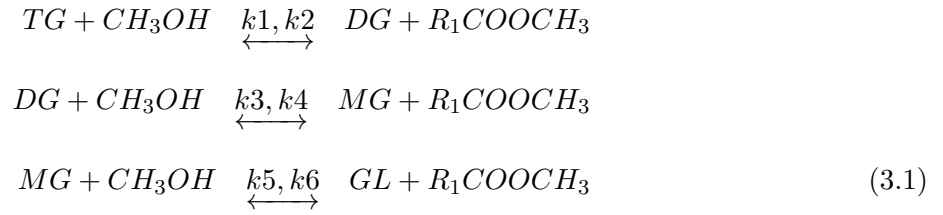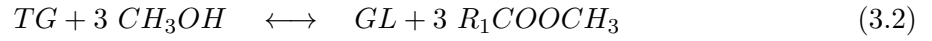
where TG, DG, MG, R_1COOCH_3, CH_3OH, GL are triglycerides, diglycerides, monoglycerides, methyl ester (i.e. biodiesel), methanol, and glycerol respectively.

$$k_i = a_i\,exp(-\frac{b_i}{T}) \qquad (3.3)$$

The mathematical model for the production of biodiesel in a batch reactor is governed by the following Ordinary Differential Equations (ODEs) Equation 3.4 to Equation 3.9 derived from the mass balance of the batch reactor (61).

TABLE XVI

VALUES OF A_I AND B_I

a_1	a_2	a_3	a_4	a_5	a_6
3.92e7	5.77e5	5.88e12	098e10	5.35e3	2.15e4
b_1	b_2	b_3	b_4	b_5	b_6
6614.83	4997.98	9993.96	7366.64	3231.18	4824.87

$$F_1 \; = \; \frac{dC_{TG}}{dt} \; = \; -k_1 C_{TG} C_A \; + \; k_2 C_{DG} C_E \tag{3.4}$$

$$F_2 \; = \frac{dC_{DG}}{dt} \; = k_1 C_{TG} C_A \; - \; k_2 C_{DG} C_E \; - k_3 C_{TG} C_A \; + \; k_4 C_{MG} C_E \tag{3.5}$$

$$F_3 \; = \frac{dC_{MG}}{dt} \; = \; k_3 C_{DG} C_A \; - \; k_4 C_{MG} C_E \; - k_5 C_{MG} C_A \; + \; k_6 C_{GL} C_E \tag{3.6}$$

$$F_4 \; = \frac{dC_E}{dt} \; = \; k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E \tag{3.7}$$

$$F_5 \; = \; \frac{dC_A}{dt} \; = \; -\frac{d_{C_E}}{dt} \tag{3.8}$$

$$F_6 = \frac{dC_{GL}}{dt} = k_5 C_{MG} C_A - k_6 C_{GL} C_E \tag{3.9}$$

where $C_{TG}, C_{DG}, C_{MG}, C_E, C_A,$ and C_{GL} are the concentration of each component.

It has been shown in the literature that the optimal constant temperatures for transesterification reaction are between 323K to 333K at atmospheric pressure (22), but reaction temperatures from 241K can also be found (84). In this work, two base cases are taken into account: 1) constant temperature of 315K and 2) constant temperature of 323K. Figure 22 shows the concentration profile for the six components for the case of 323K of reaction temperature, the set of ODEs are integrated using the explicit Runge-Kutta Fehlberg (RKF) method (85). It can be seen as the triglycerides and methanol are consumed biodiesel is produced.

3.3   Optimal control problem

Optimal control has become an interest topic in the industrial and academic field since it provides useful information for designing and controlling the reaction process. In general, a solution to these problems involves finding the time dependent profiles of the control variable so as to optimize a particular performance index (86). To solve optimal control problems, direct and indirect methods can be used (87). When direct methods are used, the problem can be discretized into partial or full discretization depending on the level of discretization. In this case, dynamic and *NLP* methods can be employed; but, since these types of problem are large, they require large-scale *NLP* solvers and most of the time they need good initial values to
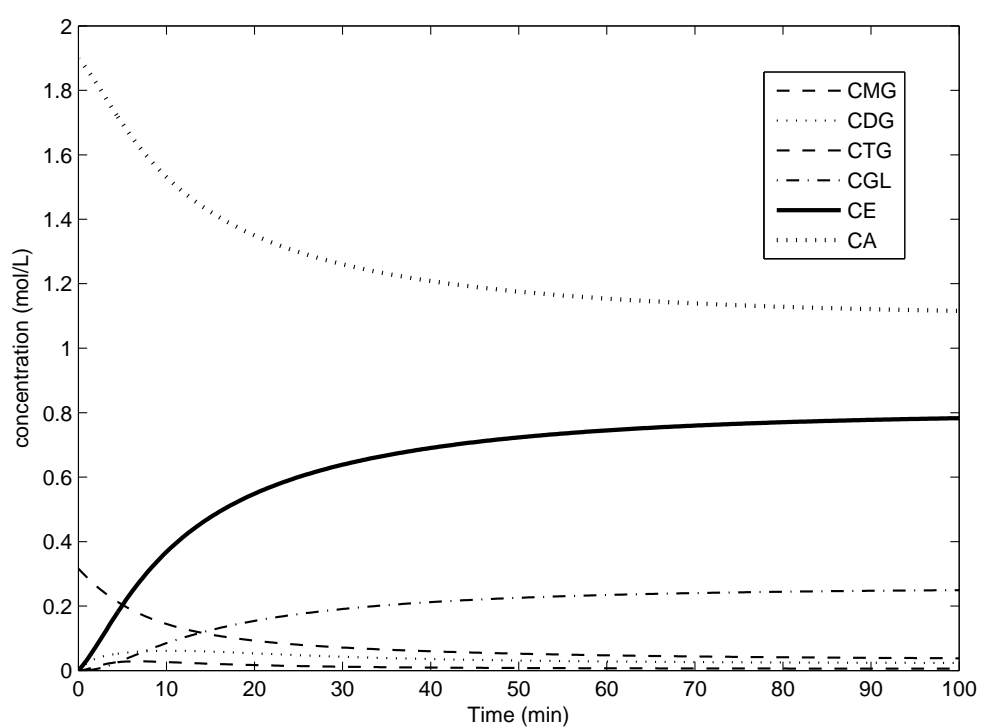
Figure 22. Concentration profile at constant temperature

TABLE XVII

OPTIMAL CONTROL PROBLEMS IN BIODIESEL PRODUCTION

Problem	Concentration	Batch time	Objective
Maximum Concentration (MCP)	Free	Fixed	Maximize C_E
Minimum Time (MTP)	Fixed	Free	Minimize t_f
Maximum profit (MPP)	Free	Free	Maximize profit

converge. Among some methods, there are: maximum principle, dynamic programming, and NLP algorithm with ODE discretization by collocation. However, using maximum principle, the solution of partial differential equations and second order differential equations can be avoid (68) as well as use of large-scales NLP solvers.

Maximum principle was proposed first by Pontryagin and coworkers (88); (89) and (90). This method has been widely used to solve a variety of optimal control problems. In the following subsections, the three optimal control problems are formulated for the case study of biodiesel production. All of them are solved using the maximum principle. Table XVII summarizes these three problems.

3.3.1   Maximum Concentration Problem *(MCP)*

The formulation of the optimal control problem for maximum concentration of biodiesel production in a batch reactor is presented in this subsection. In this problem, the objective is

to maximize the concentration of biodiesel by finding the best temperature profile given reaction time. For this case study, 100 minutes of reaction time is used to ensure that the maximum yield is reached (84) and (22).

$$\max J = \int_{t_0}^{t_f} k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E = C_E(t_f)$$

(3.10)

subject to:

State Equation 3.4 to Equation 3.9 given in the generalized form below:

$$\frac{dC_i}{dt} = f(C_i, T)$$

(3.11)

where C_i are the initial conditions for state variables and T (temperature) is the control variable. In addition:

Initial time $(t_0) = 0$ minutes

Final time $(t_f) = 100$ minutes

$C_i(t_0) = [0.3226; 0; 0; 0; 1.9356; 0]$ [mol/L]

In the maximum principle, the objective function is reformulated as a linear function in terms of final values of state variables (C_i) and the constant values (A_i), thus, the objective

function for this problem is shown in Equation 3.12:

$$maxJ = \sum_{i=1}^{n} A_i \ C_i(t_f) \ = \ \bar{A_i}^T \ \bar{C_i}(t_f) = C_E(t_f) \tag{3.12}$$

where A_i's are constant values for the linear representation of the maximum principle. Therefore, $A = [0; 0; 0; 1; 0; 0]$

The maximum principle involves the addition of n adjoint variables (one adjoint variable per state variable), n adjoint equations, and a Hamiltonian which satisfies the following relations (91):

$$H(\bar{Z}_t, \bar{C}_t, T) = \bar{z}_t^T F(\bar{C}_i, T_t) = \sum_{i=1}^{n} z_i F_i(\bar{C}_t, T_t) \tag{3.13}$$

$$\frac{dz_i}{dt} = \sum_{j=1}^{n} z_j \frac{\partial F_i}{\partial C_i} \tag{3.14}$$

where n is the number of components (i.e. 6 components) and F_i is the right hand side of differential equation for each component i (Equation 3.4 to Equation 3.9). Equation 3.15 shows the extended form of the Hamiltonian from Equation 3.13:

$$H = z_1 F_1 + z_2 F_2 + z_3 F_3 + z_4 F_4 + z_5 F_5 + z_6 F_6 \tag{3.15}$$

The adjoint equations can be compute using Equation 3.14, as it is shown next:

$$\frac{dz_1}{dt} = -z_1(-k_1 C_A) - z_2 k_1 C_A - z_4 k_1 C_A - z_5(-k_1 C_A) \tag{3.16}$$

$$\frac{dz_2}{dt} = -z_1 k_2 C_A - z_2(-k_2 C_E - k_3 C_A) - z_3 k_3 C_A - z_4(-k_2 C_E + k_3 C_A) - z_5(k_2 C_E - k_3 C_A) \tag{3.17}$$

$$\frac{dz_3}{dt} = -z_2 k_4 C_E - z_3(-k_4 C_E - k_5 C_A) - z_4(-k_4 C_E + k_5 C_A) - k_5(k_4 C_E - k_5 C_A) - z_6 k_5 C_A \tag{3.18}$$

$$\begin{aligned}
\frac{dz_4}{dt} = \; & -z_1 k_2 C_{DG} - z_2(-k_2 C_{DG} + k_4 C_{MG}) - z_3(-k_4 C_{MG} + \\
& k_6 C_{GL}) - z_4(-k_2 C_{DG} - k_4 C_{MG} - k_6 C_{GL}) - z_5(k_2 C_{DG} + k_4 C_{MG} + \\
& k_6 C_{GL}) + z_6 k_6 C_{GL}
\end{aligned} \tag{3.19}$$

$$\frac{dz_5}{dt} = z_1 k_1 C_{TG} - z_2(k_1 C_{TG} - k_3 C_{DG}) - z_3(k_3 C_{DG}$$

$$-k_5 C_{MG}) - z_4(k_1 C_{TG} + k_3 C_{DG} + k_5 C_{MG}) - z_5(-k_1 C_{TG} - k_3 C_{DG} +$$

$$-k_5 C_{MG}) - z_6 k_5 C_{MG} \tag{3.20}$$

$$\frac{dz_6}{dt} = -z_3 k_6 C_E - z_4(-k_6 C_E) - z_5 k_6 C_E + z_6 k_6 C_E \tag{3.21}$$

The boundary conditions for the adjoint variable are $z_i\,(t_f) = [0;\,0;\,0;\,1;\,0;\,0]$, which correspond to the constant values of vector A. Using backward integration along with RKF method these equations can be solved. Finally, the optimal decision vector $T(t)$ can be obtained by finding the extremum of the Hamiltonian at each time step, in other words, applying the optimality condition:

$$\frac{dH}{dT}\bigg|_t = 0 \tag{3.22}$$

3.3.1.1 <u>Solution Technique: Steepest ascent Hamiltonian method</u>

The maximum principle formulation results in two point boundary value problems because the initial conditions for the state variables C_i are known, but the conditions for the adjoint variables are only known at the final boundary. In order to obtain a solution, some iterative

techniques including the shooting method and steepest ascent of the Hamiltonian method can be used (91). To reduce the computational intensity, the optimal temperature trajectory for the system is achieved by using the approach proposed by Diwekar and co-workers (91); (92) and (93), which uses the maximum principle. This algorithm starts with the initial estimate temperature $T(t)$. Then, Equation 3.4 to Equation 3.9 and Equation 3.16 to Equation 3.21 are solved by employing the RKF method (85) with a step size equal to 0.01. Next, the values of dH/dT at each time are computed and then the convergence criterion (abs(dH/dT) < tolerance) is verified. If the convergence criterion is not satisfied, the temperature $T(t)$ is updated using this gradient, in such that the updated temperature profile improves the objective function, shown in Equation 3.23. The value of M is a suitable constant that can be small enough so that no instability will result, or large enough for rapid convergence. Figure 23 shows the flowchart for this algorithm. In order to obtain the derivative of the Hamiltonian, a novel approach was used. This approach involves new differential equations whose solutions result in the derivative of the Hamiltonian. This is described in the Appendix B.

$$T(t)^{new} = T(t)^{old} + M \left(\frac{dH}{dT}(t) \right) \tag{3.23}$$

3.3.2   Minimum Time Problem (MTP)

For the minimum time problem, the objective is to minimize the batch time given a final concentration. Although, the maximum concentration and minimum time problem result in
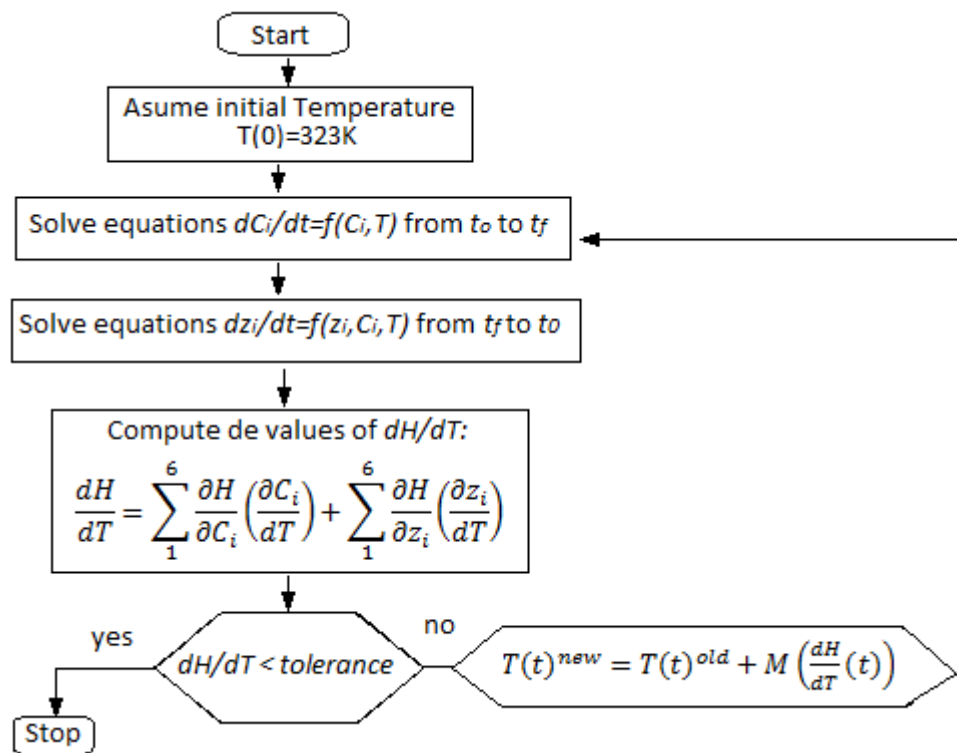
Figure 23. Flowchart of the solution technique

similar equations for maximum principle; one more equation is introduced due to the new state variable t (i.e. time). The formulation for the minimum time problem is explained next.

The objective function:

$$min \ J' = \int_{C_E(t_0)}^{C_E(t_f)} \frac{dt}{dC_E} = \int_{C_E(t_0)}^{C_E(t_f)} \frac{1}{\frac{dC_E}{dt}} = t(C_E(t_f))$$

(3.24)

Subject to:

$$\frac{dC_i}{dC_E} = \frac{\frac{dC_i}{dt}}{\frac{dC_E}{dt}} = F_i G_i$$

(3.25)

where F_i are the differential Equation: Equation 3.4 to Equation 3.9 and G_1 can be written as:

$$G_1 = \frac{dt}{dC_E} = \frac{1}{k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E}$$

(3.26)

Therefore, this problem is subject to:

$$F_1' = \frac{dC_{TG}}{dC_E} = \frac{-k_1 C_{TG} C_A + k_2 C_{DG} C_E}{k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E}$$

(3.27)

$$F_2' = \frac{dC_{DG}}{dC_E} = \frac{k_1 C_{TG} C_A \ - \ k_2 C_{DG} C_E \ - k_3 C_{TG} C_A \ + \ k_4 C_{MG} C_E}{k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E}$$

$$(3.28)$$

$$F_3' = \frac{dc_{MG}}{dC_E} = \frac{k_3 C_{DG} C_A - k_4 C_{MG} C_E - k_5 C_{MG} C_A + k_6 C_{GL} C_E}{k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E}$$

$$(3.29)$$

$$F_4' = \frac{dC_E}{dC_E} = \frac{k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E}{k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E}$$

$$(3.30)$$

$$F_5' = \frac{dC_A}{dC_E} = \frac{-k_1 C_{TG} C_A + k_2 C_{DG} C_E - k_3 C_{DG} C_A + k_4 C_{MG} C_E - k_5 C_{MG} C_A + k_6 C_{GL} C_E}{k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E}$$

$$(3.31)$$

$$F_6' = \frac{dC_{GL}}{dC_E} = \frac{k_5 C_{MG} C_A - k_6 C_{GL} C_E}{k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E}$$

$$(3.32)$$

$$F_7' = \frac{dt}{dC_E} = \frac{1}{k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E}$$

$$(3.33)$$

Again, the application of the maximum principle involves the addition of n adjoint z_i' variables, n adjoint equations and a Hamiltonian (n, in this case is equal to 7), which satisfies the following relations:

$$\left(\frac{dz_i}{dt}\right)\left(\frac{dt}{dC_E}\right) = \frac{dz_i'}{dC_E} = -\sum_{j=1}^{n} z_j' \left(\frac{\partial F_i}{\partial C_i}\right)$$

$$(3.34)$$

$$H(\bar{Z}_t', \bar{C}_t, T) = \bar{z}_t'^T F'(\bar{C}_i, T_t) = \sum_{i=1}^{n} z_i' F_i'(\bar{C}_t, T_t)$$

$$(3.35)$$

For instance, to compute the adjoint variable for triglycerides the differential Equation 3.36 can be used:

$$\frac{dz_{TG}}{dC_E} = \frac{dt}{dC_E}\left(-z_{TG}\frac{dF_1}{dC_{TG}} - z_{DG}\frac{dF_2}{dC_{TG}} - z_{MG}\frac{dF_3}{dC_{TG}} - z_E\frac{dF_4}{dC_{TG}} - z_A\frac{dF_4}{dC_{TG}}\right.$$
$$\left. -z_{GL}\frac{dF_6}{dC_{TG}}\right) - z_t\frac{d(\frac{dt}{dC_E})}{dC_{TG}}$$

$$(3.36)$$

The minimum time problem resulted from this formulation can be solved using the same approach presented in Section 3.3.1.1.

3.3.3   Maximum profit problem (*MPP*)

In the previous section, the formulation of minimum time problem using the maximum principle and the application of the steepest ascent of the Hamiltonian method as the solution technique was shown. In this section, the maximum profit problem is formulated. This problem determines the optimum batch time and concentration of biodiesel while maximizing the overall profit. Moreover, it is presented here that the maximum profit problem involves the solution of the maximum concentration problem and both the maximum concentration and minimum time problems which turn out to be special cases of the maximum profit problem.

The objective function for the maximum profit problem in the reaction section is represented by Equation 3.37 (94)

Objective function:

$$\max J'' = \frac{M_E P_r - B_o C_o}{t + t_s} \tag{3.37}$$

where *ME* is the amount if product (*kg*), *Pr* is the sales value of the product ($/kg), *Bo* is the amount of feed *F* (*kg*), *Co* is the cost of feed ($/kg), t is batch time (minutes) and t_s is the setup time for each batch. It can be seen that the energy term is not considered in this equation because it does not affect in the same proportion as the raw material. As mentioned before,

previous literature agreed that raw material is the largest contributor to the production cost. One possible reason is that the transesterification reactions are exothermic, which increase the temperature of the reactor by itself, so the energy required to heat the reactor is not significant.

In order to solve the complete optimization problem Equation 3.38 can be reformulated as:

Objective function:

$$\max J'' = \max \frac{max(M_E)P_r - B_oC_o}{t + t_s} \tag{3.38}$$

Table XVIII shows the information needed for profit function calculation. The amount of feed involves the quantity of methanol and triglycerides at the beginning of the reaction while the amount of product is the final concentration of methyl ester which is maximized by finding a temperature profile.

3.3.3.1 <u>Solution technique: Maximum principle and *NLP*</u>

The maximum profit problem is solved as two level optimization problems. This algorithm combines maximum principle and *NLP* techniques. The solution procedure is shown in Figure 24. As shown in this figure, there are two levels of optimization which are: *NLP* optimization at the outer loop with the initial value of temperatures and the inner loop involving calculation of the maximum concentration of biodiesel. In brief, it starts by giving the initial guess of temperature and solving the *MCP* which consists on the system of differential equations for the states and adjoint variables so the derivative of the Hamiltonian is calculated and a new

TABLE XVIII

INFORMATION FOR MPP

Item	Data
Soybean oil (Triol)[a]	$0.62/kg
Methanol	$0.320/Kg
Biodiesel (Methyl ester)	$3/gallon=$0.9/kg
Biodiesel density	0.88 kg/l
Triglyceride density	885.45 kg/l
Methanol density	32.04 kg/l
Setup time (t_s)	10 min
Volume	10000 l

[a](28) and (95)

temperature profile is obtained (i.e. Level 2). The integration and calculation of the control

variable T continues until the specific stopping criterion is met. This Level 2 is the same as

summarized in Section 3.3.1.1. Once, this criterion is reached, the optimal temperature profile

and maximum value of concentration calculated at the given time go to level 1 to compute the

objective function (Equation 3.38), then NLP optimization technique is used to find optimum

time corresponding to the criterion that the Kuhn Tucker error is less than an allowable toler-

ance (allowable Kuhn Tucker error), at this stage the algorithm stops, otherwise, a new value

of time is updated and the level 2 takes part in the algorithm again. This code uses SQP to

minimize ($-J''$). This approach was derived from the solution of optimal control problems in

batch distillation presented in (93).
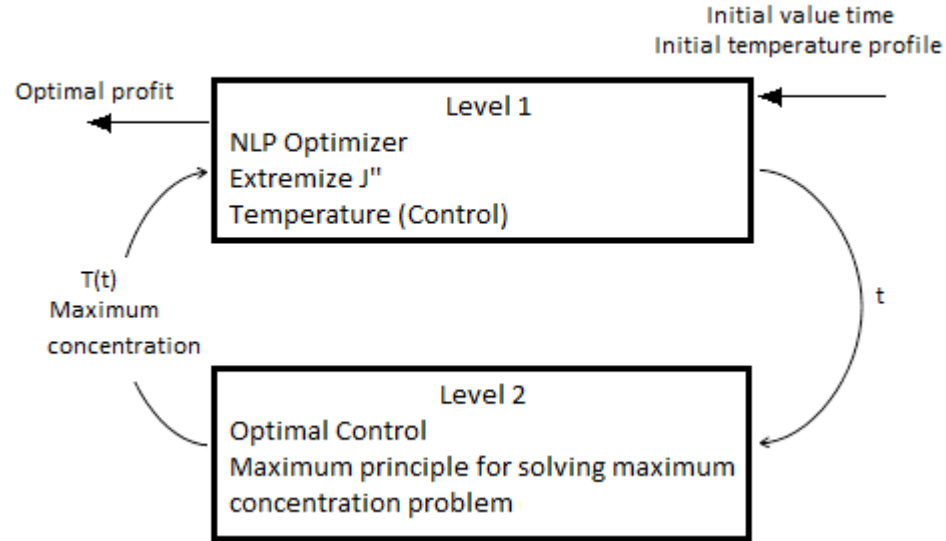
Figure 24. Combining maximum principle and *NLP* optimization techniques

3.3.4   Results and discussion

Results of the three optimal control problems for biodiesel production are shown in this section. To start with, Figure 25 and Figure 26 present the profiles of derivatives of the Hamiltonian and the temperature per iteration. From these figures, it can be seen that as the profiles of the gradients dH/dT decrease (Figure 25) the temperature profiles increase (Figure 26) which improve the objective function (Equation 3.12). The solution technique presented in this chapter proposes that the iterations proceed until the gradients reach a specific tolerance (i.e. Tolerance less than *2e-3*). The value of this tolerance was chosen based on the reaction temperature. This temperature cannot exceed the boiling point of methanol (i.e. 338K at atmospheric pressure) due to the risk of leak out of alcohol through vaporization (22); therefore,
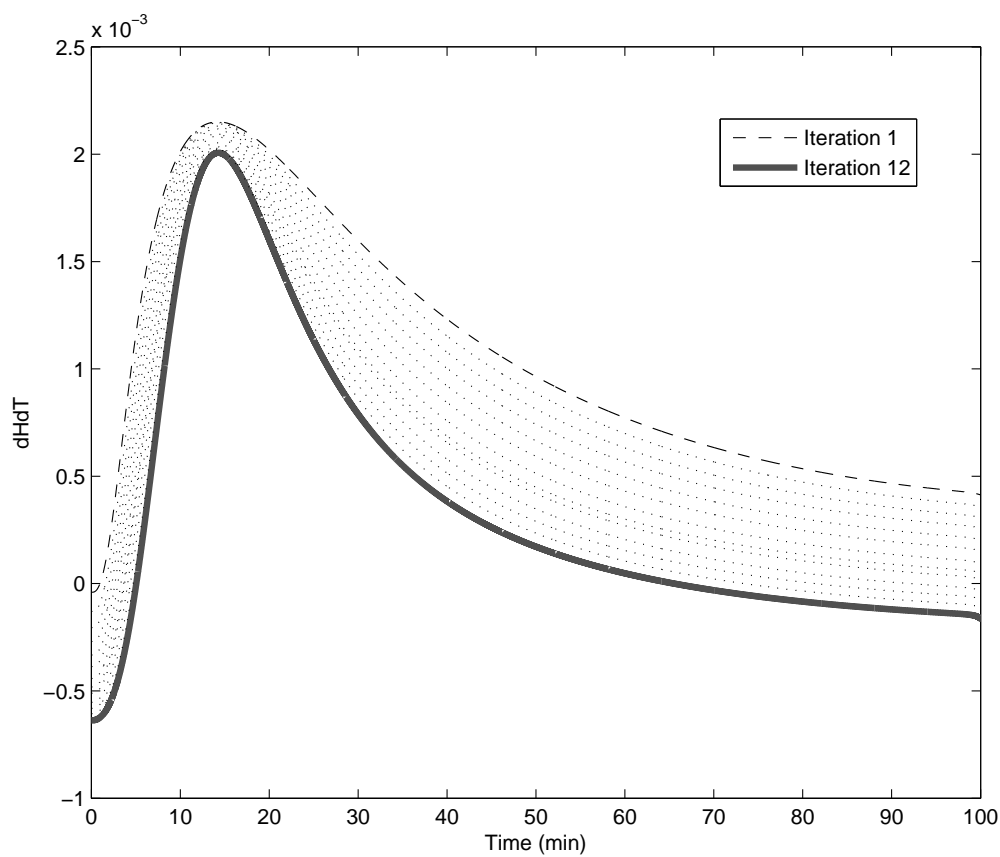
Figure 25. Values of dH/dT for all iterations

twelve iterations were deemed to be sufficient.

Figure 27 shows the initial guess of temperature $T(t)$=323K and the optimal temperature profile obtained after the stopping criterion was satisfied. This figure illustrates the significant variation of temperature with reaction time: at time zero the temperature value starts with
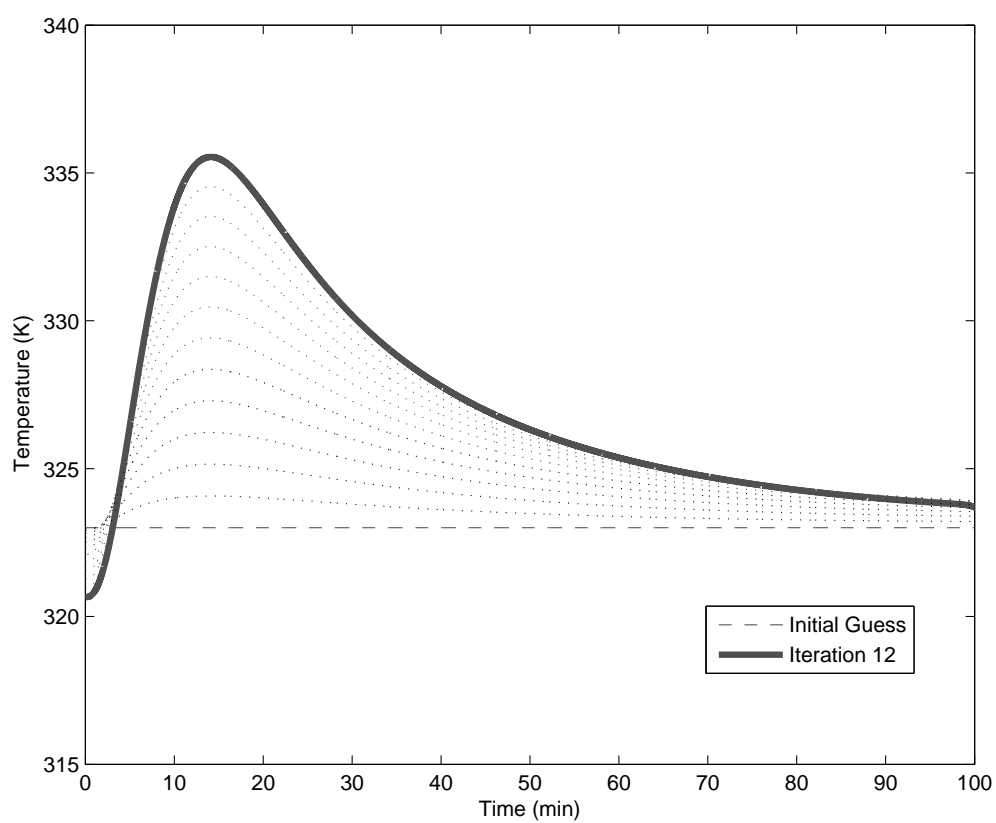
Figure 26. Temperature profiles for all iterations
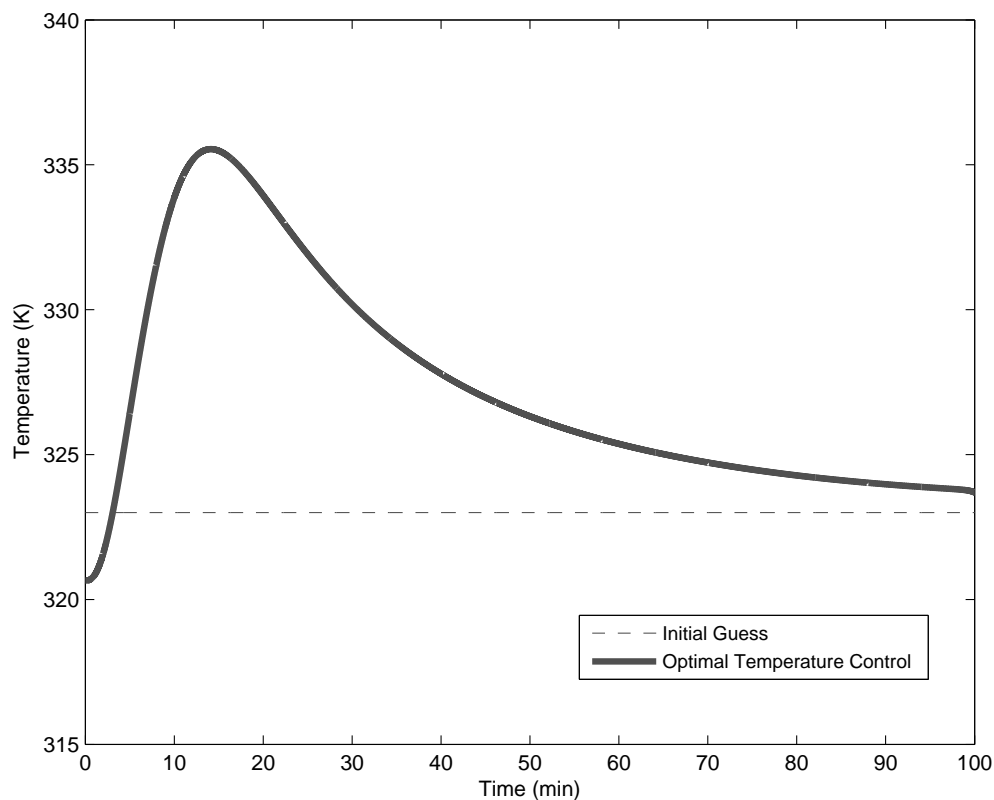
Figure 27. Comparison between initial guess and optimal temperature profiles

320.6K, then, as the reaction proceeds between 10 to 20 minutes, the temperature increases to 335.5K. According to (62); (84) and (96), if the temperature goes beyond the optimal level, the yield of biodiesel product decreases because the saponification reaction of triglycerides acceler-ates. Finally, when the reaction time is 100 minutes the temperature drops to 323.7K.
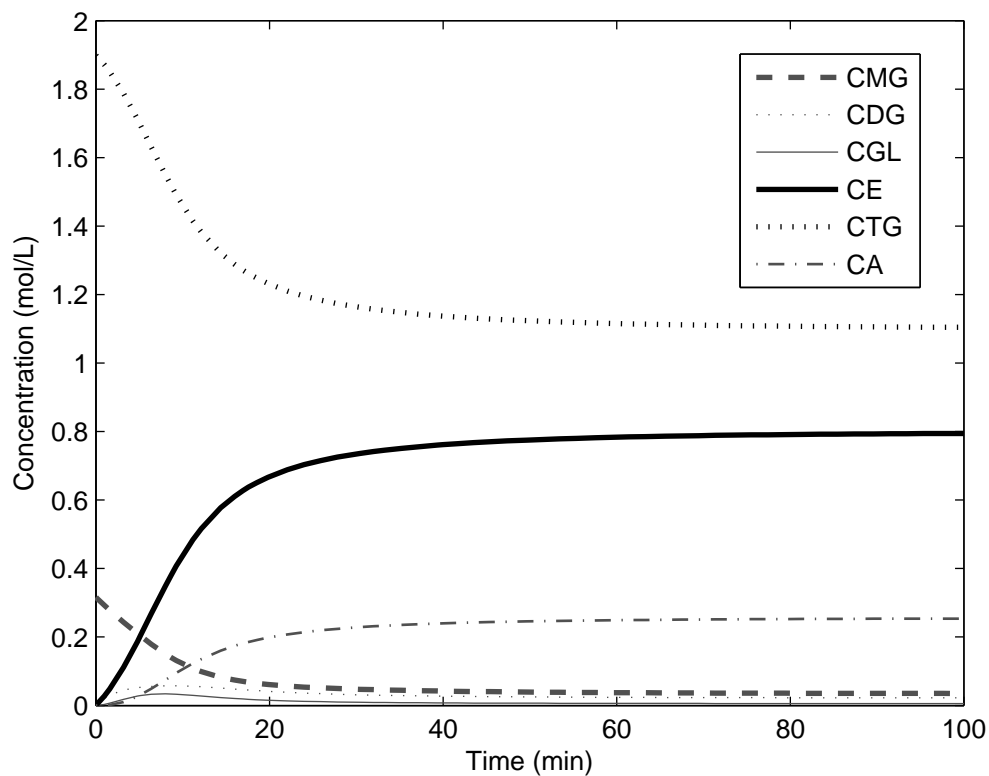
Figure 28. Concentration profiles at the end of iterations

Figure 28 presents concentration profiles for the six components. The purpose of this figure is to show that as the reaction precedes, the concentration of the desired product, methyl ester, increases; however, after 65 minutes there is no significant change in these values. This situation also happens with the rest of the components which no further change occurs after reaching this time.

Figure 29 illustrates the concentration profile of methyl ester(i.e biodiesel). Here the concentration profiles are compared at constant temperature and the values calculated at optimal temperature profile. From this figure, it is observed how the behavior of the temperature is reflected on the concentration of methyl ester, thus, when the temperature profile changes from constant values to the optimal profile, the concentration of methyl ester also changes. This situation is more significant when the optimal control is compared with base case 1. It can be seen that at 100 minutes of reaction time, the concentration of methyl ester at optimal control temperature reaches its maximum value, 0.79mol/L; while at constant temperature, the maximum concentration is 0.73mol/L. On the other hand, for the base case 2 the maximum concentration value at 100 minutes is 0.78mol/L. Comparing these values, there is an increment of 8.46% with base case 1 and 1.47% with base case 2. For base case 2, the increment is not significant since the constant profile at 323K belongs to the constant optimal profiles reported in the literature (22). Alternatively, if we fix the concentration at 0.73mol/L, the reaction time needed would be 69.5% less than it was at the beginning. In the base case 2, the reduction on time represents 46% of the original reaction time if the concentration is fixed to 0.78mol/L. This condition is the expected result from solving the minimum time problem. This improvement does not affect the other components because at the 50th minute of the reaction time, their concentration values are almost constant as shown in Figure 28.

The next part of this section is the minimum time problem (MTP) results. Figure 30 illustrates the time profile of methyl ester for the MTP. Here, we are comparing the concentration
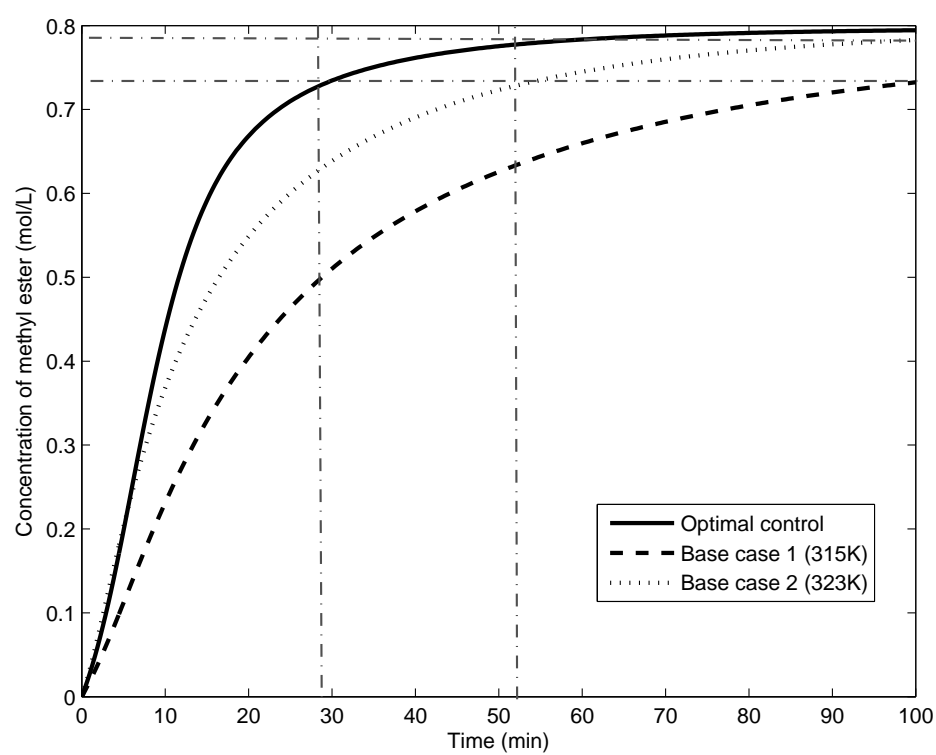
Figure 29. Concentration profile of biodiesel

values at constant temperature (i.e. base cases) with the values calculated at optimal temperature profile. As it can be observed, after fixed the concentration of methyl ester to 0.73mol/L the minimum reaction time reached is around 30.6 minutes when optimal control approach is applied, while in base case 1 and 2 their minimum time is reached at 100 and 54 minutes, respectively. If this figure is compared with Figure 29, it can be easily shown that the maximum concentration and minimum time problem results in similar equations for maximum principle and also results in similar profiles.

Figure 31(a and b) compares the temperature profiles for MCP and MTP. The first figure presents how temperature increases up to 336K at minute 16th and then starting to decrease until 330K at minute 30.5^{th}. This behavior is also reflected in the concentration profile (Figure 29) where most part of the reaction occurs in the beginning since this reaction is favored by the increase of temperature (84). On the other hand, Figure 31b shows a different temperature profile. In this case, the temperature decreases until 326K and then it reaches 342K at final concentration of methyl ester (i.e. 0.73mol/L). Although, the optimal control profiles shown in this figure for the two optimal control problems are significantly different, their results are similar showing that this problem has multiple solutions.

Finally, the maximum profit problem results are presented next. Figure 32 compares the concentration profile of methyl ester using optimal control problem (i.e. maximum profit problem) with the two base cases. It can be seen that at 50 minutes of reaction time, there is an
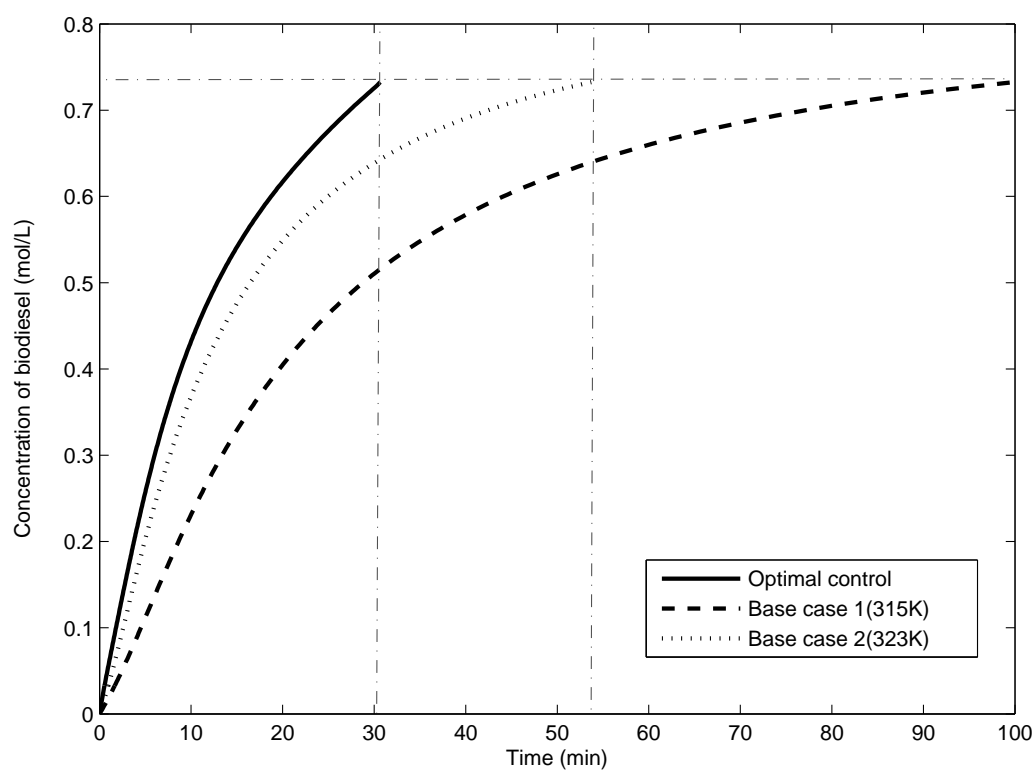
Figure 30. Time profile for methyl ester (MTP)
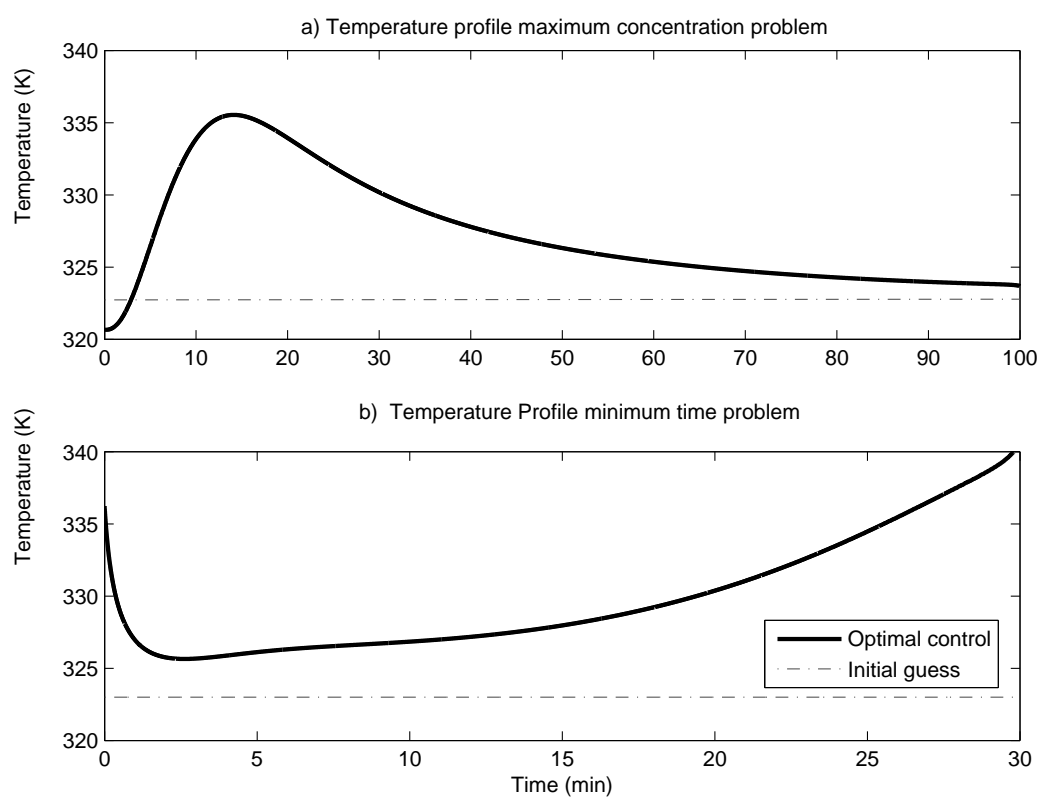
Figure 31. Temperature profile for methyl ester.a) Maximum Concentration Problem. b) Minimum Time Problem

TABLE XIX

COMPARISON OF THE OPTIMAL CONTROL PROBLEMS

Parameter	Maximum concentration problem	Minimum Time problem	Maximum profit problem
Concentration of methyl Ester (mol/L)	0.79	0.73	0.78
Time (min)	100	30.5	50
Profit ($/h)	103.10	32.89	149.83

increase of methyl ester concentration of 25.56% (for base case 1) and 8.50% (for base case 2). Moreover, if the profit values of the *MCP* and *MTP* are computed (using Equation 3.38) and then compared them with the profit value found in the *MPP*, there is an increment of 45.32% and 355.58%, respectively; this information is summarized in Table XIX. These results show that the *MPP*, which combines the maximum concentration and minimum time problem, give better outcomes than employing the problems individually. The optimal temperature profile of *MPP* is presented in Figure 33. As it is observed, this optimal profile has higher values of temperature compared with the *MCP* profile (Figure 31a). This situation evidences what it is shown in Figure 32, where the production of methyl ester is favored using optimal control strategies since it can produce more of methyl ester in less time.
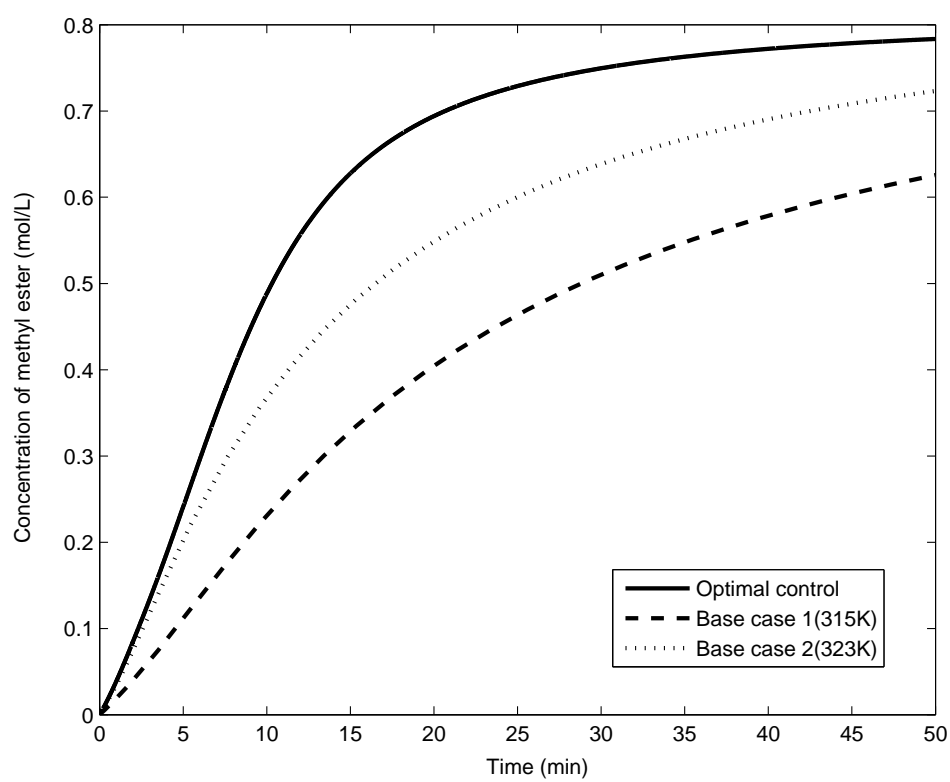
Figure 32. Concentration profiles for maximum profit
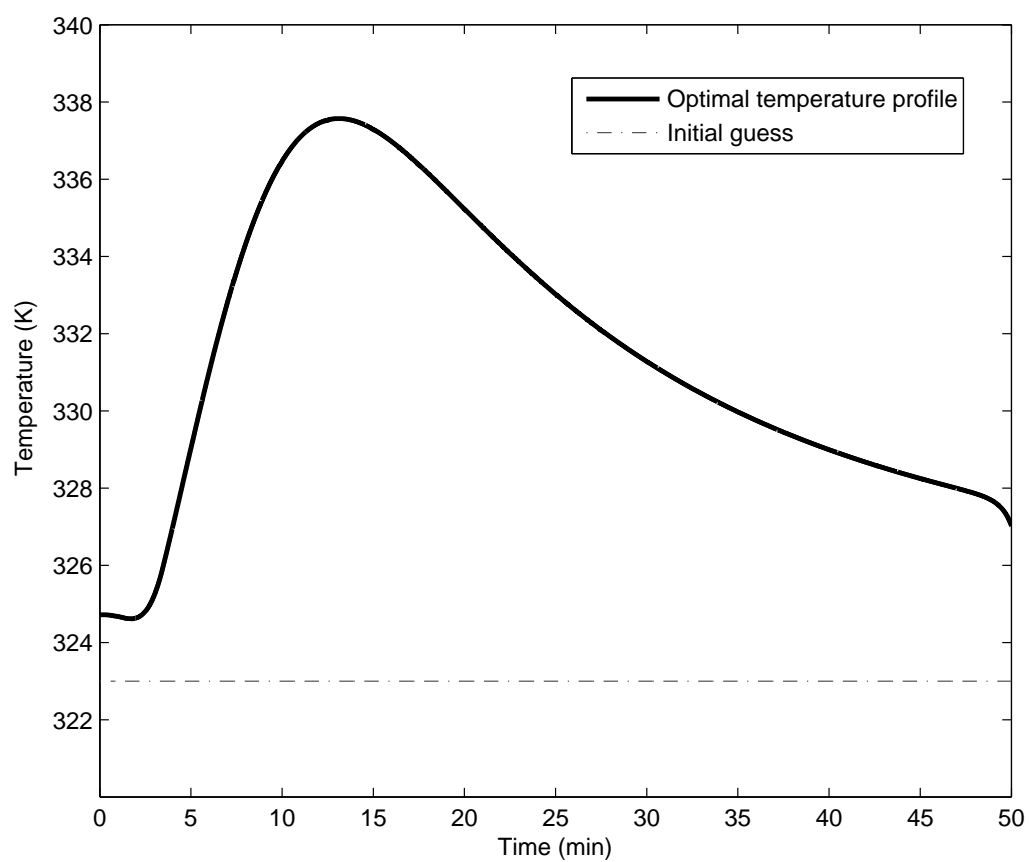
Figure 33. Temperature profile for maximum profit

3.3.5 Conclusion

This chapter presented three optimal control problems encountered in biodiesel batch production. These problems involved determining the deterministic optimal temperature profile so as to maximize or minimize performance indices, namely, concentration, time and profit. The maximum principle along with the steepest ascent of the Hamiltonian method was used to solve the optimal control problems. The advantage of this method is that avoids the solution of second order differential and partial differential equations that are required in other techniques, such as calculus of variation and dynamic programming. For the maximum concentration problem, numerical results showed that twelve iterations were enough to reach the maximum concentration of methyl ester. The deterministic profile was compared with two base cases: (I) constant temperature of 315K and (II) optimal temperature of 323K. As a result, it was presented that at 100 minutes of reaction time the concentration value of methyl ester increased 8.46% for base case 1 and 1.47% for base case 2 when the optimal temperature profile was employed. On the other hand, it was shown that the methyl ester profile obtained can reach the maximum concentration in less time when the optimal control of temperature is used; in other words, the values of concentration reached 0.73mol/L at 30.5 minutes for base case 1 and 0.78mol/L at 54 minutes for base case 2, which implied a reduction of 69.5% and 46% in batch time, respectively. Moreover, the solution of the *MCP* and *MTP* results in similar equations for maximum principle. It was also shown that the solution of maximum profit involves the solution of maximum concentration in the inner loop and minimum time problem in the outer loop, combining the maximum principle and *NLP* techniques. The maximum profit found

using optimal control was 149.83\$/h. For this reason, optimal control provides improvement to the effectiveness of batch processing, specially, in the case of the maximum profit problem. The MPP's results indicated that solving this problem gives better results than solving the maximum concentration and minimum time problem individually.

CHAPTER 4

UNCERTAINTY IN BIODIESEL PRODUCTION

4.1   Introduction

Uncertainty is present in all systems, from natural systems to industrial system with the detailed process description. Modeling and managing uncertainty is important in any process since the successful utilization of the resulted models relies heavily on the ability to handle system variability. In the recent years, modeling, planning and scheduling under uncertainty has received a lot of attention in the open literature from chemical engineering and operations research communities (97).

There are two kinds in which uncertainties can be classified: static uncertainties and dynamic uncertainties. Examples of static uncertainties are variations observed in initial variables, input conditions or model parameters while process conditions that change with respect to time are described as dynamic uncertainties. Most of the time, static uncertainties can affect other parameters in the process that change with time, which is an exclusive characteristic of dynamic processes. Therefore, static uncertainties lead to dynamic uncertainties. Processes that explicitly consider randomness may be much more valuable and it can be more useful for actual operation (98). For instance, in batch distillation, relative volatility is a thermodynamic parameter which provides the equilibrium relationship between the vapor and the liquid phases.

This parameter changes with respect to time and at each plate due to the changes in the chemical composition. However, to use faster and efficient optimal control calculation, the relative volatility is assumed to be constant, as a result, the performance of the process is reduced (99). This drawback may limit the usefulness of finding an optimal solution.

Models of uncertainty are predominant in many optimization problems of batch operations. For instance, Fotopoulos et al. (100) presented an approach for modeling and optimization of batch reactors using the tendency modeling techniques. Since this technique was an approximation of the stoichiometric and kinetic models, the introduction of the process model mismatch may have significant effect on the success of the optimization involving the uncertainty in the model parameters. Their methodology was to determine the sensitivity of the optimal input policy to uncertain model parameters resulting in two point boundary value problems that are solved using orthogonal collocation. In (101), an algorithm for generating stochastic optimal adaptive controls for stochastic systems was illustrated. They studied an application to the temperature control of a batch reactor with stochastic features arising from random noise. Ruppen et al. (102) described a method for optimizing batch reactors when the models -at hand- are characterized by parametric uncertainty using the method of orthogonal collocation. The nominal optimization, minimax optimization, and robust worst-case optimization are investigated as case studies, and for each case they assumed linear temperature profile. Furthermore, they assumed that the uncertain values lie at the boundary of constraints. However, this approach leaded to conservative results, according to (103). Finally, papers by Terwiesch et al. (104) and

Srinivasan et al. (105) presented industrial viewpoints, requirements, and the corresponding modeling and practices together with a selection of optimization methods and strategies that take into account the characteristic uncertainties of batch models.

In this chapter, the main objective is to develop a general systematic approach to model and characterize uncertainties found in batch reactor. The potential of this approach will be explored in the case of biodiesel production where the effect of these uncertainties on optimal control profiles will be studied in the following chapter.

4.2   From static to dynamic uncertainties

Modeling and control of batch reactors result in a difficult and challenging task due to several consideration, such as time-varying characteristics, nonlinear behavior, constraint operations, and presence of disturbances (81). In addition, due to the innovative characteristic of batch products, only a minimum number of modeling runs are performed in the laboratory before scale-up to the production plant (104) which reduces the possibility of having accurate information. All these situations lead to factors of uncertainty, and consequently, in some associated parameters, making significant the consideration of uncertainty in a model. For instance, the kinetic parameters and the initial composition can be common source of uncertainty and good examples of static uncertainties. Since they affect other process parameters that change with time (i.e. concentration of reactants), these static uncertainties lead into dynamic uncertainties. In this work, the static uncertainties are characterized using probability distribution functions

and propagated into the models using stochastic modeling iterative procedures, whereas the dynamic uncertainties are represented by using stochastic differential equations in terms of stochastic processes, namely Ito processes which originate from real options theory in finance (106).

Before going into the details of stochastic modeling used to characterize the uncertainty in biodiesel production, background information about uncertainty analysis and sampling, as well as, various Ito processes are explained in the following subsections. For a more thorough discussion on stochastic and Ito processes reader may refer to these sources in literature (106) and (91).

4.2.1 Uncertainty analysis and sampling

The probabilistic or stochastic modeling iterative procedure involves (I) specifying the uncertainties in key input parameters in term of probability distributions, (II) sampling the distribution of the specified parameter in an iterative fashion, and (III) propagating the effects of uncertainties through the process flow sheets (107).

4.2.1.1 Specifying uncertainties using probability distribution

In order to model a system under uncertainty, a quantitative description of the expected variations must be established. Thus, probability distribution functions can be used to characterize the uncertainty. These distributions define the rule for describing the probability measures associated with the values of uncertain variable. Some of the most representatives

distributions are: uniform, normal, triangular, and lognormal. The type of distribution chosen for an uncertain variable reflects the amount of information that is available. For instance, uniform and log-uniform distributions represent an equal likelihood of a value lying anywhere within a specific range, on either a liner or logarithmic scales, respectively.

4.2.1.2 Sampling the distribution of the specified parameter in an iterative fashion

After assigning the probability distributions to the uncertain parameters, the next step is to perform a sampling operation from the multivariable uncertain parameter domain. Alternatively, one can use analytical methods to obtain the effects of uncertainties on the output; but, these methods tend to be applicable to special kind of uncertainty distributions and optimization surfaces only. The sampling approach, on the other hand, provides wider applicability. Several techniques are available such as Monte Carlo technique (MCT), Latin Hypercube sampling (LHS), Importance sampling, and Hammersley sequence sampling (HSS). MCT is the most widely used sampling technique. This technique is based on the pseudo-random number generator to approximate a uniform distribution (i.e. having equal probability in the range of 0 to 1). The specific values for each input variable are selected by inverse transformation over the accumulative probability distribution. The LHS (108) is one form of stratified sampling technique that can yield more precise estimates of the distribution function. The importance sampling (109) is a stratified sampling technique that ensures more samples are generated from high probability regions. Finally, the HSS (110) uses an optimal design scheme for placing N

sample points on a K-dimensional hypercube. This scheme certifies that the sample set is more representative of the population showing better uniformity in the multidimensional uncertainty surface.

4.2.1.3   Propagation the effects of the uncertainties through the process flow sheets

The next step is to propagate the uncertainties through the model. The output variables of interest are collected for the first iteration. Then, the simulation is repeated for a new set of samples selected from the probabilistic input distributions. All observations are evaluated through the simulation cycle for a specified number of times (e.g. typically 100) and the output variables are used to generate an approximation of the cumulative probability density functions. The stochastic simulation is run at each sample point, and hence, 100 samples are propagated into the model.

4.2.2   Stochastic and Ito processes

A stochastic process is a variable that evolves over time in a way that is at least in part random. One example of stochastic process is the temperature of a city. Its variation through time is random and unpredictable. Figure 34 shows the variation of the temperature of Chicago from the last 50 years.
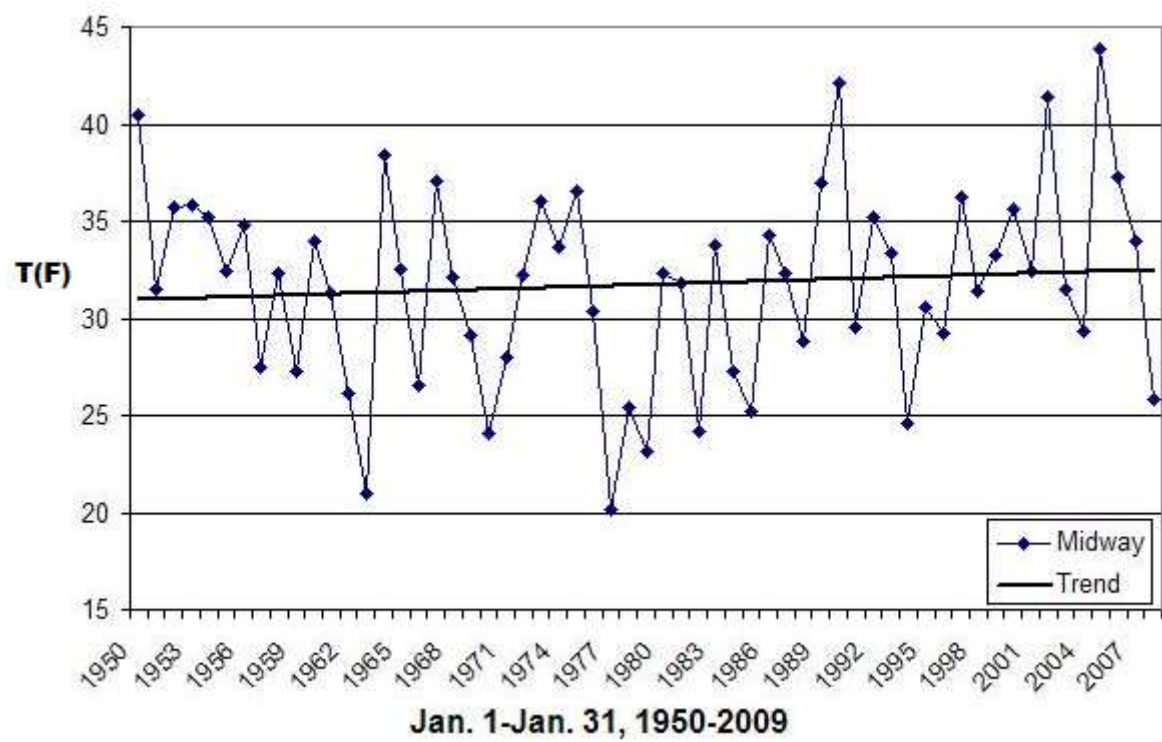
Figure 34. Average temperature of Chicago(Source:www.chicago.straightdope.com)
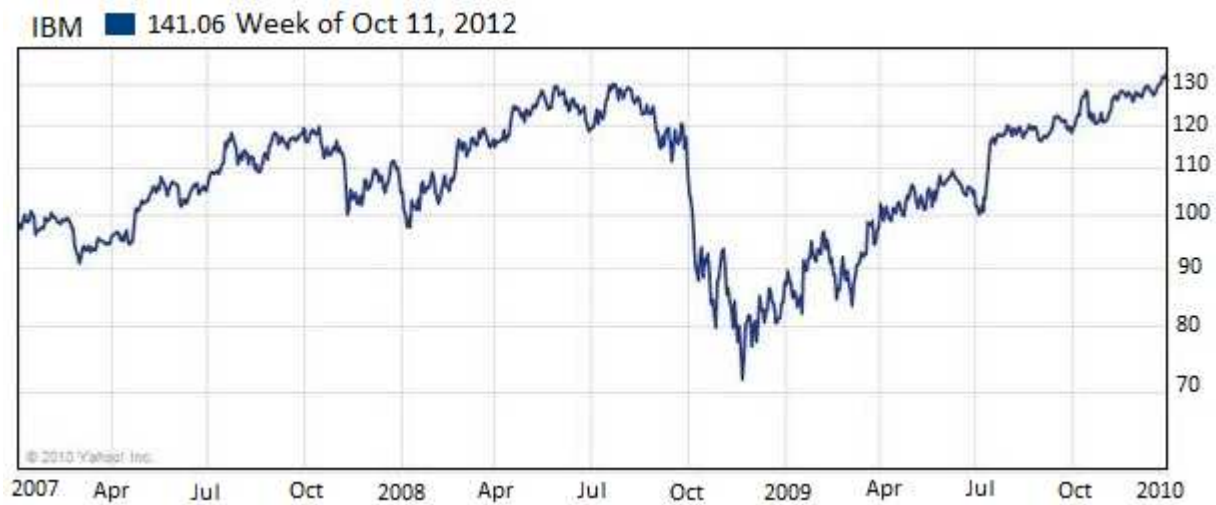
Figure 35. Price of IBM stock(Source:financegourmet.com)

Another example is the price of IBM stock, which also fluctuates randomly (See Figure 35) This variable is considered a non-stationary process since the expected value of this price can grow without bound, and the variance of price Y years from now increases with Y whereas the temperature values can be considered as stationary process.

These two variables are both continuous-time stochastic processes, in the sense that the time index t is a continuous variable. Since stochastic processes do not have time derivative in the conventional form, they cannot always be manipulated using the ordinary rules of calculus(111). This is because, in general, the solution to a stochastic differential equation is not a single value for the function, but rather is a probability distribution. Therefore, models under uncertainty

can be portrayed through Ito processes that characterize their stochastic dynamics.

Ito processes are a large class of continuous time stochastic processes used in finance literature to price assets that exhibit dynamic uncertainties. One of the simplest examples of a stochastic process is the random walk process in which a random variable that begins at a known value, takes a jump in either direction with a 50% probability. The Wiener process, also called a Brownian motion, is a continuous limit of the random walk and serves as a building block for Ito processes, through the use of proper transformations. Three important properties characterize a Wiener process:

- It follows the Markov property: the probability distribution for all future values of the process depends only on its current value.

- It has independent increments: the probability distribution for the change in the process over any time interval is independent of any other time interval.

- Changes in the process over any finite interval of time are normally distributed, with a variance which is linearly dependent on the length of time interval, dt.

An Ito process can be defined by Equation 4.1:

$$dx = a(x,t)dt + b(x,t)dz \tag{4.1}$$

where dz is the increment of the Wiener process equal to $\varepsilon_t\sqrt{\Delta t}$, and $a(x,t)$ and $b(x,t)$ are known functions. The random value ε_t has a unit normal distribution with zero mean and

standard deviation of one. The simplest generalization of Equation 4.1 is the equation for the Brownian motion with drift given by Equation 4.2:

$$dx = a(x,t)dt + b(x,t)dz \qquad (4.2)$$

where α is called the drift parameter, and σ is the variance parameter. Over the time interval Δt, the change in x, denoted by Δx, is normally distributed and has an expected value variance:

$$E[\Delta t] = \alpha \Delta t \qquad (4.3)$$

$$v[\Delta x] = \sigma^2 \Delta t \qquad (4.4)$$

For calculation of σ, the average value of the differences in x (i.e. $E[x_t - x_{t-1}]$) is computed. Then this value is divided by the time interval Δt to obtain α. On the other hand, for σ, is the variance of the difference in x is found and divided by the interval time Δt. Then the square root of this value is computed.

Other examples of Ito processes are the geometric Brownian motion with drift and the mean reverting process, which are represented in Equation 4.5 and Equation 4.6, respectively.

$$dx = \alpha x dt + \sigma x dz \qquad (4.5)$$

$$dx = \eta(\bar{x} - x)dt + \sigma dz \qquad (4.6)$$

where η is the speed of reversion and $\bar{x}$ is the nominal level that x reverts to.

In geometric Brownian motion, the percentage changes in x and $\Delta x/x$ are normally distributed (i.e. absolute changes are log normally distributed). While in the mean reverting process, the variable may fluctuate randomly in the short run, but in the longer run it will be drawn back towards the marginal value of the variable. Figure 36 (91) presents the sample paths for the Brownian motion with drift and for the mean reverting process. For example, Brownian motion can be used when the model has non-stationary behavior whereas the mean reverting process is commonly used when the model has stationary behavior.
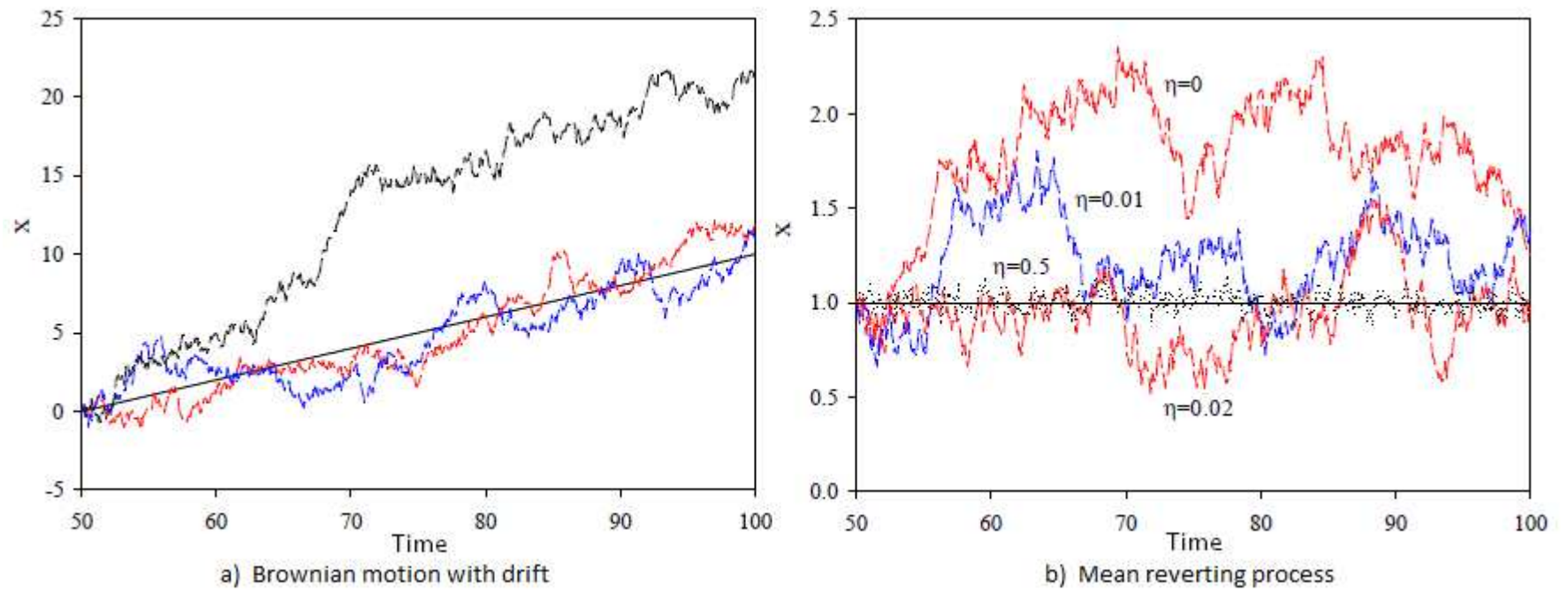
Figure 36. Sample paths for two Ito processes

Applications of Ito processes are prevalent in finance literature since provide a convenient way of analyzing investment timing and option valuation problems. However, these processes can also be used to represent the time dependent changes in a process parameter which are characteristic of optimal control problems. It has been shown in previous works by (112); (113) and (99) that in batch reactor and batch distillation static uncertainties can result in dynamic uncertainties and these uncertainties can be represented by Ito processes. Thus, under uncertainty conditions, these control problems are more difficult to solve since the mathematical model of the process dynamic is not expressed in the conventional sense and techniques such as calculus of variation, dynamic programming, and maximum principle cannot be used. As a result, we use the stochastic processes in order to solve these types of problems in biodiesel production.

4.3   Uncertainties in biodiesel production

Biodiesel production is subject to uncertainties arising out of different parameters that can significantly affect the product quantity, quality, and process economics. Some of the sources of uncertainties in the biodiesel production are the variation of feed composition of vegetable oils, the ratio of methanol to oil, and the reactor operating parameters. Particularly, the feedstock composition is highly variable and even in the same feedstock the range of a single component is very broad (84); (114); (115). Moreover, the operation of the transesterification reactors involves some difficulties that can be associated with frequent overshoot of reaction temperature, oscillation of its internal pressure, the variation in the reactor conversion, and fluctuation in the cooling jacket temperature (79), which are also considered as disturbances to the reactor.
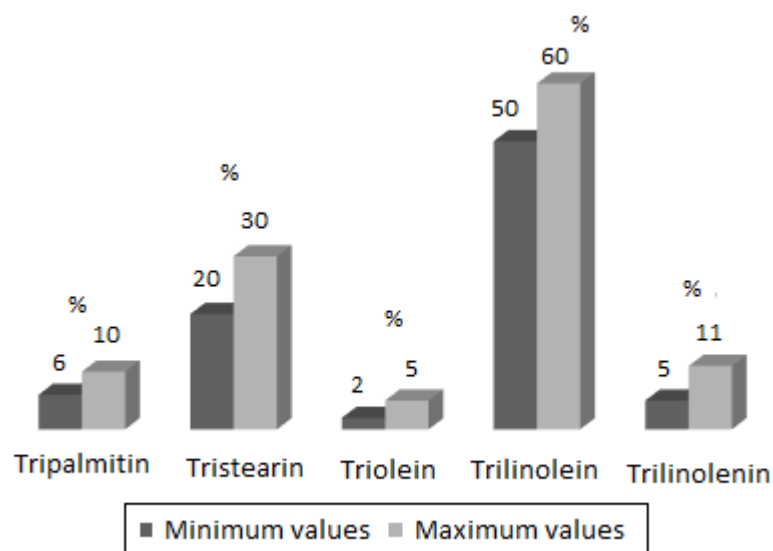
Figure 37. Types and percentage of hydrocarbon chains in soybean oil

In this work, the variation in the feedstock composition is considered as uncertain.

As it was shown in Chapter 2, the transesterification reaction consists of a number of consecutive reversible reactions wherein the triglycerides are converted stepwise to diglycerides, monoglycerides and glycerol and one mole of ester is liberated at each step. As it can be seen in Figure 37, the triglyceride composition existing in soybean is very broad and contains five types of hydrocarbon chains which are tripalmitin 6-10%, tristearin 20-30%, triolein 2-5%, trilinolein 50-60% and trilinolenin 5-11% (115).

The type and amount of triglycerides in the feedstock varies considerably because of nature as a bio-based material (116). This variation is important to consider in the biodiesel production since it can affect the design, modeling, and control of the process. The variability in the feed composition turns out to be one of the most influential parameters in the process. As mentioned before, this uncertainty can be modeled using probabilistic techniques, and can be propagated using stochastic modeling iterative procedures, which involves the following steps presented in Section 4.2.2. Therefore, the first part of this procedure is the representation of the uncertainty in term of probability distribution. Figure 38 shows the probability distribution for the composition of the five triglycerides presented in soybean. The probability distribution used to represent the uncertainties in the feedstock composition is the modified form of uniform distribution, which is uniform* (i.e. uniform Star). A more complete review of the characterization may be found in (107). According to (107), this distribution is better than a uniform distribution because it allows several intervals of the range to be distinguished and captures the range of values in a single feedstock source.

The second part of the stochastic modeling iterative procedure is related with the sampling technique. In this work Latin Hypercube Sampling (LHS) technique was employed. As mentioned before, this technique provides precise estimates of the distribution function compared with other techniques like Monte Carlo techniques. In the LHS method, a distribution is divided into non-overlapping intervals of equal probability and one sample from each interval is selected at random with respect to the probability density in the interval (91) and (117). LHS
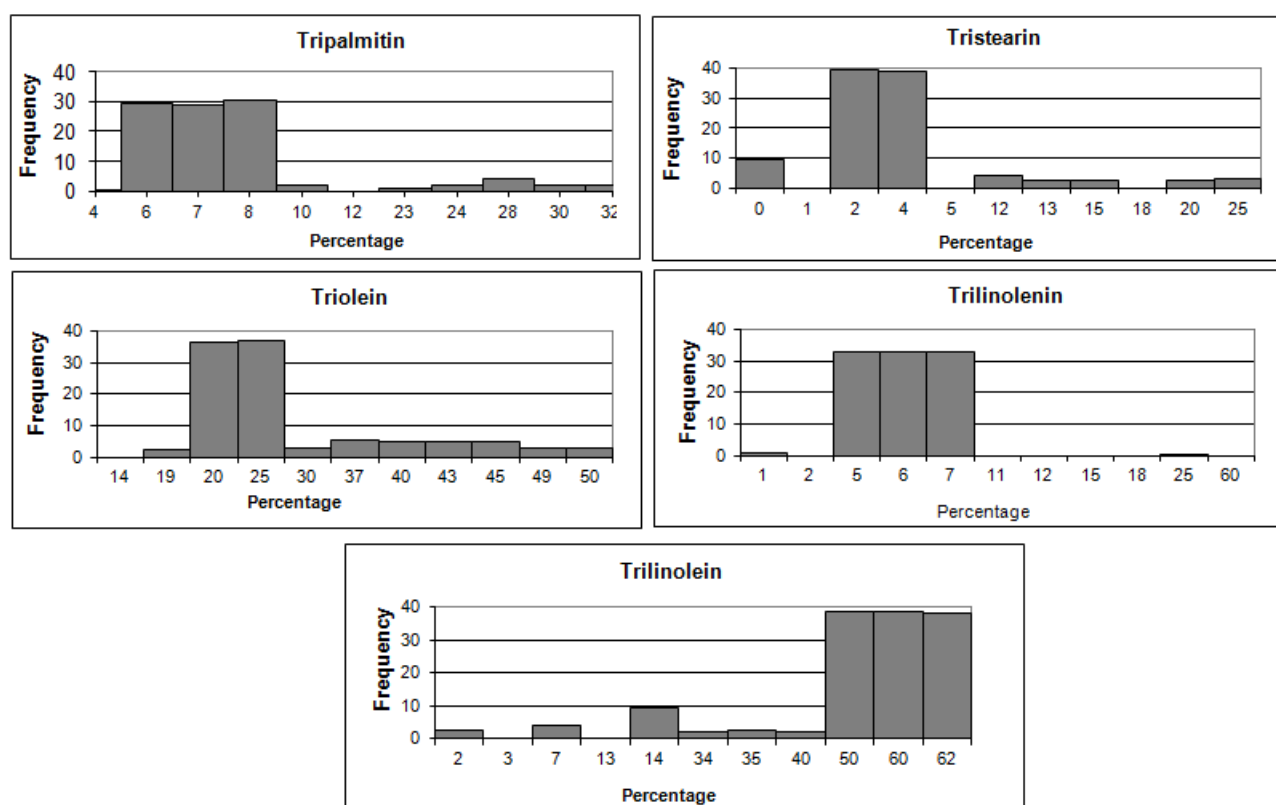
Figure 38. Probability distribution for composition of triglycerides

guarantees that the values from the entire range of the distribution are sampled in proportion to the probability density of the distribution. The procedure to select samples using LHS is described in (117). Thus, 100 samples for the feed composition (i.e. initial triglycerides concentration) were generated.

Finally, the uncertainty parameters (i.e. initial composition of the feedstock) are propagated through the batch reactor model. Figure 39 presents the variation of concentrations for each component with respect to time for each sample. It can be seen from the figure how the variation in the feed composition affects the concentration for each component showing that the static uncertainties result in dynamic uncertainties in concentration. For instance, in the methyl ester case (biodiesel), at 100 minutes of reaction time the concentration can take values between 0.42mol/L to 1.87mol/L. The thick black line in each profile represents the average value of concentration which was the profile used in the deterministic case (Chapter 3).

4.4   Capturing the uncertainties with Ito process

As it was mentioned before, stochastic processes called the Ito process can be used to represent dynamic uncertainties in batch reactor and batch distillation column. This section deals with characterizing the time dependent uncertainties shown in Figure 39 as Ito processes so that the optimal control problem under uncertainty can be solved using the stochastic maximum principle.
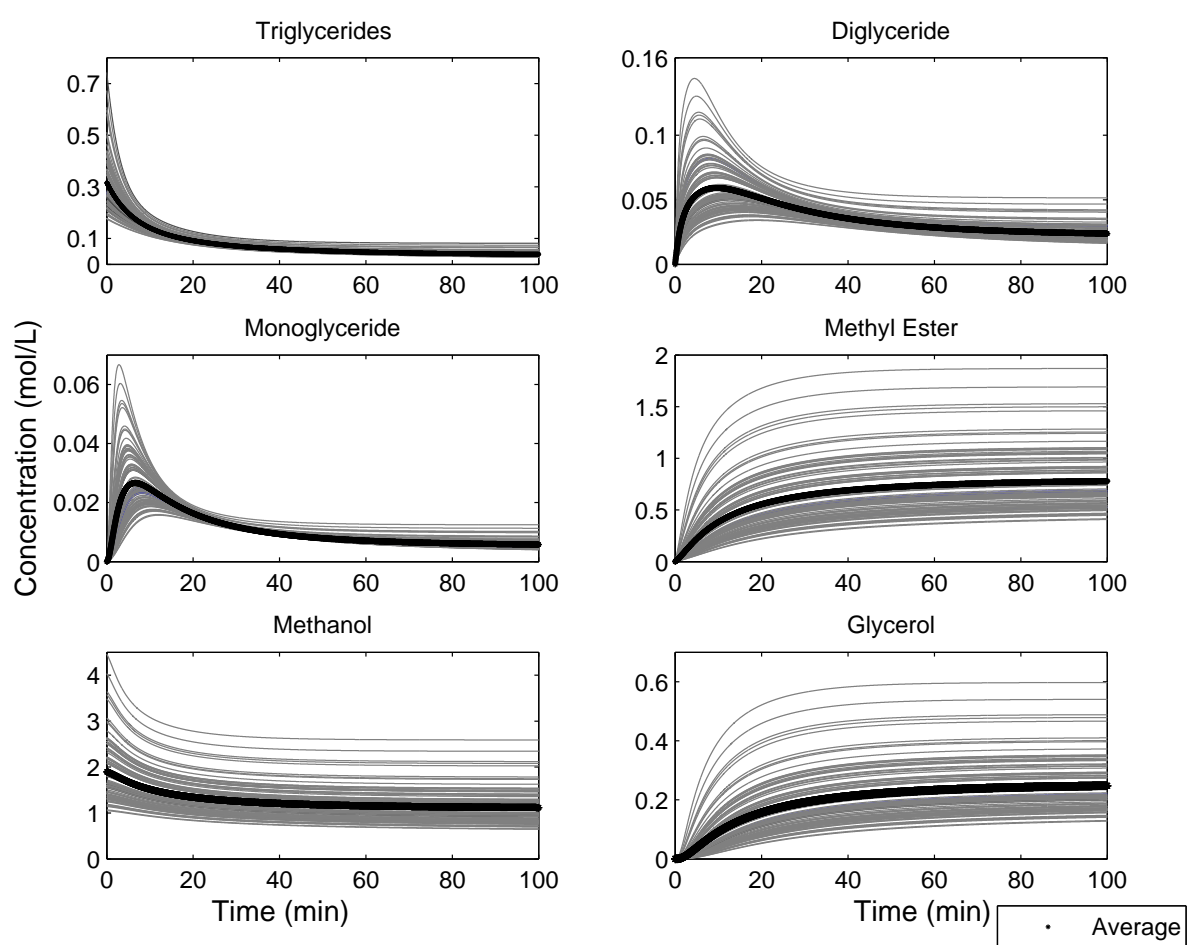
Figure 39. Concentration profiles for each component of biodiesel production

For the case study, a simplification of Equation 4.1 is used to represent time dependent uncertainties in the concentration for each component, known as the Brownian motion with drift:

$$dC_i = F_i(C,t)\Delta t + g_i \epsilon_t \sqrt{\Delta t} \tag{4.7}$$

where C_i represents the state variable, which is the concentration for each component. $Fi(C,t)$ is the right hand side of the differential equation shown in Chapter 3 (Equations 3.4 to 3.9) and g_i is the variance parameters. As mention in Section 4.2.1, over any time interval Δt, the change in C_i is normally distributed and the value of g_i can be calculated by computing the square root of the variance of the differences in C_i and divided by the interval time Δt:

$$g_i = \sqrt{\frac{var(\Delta C_i)}{\Delta t}} \tag{4.8}$$

Therefore, the discrete form of Equation 4.7 is expressed for each component of the biodiesel reaction as:

$$C_{TG}(t+1) = C_{TG} + F_1(C,t)\Delta t + g_{TG} \epsilon_t \sqrt{\Delta t} \tag{4.9}$$

$$C_{DG}(t+1) = C_{DG} + F_2(C,t)\Delta t + g_{DG}\epsilon_t\sqrt{\Delta t} \qquad (4.10)$$

$$C_{MG}(t+1) = C_{MG} + F_3(C,t)\Delta t + g_{MG}\epsilon_t\sqrt{\Delta t} \qquad (4.11)$$

$$C_E(t+1) = C_E + F_4(C,t)\Delta t + g_E\epsilon_t\sqrt{\Delta t} \qquad (4.12)$$

$$C_A(t+1) = C_A + F_5(C,t)\Delta t + g_A\epsilon_t\sqrt{\Delta t} \qquad (4.13)$$

$$C_{GL}(t+1) = C_{GL} + F_6(C,t)\Delta t + g_{GL}\epsilon_t\sqrt{\Delta t} \qquad (4.14)$$

where C_{TG}, C_{DG}, C_{MG}, C_E, C_A, and C_{GL} are the concentrations of triglycerides, diglycerides, monoglycerides, methyl ester, methanol, and glycerol, respectively. These discrete equations are solved from $t=0$ to $t=100$ minutes. Figure 40 shows the Ito process representation (i.e. Brownian motion with drift) of time-dependent uncertainties in the concentration for each composition. It can be observed that 95% confidence interval covers the range of these uncertainties. The comparison of Figure 39 and Figure 40 show that the time dependent uncertainties resulting from the feed composition can be easily captured by the Ito process represented by Equation 4.9 to Equation 4.14.
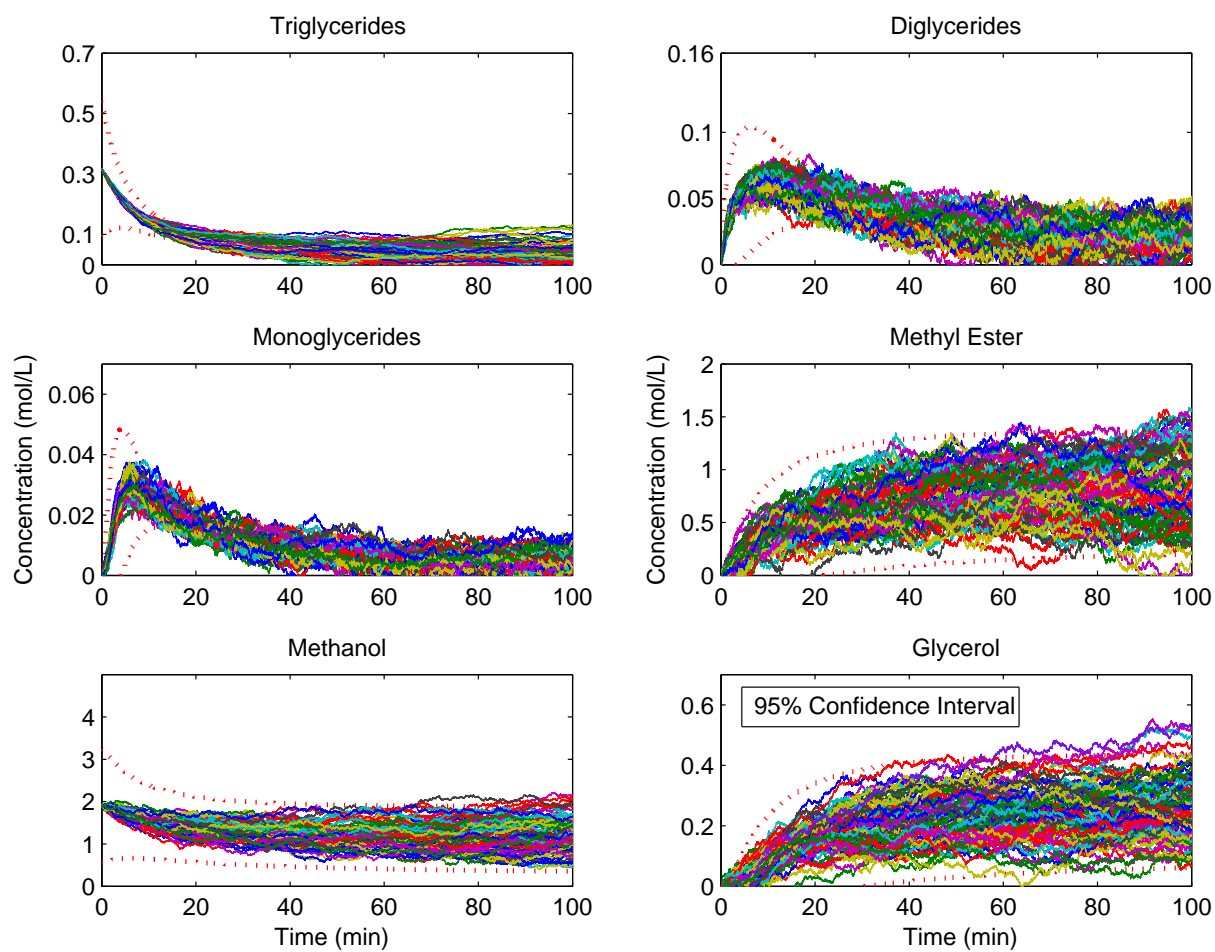
Figure 40. Concentration profiles for each component of biodiesel production after applying Ito process

4.5 <u>Conclusion</u>

In this chapter, the importance of stochastic processes, represented by Ito processes, were introduced. As an example, the uncertainties in biodiesel production in a batch reactor were modeled using uniform* (star) distribution and propagated into the model. The static uncertainties encountered in biodiesel production led to dynamic uncertainties and it was shown that these dynamic uncertainties can be captured by the Ito processes.

CHAPTER 5

STOCHASTIC OPTIMAL CONTROL PROBLEM IN BIODIESEL PRODUCTION

5.1 Introduction

In previous chapters it was shown that optimal control problems provide an improvement to the effectiveness of batch processing; nevertheless, the scope of these problems was limited to the deterministic case where no uncertainty was considered. This is not a realistic assumption given that there are inherent uncertainties in biodiesel feed composition. Some papers have included uncertainty in the manufacturing of biodiesel. For instance, (118) dealt with the uncertainties of the facility location planning applied to biodiesel supply chain of vegetables oils. They presented an integrated analysis of the biodiesel supply chain from family-owned farms regarding the production and transport of grain and vegetable oils. Thus, the productivity rate variability of the grain producers was considered as the uncertainty factor, mainly due to climatic conditions. On the other hand, (119) described recent development in U.S. biofuel markets and a set of market projections. Here a stochastic analysis was used to demonstrate the wide range of possible outcomes for biofuel and agricultural market and its impact on high energy prices and food security. The uncertainty was introduced through petroleum prices. This study was developed by the Food and Agricultural Policy Research Institute (FAPRI). They presented the FAPRI stochastic model of the US agricultural sector, which was based on

a simplification of the deterministic model. Finally, (120) investigated whether a model-based analysis allowed for a clear evaluation of biofuel policies despite prevalent uncertainties. These uncertainties were represented in the rapid increase of both oil and feedstock prices in 2007 and 2008 and the performance and costs of advanced biofuels. In this work, a risk assessment was applied to the biofuel model BioPOL, which was a recursive dynamic model that determines the level of biofuel production in the European Union. However, none of the previous works considered time dependent uncertainties as a result of the feed composition variability or considered time dependent decisions like temperature profile.

In this Chapter, the optimal control for biodiesel production in a batch reactor is extended to a problem when uncertainty in the feed composition is considered. Under control of reactor temperature, a numerical method is applied based on the Steepest Ascent of Hamiltonian to solve the stochastic optimal control problem that involves the application of Ito processes and the stochastic maximum principle. Two stochastic optimal control problems are formulated in this chapter: the stochastic maximum concentration and the stochastic maximum profit problem.

5.2   Stochastic Maximum Concentration Problem ($SMCP$)

As it was mentioned in Chapter 3, the maximum principle can be employed to solve optimal control problems. This approach requires addition of adjoint variables, corresponding adjoint equations, and the Hamiltonian (91). In this chapter, this approach is extended to the

stochastic case since the model deals with uncertainties (i.e. stochastic processes). Therefore, the optimal control problem for the stochastic maximum concentration problem is formulated next. The objective is to maximize the expected value of concentration of biodiesel, considering the uncertainties in the feed composition by finding the best temperature profile in a given reaction time (i.e. 100 minutes).

Objective function:

$$\max J = E\left[\int_{t_0}^{t_f} (k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E)\ dt\right]$$

$$(5.1)$$

In other words,

$$\max L = E\left[C_E(t_f)\right] \tag{5.2}$$

Subject to an Ito process (Equations 4.9 to 4.14):

$$dC_i = F_i(C, t)\Delta t + g_i \epsilon_t \sqrt{\Delta t} \tag{5.3}$$

where $E[]$ is the expected value. The corresponding optimality condition for Equation 5.2 is:

$$0 = \max_{T_t}\left[\frac{1}{dt} E(dL)\right] \tag{5.4}$$

To work with stochastic processes, one must make use of Ito's lemma which allows us to differentiate and integrate functions of the stochastic process (91)and (106). This lemma is called the fundamental stochastic calculus theorem and it is the stochastic calculus counterpart of the chain rule in ordinary calculus. Therefore, Itos lemma is easier to understand as a Taylor series expansion. For instance, suppose that $x(t)$ follows the process of Equation 4.1 (i.e. Ito process), and the idea is to find the total differential of this function dF. The usual rules of calculus define this differential in terms of first-order changes in x and t, but suppose that the high-order terms for changes in x are also included:

$$dF = \frac{\partial F}{\partial t}dt + \frac{\partial F}{\partial x}dx + \frac{1}{2}\frac{\partial^2 F}{\partial x^2}(dt)^2 + \frac{1}{6}\frac{\partial^3 F}{\partial x^3}(dx)^3 + ... \tag{5.5}$$

In ordinary calculus, these high-order terms all vanish in the limit. For an Ito process following Equation 4.1, it can be shown that the differential dF is given in terms of the first-order changes in t and the second-order changes in x. Hence, Itos lemma gives the differential dF by substituting Equation 4.1 and $dz^2 = dt$ in Equation 5.5:

$$dF = \left[\frac{\partial F}{\partial t} + a(x,t)\frac{\partial F}{\partial x} + \frac{1}{2}b^2(x,t)\frac{\partial^2 F}{\partial x^2}\right]dt + b(x,t)\frac{\partial F}{\partial x}(dz) \tag{5.6}$$

Thus, applying the Itos lemma to Equation 5.4 results in:

$$0 = \frac{\partial L}{\partial t} + \sum_{i=1}^{6}\frac{\partial L}{\partial C_i}F_i(C_t, T_t) + \sum_{i=1}^{6}\frac{g_i^2}{2}\frac{\partial^2 L}{\partial C_i^2} + \sum_{i\neq j}^{6}g_i^2 g_j^2\frac{\partial^2 L}{\partial C_i \partial C_j} \tag{5.7}$$

where T_f represents the optimal solution to the maximization problem and g_i is the variance parameter of the state variable C_i. Note that if the uncertainty terms in Equations 4.4 to 4.9 are not correlated, the last term in Equation 5.7 can be eliminated.

$$
\begin{aligned}
0 = \ & \frac{\partial L}{\partial t} + max[\frac{\partial L}{\partial C_{TG}}F_1 + \frac{\partial L}{\partial C_{DG}}F_2 + \frac{\partial L}{\partial C_{MG}}F_3 + \frac{\partial L}{\partial C_E}F_4 + \frac{\partial L}{\partial C_A}F_5 + \frac{\partial L}{\partial C_{GL}}F_6 \\
& \frac{g_{TG}^2}{2}\frac{\partial^2 L}{\partial C_{TG}^2} + \frac{g_{DG}^2}{2}\frac{\partial^2 L}{\partial C_{DG}^2} + \frac{g_{MG}^2}{2}\frac{\partial^2 L}{\partial C_{MG}^2} + \frac{g_E^2}{2}\frac{\partial^2 L}{\partial C_E^2} + \frac{g_A^2}{2}\frac{\partial^2 L}{\partial C_A^2} + \frac{g_{GL}^2}{2}\frac{\partial^2 L}{\partial C_{GL}^2}] \quad (5.8)
\end{aligned}
$$

Where $\frac{\partial L}{\partial C_i}$ and $\frac{\partial^2 L}{\partial C_i^2}$ are adjoint variables z_i and ω_i for triglycerides, diglycerides, monoglycerides, methyl ester, methanol, and glycerol. The adjoint variables ω_i come from the randomness considered in the problem.

The Hamiltonian:

$$
H = z_1F_1 + z_2F_2 + z_3F_3 + z_4F_4 + z_5F_5 + z_6F_6 + \frac{g_{TG}^2}{2}\omega_1 + \frac{g_{DG}^2}{2}\omega_2 + \frac{g_{MG}^2}{2}\omega_3 + \frac{g_E^2}{2}\omega_4 + \frac{g_A^2}{2}\omega_5 + \frac{g_{GL}^2}{2}\omega_6
$$

$$(5.9)$$

The adjoint equations to be solved in the stochastic maximum principle formulation are:

$$\frac{dz_j}{dt} = \sum_{i=1}^{6} \left[z_i \frac{\partial F_i}{\partial C_j} - \frac{1}{2} \left(\frac{\partial g_i^2}{\partial C_j} \right) \omega_i \right] \tag{5.10}$$

$$\frac{d\omega_j}{dt} = \sum_{i=1}^{6} \left[-2\omega_i \frac{\partial F_i}{\partial C_j} - -z_i \frac{\partial^2 F_i}{\partial C_j^2} - \frac{1}{2} \left(\frac{\partial^2 (g_i^2)}{\partial C_j^2} \right) \omega_i \right] \tag{5.11}$$

where the boundary conditions are: $z(t_f) = c$(constant) and $\omega(t_f) = 0$.

Once again, the stochastic problem leads to a two-point boundary value problem, in which the initial conditions for the state variable C_i are known but the conditions for the adjoint variables (i.e. z_i and ω_i) are unknown. Therefore, to obtain the solution of this problem, it is necessary to use an iterative procedure (shown in Section 3.3.1.1). This approach works for deterministic as well as stochastic, with the difference that in the stochastic case requires 6 additional equations due to the uncertainty parameters (Equation 5.11). Appendix A.3 shows the calculation of the derivation of the Hamiltonian for the stochastic case.

Note: as it was presented in Chapter 3, the maximum concentration problem and the minimum time problem resulted in similar equations and formulation, therefore, the stochastic minimum time problem was not studied for stochastic optimal control formulation.

5.3   Stochastic Maximum Profit Problem (*SMPP*)

In this section, the stochastic maximum profit problem (*SMPP*) for the biodiesel production is formulated. Now, the objective function is to determine the expected value of the maximum profit subject to fluctuations due to the variability in the feedstock composition. Then, the *SMPP* can be formulated as it is shown in Equation 5.12.

Objective function:

Objective function:

$$\max J'' = E\left[\frac{max(M_E)P_r - B_oC_o}{t + t_s}\right] \tag{5.12}$$

where the values of P_r, B_o, C_o and t_s are the same values shown in Table XVIII. To solve this problem, the strategy presented in Section 3.3.3.1 is used.

5.4   Results and discussion

The results of the stochastic maximum concentration problem are shown in the first part of this section. To start with, the derivative of the Hamiltonian at different iterations is presented in Figure 41. As it is shown in this figure, the values of the derivatives decreases as the iteration increases, until the stopping criterion is reached (i.e. when the gradients are less than *1.9x10-3*). The reason of deciding this value is because the reaction temperature cannot exceed the boiling point of methanol (i.e. 338K at atmospheric pressure) due to the risk of leak out of alcohol through vaporization (22). Twelve iterations were sufficient to obtain the optimal
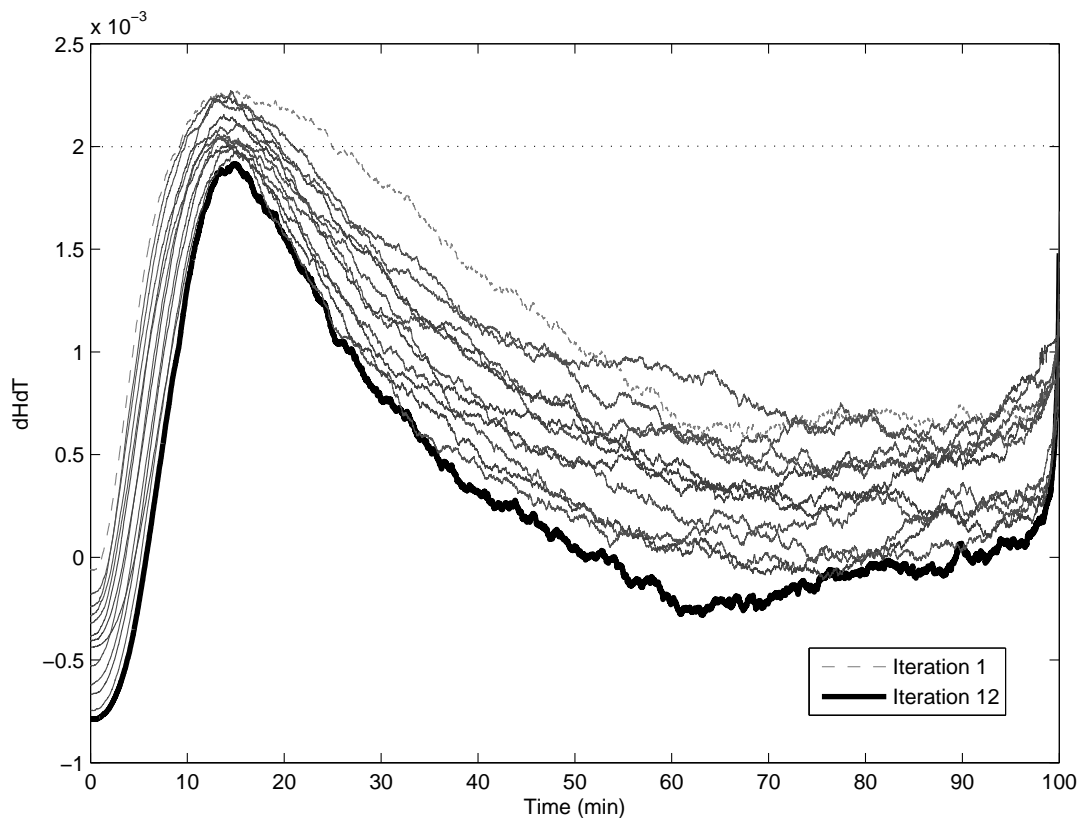
Figure 41. Profiles of Hamiltonian gradients (dH/dT) for all iterations

temperature profile that is shown in Figure 42.

Figure 42 shows how the temperature varies with time. In the first two iterations the temperature remains between 323K and 324K; however, from iteration three, the temperature values start to have significant change. Thus, temperature values go higher between minutes 10 and 20, and then decrease until minute 80th. After 90 minutes, these values increase again,
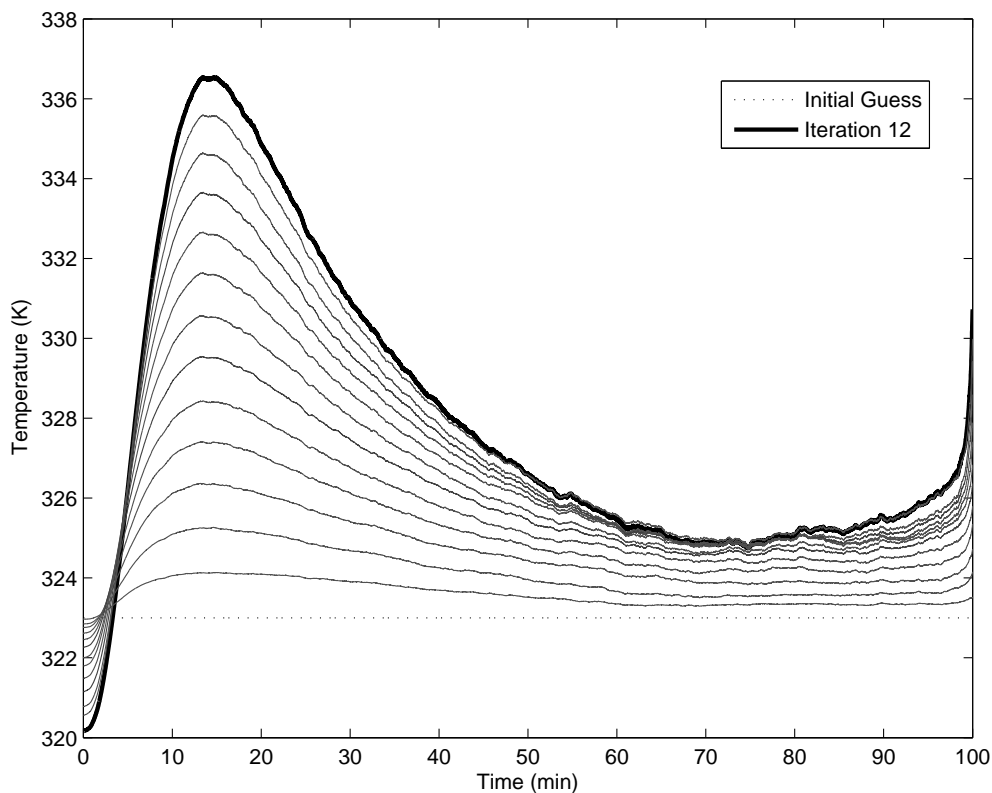
Figure 42. Temperature profiles for all iterations

especially for the last iterations. This behavior results from the values found of derivatives of Hamiltonian as was presented in Figure 41. Comparing Figure 41 and Figure 42, it can be observed that as the gradient profiles decrease the temperature profiles increase.

Figure 43 compares the optimal temperature profile found for the deterministic (shown in Chapter 3) and stochastic case. These two profiles are similar at the beginning of the reaction;
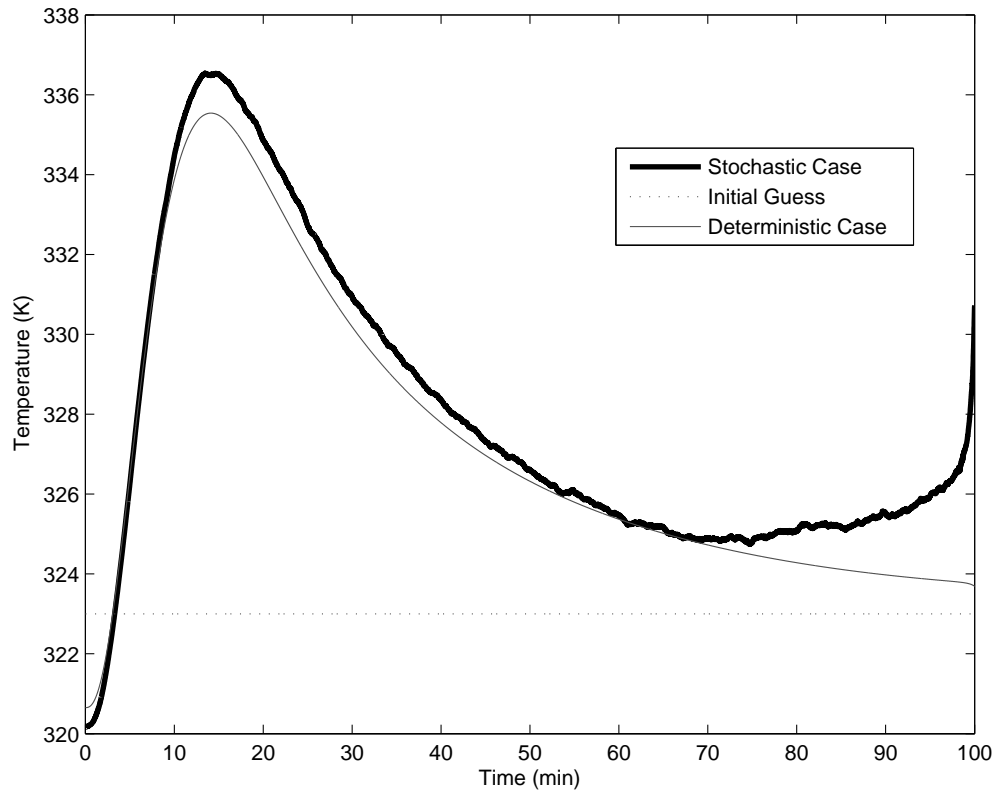
Figure 43. Temperature profiles comparison between deterministic and stochastic case

however, after 10 minutes the stochastic profile reaches higher temperatures due to the derivatives of Hamiltonian reach lower values in the stochastic case. The maximum temperature reached is 336.6K, which still lower than the boiling point of methanol, then the temperature starts to decrease until 68 minutes, when, unlike to deterministic case, increases again.

Figure 44 shows the comparison of concentration profiles between stochastic and deterministic optimal case. These profiles are obtained by propagating them through the stochastic model for both cases. Further, these two cases are also compared with the base case constant temperature profiles: 323K and 315K (using stochastic model). This figure shows how the expected value of methyl ester concentration varies with respect of time and temperature for the different cases. For instance, at 100 minutes of reaction time, the concentration of methyl ester under uncertainty reaches its maximum concentration (i.e. 0.793mol/L). Comparing the stochastic and deterministic case profiles, it can be seen that concentration values of stochastic case are slightly greater than deterministic only between 10 and 50 minutes, where the temperature values are also greater according to Figure 43. However, from this time to the moment when the reaction finishes, no appreciable change is observed between these two cases and at 100 minutes of reaction time the increment is only 0.25% using the stochastic profile.

Table XX presents the expected values of concentration of methyl ester within 95% confidence intervals. As it is shown in this table, the stochastic profile gives 7.82% improvement to the constant temperature case (i.e. 315K) and 1.64% to constant temperature case (i.e. 323K). This latter percentage is not significant since is a constant optimal profiles reported in the literature (22). However, if we consider the minimum time problem, the stochastic optimal profile reaches the desired concentrations of the base cases (0.731mol/L and 0.780mol/L) at 27 minutes and 56 minutes, which represent a reduction of 73% and 43%, respectively. On the other hand, to reach the concentration value of 0.780mol/L, the stochastic and deterministic
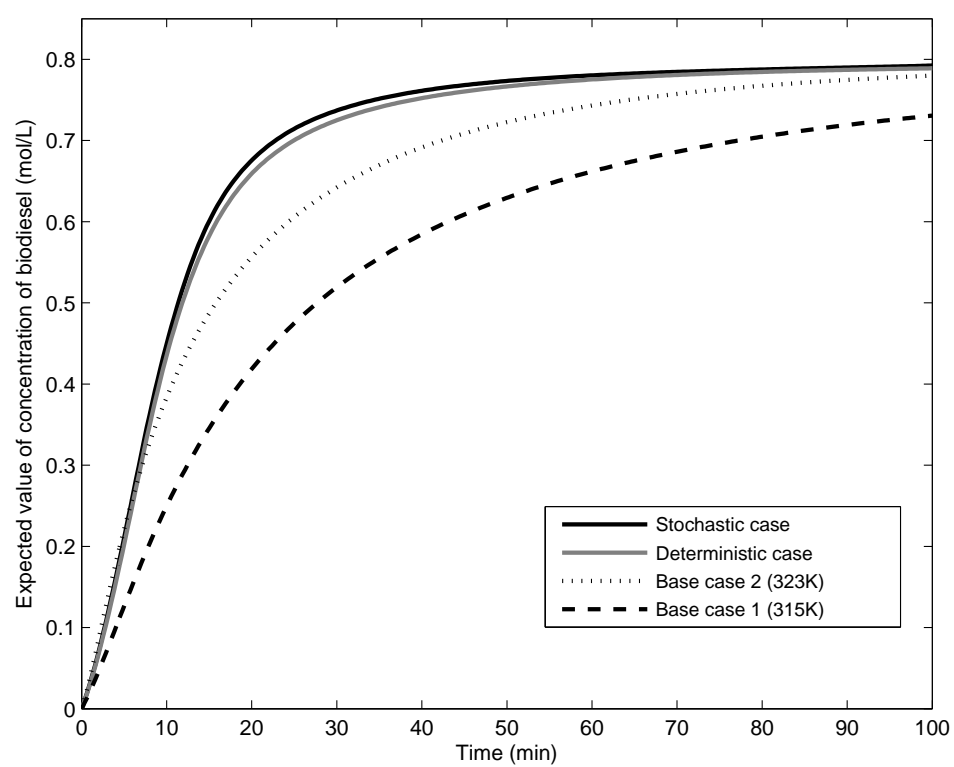
Figure 44. Comparison of concentration profiles of methyl ester

TABLE XX

RESULTS OF COMPARISON BETWEEN STOCHASTIC, DETERMINISTIC AND
CONSTANT TEMPERATURE CASES

Case	Expected value methyl ester concentration (at 100 min)	% increment (Compared to Stochastic case)	Time to reach 0.731mol/L (min)	Time to reach 0.780mol/L (min)
Stochastic	0.793±0.055	N.A	27	56
Deterministic	0.791±0.056	0.25	30	56
Constant Temp (315K)	0.731±0.059	7.82	100	N.A
Constant Temp (323K)	0.780±0.058	1.64	55	100

case will take 56 minutes in both situations. The behavior of the two optimal cases is almost the same, which shows that the uncertainty in the feed composition does not influence the final optimal time even if the profiles are different. This shows that the stochastic optimal solution is robust in feed composition uncertainties.

Finally, Figure 45 shows the expected value of biodiesel concentration and their minimum and maximum bounds based on the 95% confidence interval. These bounds allow us to determine the ranges of values that the biodiesel concentration can take in the process. At 100 minutes of reaction time the concentration of the stochastic case varies from 0.24mol/L to 1.35mol/L.
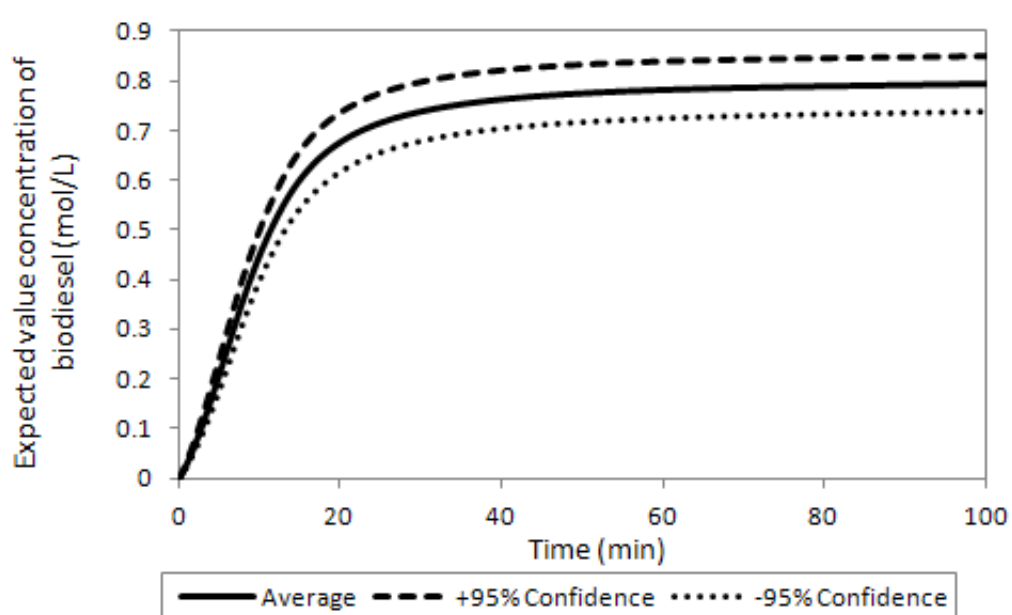
Figure 45. Minimum and maximum values of concentration for the stochastic case based on the 95% CI

TABLE XXI

SENSITIVITY ANALYSIS RESULTS

Case	Actual value of variance (g_i)	Modification	Concentration of methyl ester at 100 min (Stochastic case)
1	g_{TG}=0.003	g_{TG}=0.006	0.792
2	g_{DG}=0.004	g_{DG}=0.008	0.792
3	g_{MG}=0.0016	g_{MG}=0.003	0.790
4	g_{CE}=0.005	g_{CE}=0.009	0.791
5	g_A =0.051	g_A =0.090	0.795
6	g_{GL}=0.012	g_{GL}=0.020	0.791
7	h(step size)=0.01	h=0.005	0.789

In order to confirm the robustness of the optimal control profile, a sensitivity analysis is carried out through a series of multiple runs by changing the variances (i.e. g_i) Equations 4.9 to 4.14. Seven cases were studied. In the first six cases, the variance for each component was changed; however, in the last case, only the step size was changed. These variations are summarized in Table 5.2. The changes on the variance depend on the stochastic simulation presented before. Therefore, these values were slightly changed with respect to the originals, taking in to account that the profiles needed to remain within the boundaries presented in Figure 40. As it can be observed from Table XXI, the new values of methyl ester concentration do not have significant change compared with the original value (i.e. 0.793mol/L at 100 minutes of reaction time).

Another objective of this chapter is to show how the uncertainty in the feed composition affects to maximum profit problem. Figure 46 presents the optimal temperature profile comparison between deterministic (Chapter 3) and stochastic case for this problem. Although three curves are shown in this figure, the dashed curve is the smoothed version of the stochastic temperature profile. It is observed two noticeable differences, one is that the temperature profile from the stochastic cases (both) maintains higher values after minute 16th, and second, the stochastic case finishes earlier than deterministic case (i.e. around 5 minutes earlier). These two characteristics are reflected in the optimal profit value since there is an improvement of 6.7% in the stochastic case as compared to the deterministic case and a very significant improvement compare with the two base cases. In other words, as it is shown in Table XXII, the stochastic maximum profit problem gives 10.01$/h more than the deterministic case of this problem, and 148.18$/h and 76.97$/h more than base case 1 and 2, respectively. It can be also seen that the profit value using both the original temperature profile and the smoothed curve are presented in this table, and their values do not have significant difference. However, the smoothed temperature profile is preferred since the ease to implement the control into the process. Therefore, applying optimal control under uncertainty in the feed composition in biodiesel production (batch reaction section) can provide a better reaction time to produce the same amount of biodiesel compared to the deterministic case.
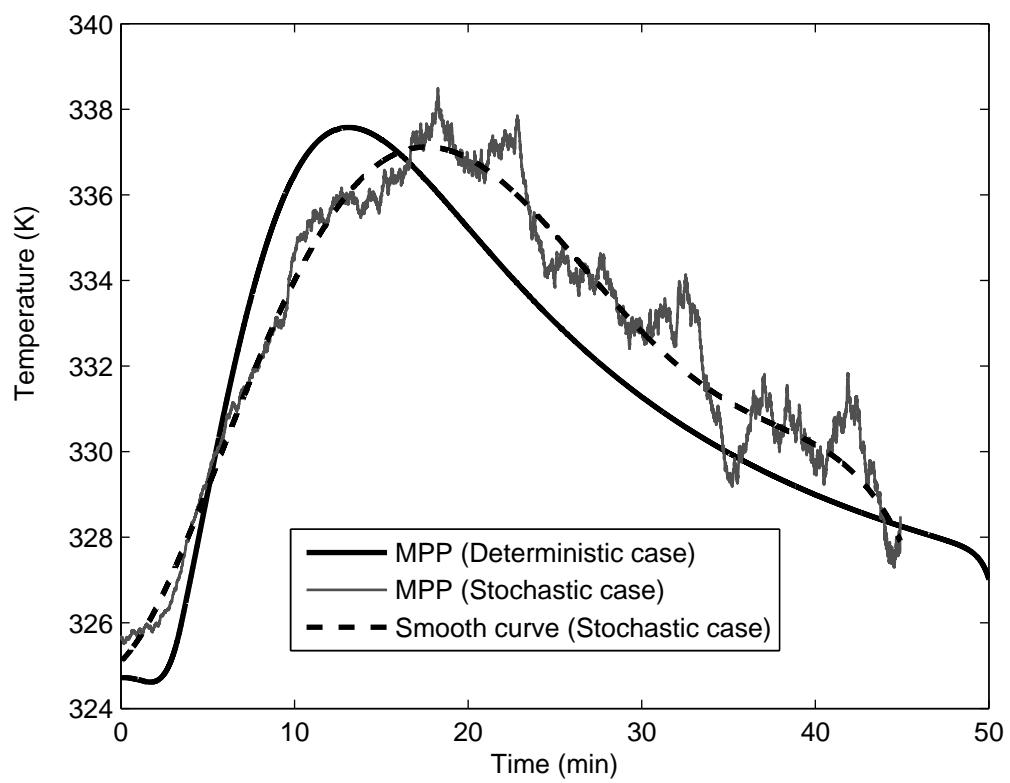
Figure 46. Temperature profile comparison between deterministic and stochastic case

TABLE XXII

COMPARISON BETWEEN STOCHASTIC, DETERMINISTIC AND CONSTANT
TEMPERATURE CASES FOR *MPP*

Parameter	Concentration of biodiesel (mol/L)	Time (min)	Profit (within 95%confidence intervals)($/h)
Base case 1 (315K)	0.732	100	11.20±10.97
Base Case 2 (323K)	0.777	92.65	82.41±10.95
Deterministic Case	0.780	50	149.37±21.17
Stochastic Case	0.779	44.91	160.87±24.15
Stochastic Case (smooth curve)	0.779	44.91	159.38±24.14

5.4.1 Conclusion

In this Chapter, two optimal control problems for biodiesel production under feed variability were formulated. For the first problem, the stochastic maximum principle was employed to determine the optimal temperature profile that maximizes the concentration. The second problem used the stochastic maximum principle along with *NLP* optimization techniques so the profit was maximized. The most important aspect of this chapter was to solve the stochastic optimal control problem which involved the application of Ito processes, Ito's lemma, and the stochastic maximum principle. Both problems were compared with two base cases (i.e. constant temperatures: 323K and 315K) as well as the deterministic case studied in Chapter

3. When the maximum concentration problem was solved, the stochastic problem resulted in a slightly different temperature profile compared with the deterministic case but the concentrations showed no major difference between them. Although, the application of an optimal control strategy (regardless deterministic or stochastic) brought significant improvement in the process when were compared with the base cases, the results showed that the optimal profiles were robust in the presence of uncertainties in feed composition. Finally, it was found that the stochastic maximum profit problem provided 6.7% improvement over the deterministic problem and significantly greater improvement over the base cases as well the deterministic case.

CHAPTER 6

IMPLEMENTATION OF THE OPTIMAL TEMPERATURE CONTROL

6.1   Introduction

In the previous chapters, the mathematical model for the reactor temperature dynamic was study under deterministic and stochastic conditions. It was found that through the optimal control strategy (i.e. temperature control), the biodiesel concentration was maximized as well as the profit value whereas the reaction time was minimized. However, these models were simple models since some operating conditions, such as reactor cooling/heating system, and energy balance were not included. In this chapter, some aspects for the implementation of the optimal temperature control in the biodiesel reactor are presented.

Several papers have studied control strategies for the reactor temperature control. For instance, Cott et al. (121) developed a model-based controller for the initial heat-up and subsequent temperature maintenance of exothermic batch reactors. Their model provided an effective way of incorporating a nonlinear energy balance model of the reactor and the heat-exchange apparatus into the controller. Therefore, their model consisted on a deterministic on-line estimator used to determine the amount and rate of heat released by the reaction, with this information they determined the change in jacket temperature set point in order to keep the reaction temperature on its desired trajectory. Another example is presented by Louleh et

138

al. (122). In their investigation, they worked on a multipurpose batch reactors using a cascaded model based control to control the reactor temperature. This strategy was based on the use of the thermal flux (i.e. heat load) as the manipulated variable, therefore, at each sampling time, the master controller computed the thermal flux to be exchanged between the reactor content and thermal fluid flowing inside the jacket. One of the advantages of their methodology was the implicit management of several cooling/heating fluids by the control system, since based on the heat load required by the reactor, the model-based supervisory allowed to choose the right fluid according to the limit capacities of the different fluid configurations. As it can be seen, the energy balance is an important issue to be considered for the determination of the overall temperature control.

Therefore, the optimal control of the reactor temperature goes beyond the calculation of the optimal reactor temperature profile. This temperature is affected by external heating or cooling depending whether the reaction is endothermic or exothermic. As it was mentioned before, the biodiesel reaction is an exothermic reaction. In this sense, to complete the optimization of the batch reactor operation, a jacket configuration and operation of the coolant flow is also needed. The coolant is the fluid used to maintain the optimal temperature and its conditions can be determined by the energy balance in the batch reactor.

6.2   Jacketed reactor configuration

In this section, the configuration parameters of the cooling jacket system are presented based the reactor design. A typical batch reactor with associated heating and cooling configuration is shown in Figure 47, this scheme consists of a reaction vessel with a jacket into which is injected with either a mono-fluid heating or mono-fluid cooling (123). This decision depends on the heat requirements of the reaction. In this case, the transesterification reaction generates heat which tends to increase the reactor temperature (since it is exothermic reaction); therefore, a cooling system is required. The cooling fluid, in this case water, can be injected into the reactor jacket via nozzles which increases the annular velocity and improves the heat transfer coefficient to the inner wall. This configuration has been found to work well for many applications. In industrial batch reactors, it can be found that to control the temperature of the reaction mixture, a control system manipulates the inlet jacket reactor temperature using an electrical resistance and two plate heat heat-exchangers (124) or coolant/heating fluid temperature inside of the jacket.

Table 6.1 summarizes the parameters of the design of the cooling jacket system. This table also presents equations for calculation of some of these parameters. In this table, P is the reactor design pressure (126.66562 KPa), S is the maximum allowable work stress (6900Kpa), and Ej is the efficiency of the joints (0.85). More detailed information can be found in (125).
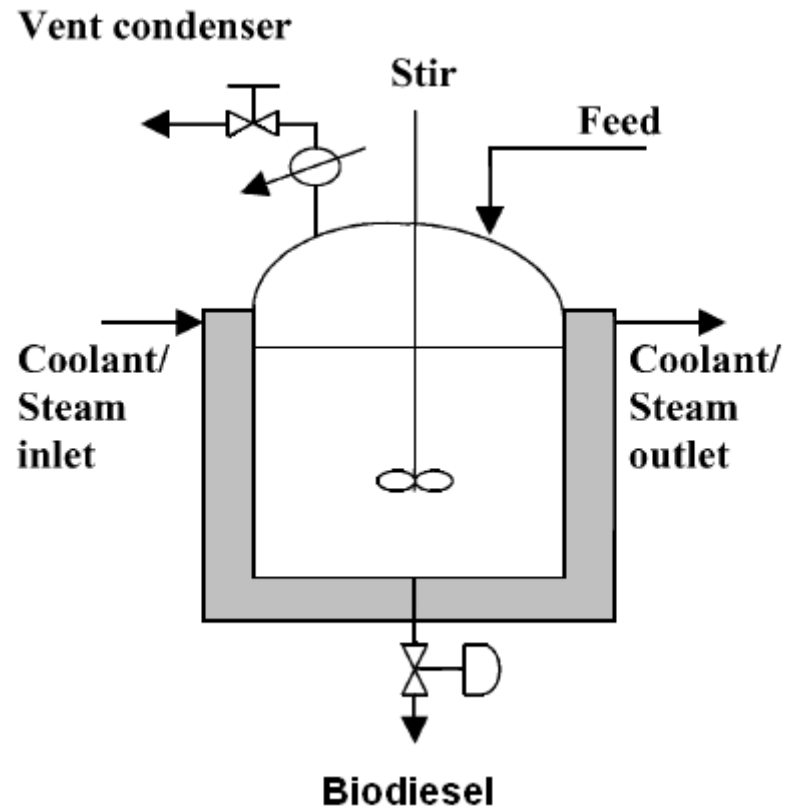
Figure 47. Schematic diagram of a jacketed mixing batch reactor

Note: For simplicity, the physical parameters, such as density and the heat capacities, are assumed to be constant.

6.3 Heat removal through reactor wall

One important consideration in the reactor is the heat load necessary to control the reactor temperature. The heat can be removed from or added to the reactor through heat exchange

TABLE XXIII

RESULTS OF COMPARISON BETWEEN STOCHASTIC, DETERMINISTIC AND
CONSTANT TEMPERATURE CASES

Parameter	Equation	Value
Volume of reactor	V_r	3.9m
Length to diameter ratio	LoD	3
Volume of cylinder (V_{cyl})	$1.2 * V_r$	4.68m^3
Cylinder diameter (d_{cyl})	$\frac{4V_{cyl}}{LoD\pi}^{\frac{1}{3}}$	1.25m
Cylinder height (h_{cyl})	$LoD\ d_{cyl}$	3.77m
Metal wall internal diameter (ID)	$d_{cyl} + 2t_{ref_1}$	1.46m
Wall thickness (t_{wall})	$\frac{P(ID/2)}{(s\ E_j)+(0.6P)}$	0.017m
Volume of the cylinder shell (V_{shell}) / Volume of the jacket	$\pi h_{cyl}\left(\left(\frac{ID}{2}+t_{wall}\right)^2 - \left(\frac{ID}{2}\right)^2\right)$	0.297m^3
Mass of the cylinder shell	$\rho_{metal}V_{shell}$	2334.78Kg
Coolant flow rate	F_c	3.648 m^3 /h
Specific heat of coolant	Cp_C	4.187KJ/Kg K
Density of coolant	ρ_c	1000 Kg/m^3
Heat transfer coefficient	U	759.198 W/m^{2}K
Initial coolant fluid temperature	T_{CO}	303 K

across the walls, that is, the heat exchanges between the reaction mixture and the jacket (126).

This heat load can be computed by Equation 6.1:

$$\dot{Q} = U A_c (T - T_c) \tag{6.1}$$

Where:

Q: The rate of heat removal from the reactor (KJ/min)

U: Heat transfer coefficient in energy per area (W/Km^2)

A_c: Area across which heat exchange occurs between the reactor and coolant (m^2)

T: Reactor Temperature (K)

T_c: Coolant temperature (K)

The rate of heat Q is considered to be positive since the temperature of the reactor is greater that the temperature of the coolant, meaning that the heat flows from the reactor to the jacket. On the other hand, the temperature of the coolant fluid can be to calculated using Equation 6.2

$$\frac{dT_c}{dt} = \frac{F_c}{V_c} (T_{c_o} - T_c) + \frac{U A_c (T - T_c)}{Cp_c V_c \rho_c} \tag{6.2}$$

Where: F_C, V_C, T_{c_o}, U, A_C, Cp_c, ρ_c are defined in Table XXIII. Therefore, to find temperature profile of the coolant fluid, Equation 6.2 is solved. A Runge Kutta method was used to solve this equation (85).

6.4   Results and discussion

Figure 48 presents the optimal control profiles as well as the cooling temperature profiles for the three deterministic problems studied in this work (i.e. maximum concentration, minimum time and maximum profit problem). For all cases, there was a significant rise of temperature of the coolant fluid in the begging of the reaction, from 303K, which is the initial temperature of the fluid, to 317K, 328K, and 321K, for the maximum concentration, minimum time, and maximum profit problems, respectively. After these raises, the temperature values of the cooling fluid follow the same pattern of the optimal temperature profile. For example, Figure 48a shows the profiles for the maximum concentration problem. It can be observed that the temperature of the coolant fluid increases in the begging of the reaction as the result of the rise of the reactor temperature. This increase is due to the exothermic nature of the transesterification reaction. Similar behavior occurs with Figure 48c (i.e. maximum profit problem), when the reactor temperature increases the coolant temperature also increases and vice versa. Temperature profiles for the minimum time problem are shown in Figure 48b. In this case, the temperature of the coolant smoothly falls at the same pace as the optimal temperature profile, but after the 5th minute both temperature increase proportionally. These outcomes were expected since the main goal is to operate the coolant fluid temperature so the optimal temperature profile can
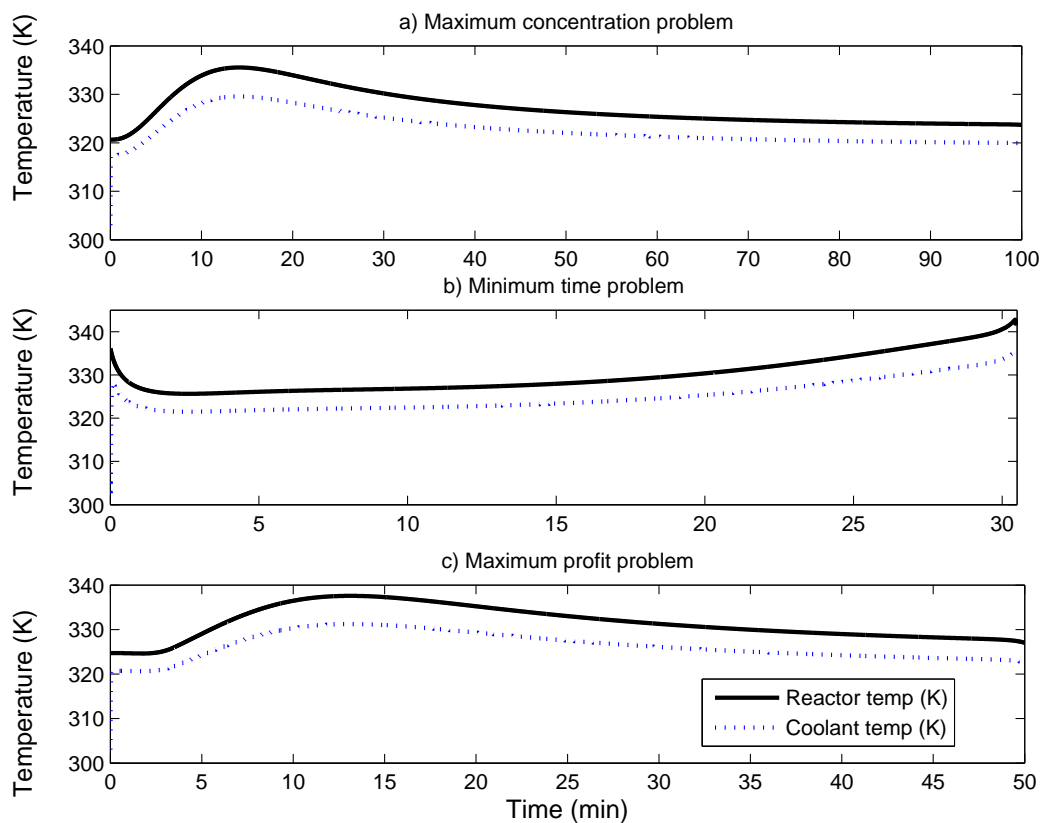
Figure 48. Coolant fluid temperature profiles for deterministic cases

be maintained throughout the reaction.

On the other hand, Figure 49 shows the rate of heat removal from the reactor to the coolant fluid of the three deterministic problems. In the very beginning of the reaction, the heat rate drastically drops for the three problems, especially for the minimum time problem profile where the heat rate goes from 40000KJ/min to 8000KJ/min. This situation is attributed to the delay
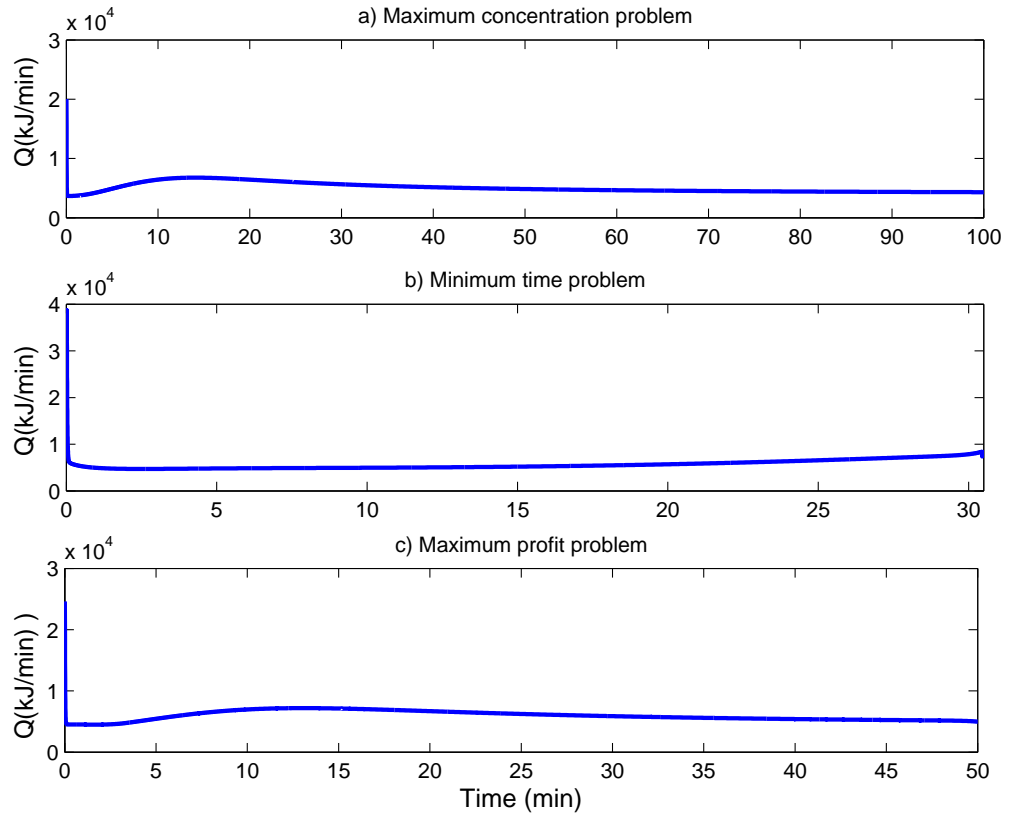
Figure 49. Rate of heat for deterministic cases

in the initial temperature of the coolant fluid shown in Figure 48. It can be observed for the three problems that the response of the heat rate is linked with the behavior of the temperature of the reactor. Thus, if this temperature increases, the heat rate also rises which allows the heat load flowing from the reactor to the wall heating the fluid in the jacket resulting in the increase of the coolant fluid temperature (See Figure 48).

Figure 50 and Figure 51 present the temperature profiles and the heat rate for the stochastic maximum concentration and stochastic maximum profit problem. The smoothed curve showed in Chapter 5 was used to compute the coolant fluid temperature. Similar behavior was found when comparing these profiles with the ones presented in Figure 48a and Figure 48c and Figure 49a and Figure 49c. In other words, when reactor temperature raises the coolant temperature also raises which affects the heat rate of the reactor by increases its values.

6.5   Conclusions

In this chapter, aspects for the implementation of temperature control were studied. In order to control the temperature of the reactor, the temperature of the coolant fluid needs to be manipulated due to the exothermic nature of the transesterification reaction, so the performance indexes such as concentration, time, and profit can be optimize. In that sense, to maintain the optimal temperature profile for the different optimal control problem, the temperature of the cooling fluid and the heat rate were computed using the energy balance.
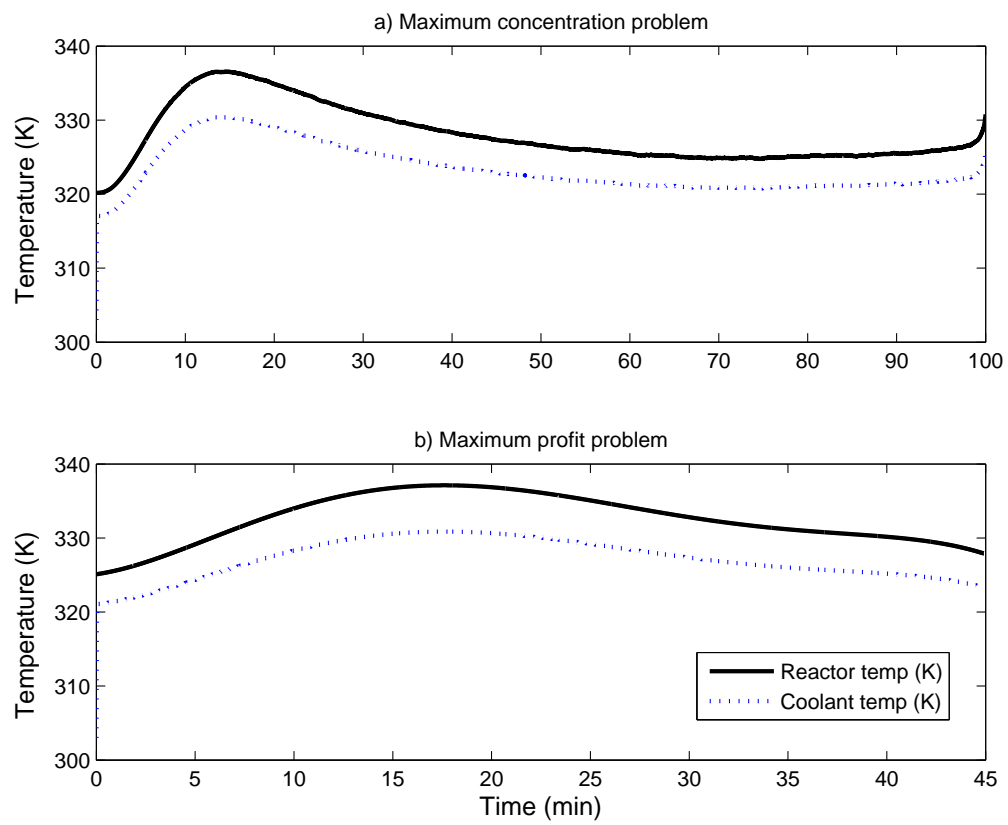
Figure 50. Coolant fluid temperature profiles for stochastic cases
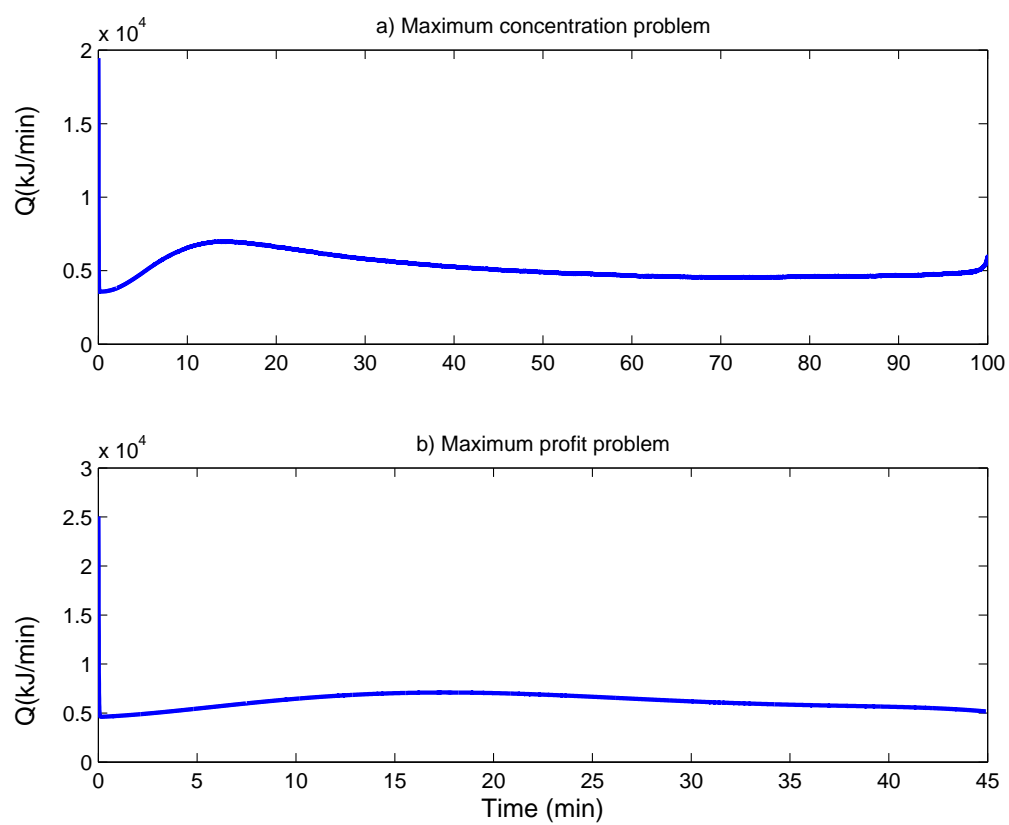
Figure 51. Rate of heat for stochastic cases

CHAPTER 7

SUMMARY, CONCLUSIONS AND FUTURE RESEARCH

7.1 Summary and conclusion of the work

The intensification of human activities resulting from continuous technological, economic, and social evolution has severely depleted and deteriorated the earth's natural resources. This situation has challenged the scientific, political, and social communities to explore alternatives that allow them to understand and manage the effects of development. Their efforts have focused mainly on achieving an environmentally friendly industrial sector from waste treatment and management to green engineering and green processes. One example of these efforts is biodiesel production. Biodiesel is well accepted as a renewable energy, and it can be considered one of the best alternatives to reduce the negative environmental impact of the conventional fuels such as petroleum-based diesel due to the similarity of properties.

Biodiesel is getting more attention because of the extensive research and promising results shown by industry and academia in the last decade. In order to produce biodiesel, optimal processes are needed to make future energy production cost effective and efficient. This thesis was concentrated on biodiesel production. Currently, biodiesel is produced in continuous plants, however, in the first part of this work, performance and cost of biodiesel production in batch versus continuous plants was compared. Computer simulation of biodiesel batch plants

as well as continuous plants was used and an economic assessment was performed. Based on the different scenarios of batch capacities and soybean distribution to the continuous plant, it was found that producing 21000ton of biodiesel per year using a continuous process involves higher costs (e.g. higher utility, water waste treatment, and soybean oil costs) as compared to performing this operation in three batch plants located in three different states (i.e. Missouri, Illinois, and Iowa).

In the second part of this thesis, dynamic optimization (i.e. optimal control) was the main subject of study. Batch processes offer the most interesting and challenging problems in modeling and control because of their inherent dynamic nature. In batch processes, batch reactors are used. These types of reactors are important unit operations in biodiesel production. In fact, they are considered the heart of any biodiesel manufacturing plant. Using optimal control, a temperature control policy was developed so three objective functions, namely, maximum concentration, minimum time, and maximum profit problem were optimize. Different methods were employed for their solutions such as maximum principle and NLP techniques.

Another important contribution of this thesis regards optimization under uncertainty, which is necessary for a realistic analysis. There are inherent uncertainties in biodiesel production, so in order to obtain robust optimal control, feed composition uncertainties (i.e. variability) were incorporated in the analysis. These static uncertainties led to dynamic uncertainties. Therefore, the dynamic uncertainties in biodiesel production were modeled and incorporated into math-

ematical formulations for time-dependent decision making. Ito processes were used to model these dynamic uncertainties. In addition, Ito calculus and stochastic optimal control were also used to derive robust optimal control strategies for the optimal control problems studied.

In the last part of this thesis, the focus of the study was regarding some aspects for the implementation of the temperature control. It was found that the control of batch reactors is strongly affected by the characteristic of the heating/cooling system. As a result, a jacket configuration and the operation of the coolant flow were incorporated. This strategy was developed to maintain the optimal temperature and its conditions were determined by energy balances in the batch reactor.

In conclusion, the main contribution of this work was the demonstration of the successful optimal control strategies for biodiesel production in batch process under deterministic and uncertain conditions. These strategies were based on the calculation of reactor temperature control which was achieved by the implementation of algorithms such as maximum principle and NLP techniques as well as the use of numerical methods.

7.2   Recommendation for future research

The results obtained from this research can be applied to many different areas and can serve as a starting point for future studies. In this section, several ideas are proposed that can be

the building blocks for future research.

In Chapter 2, a comparison between continuous and batch processes for biodiesel production was studied. It was shown that batch processes were more attractive to produce biodiesel. This conclusion was confirmed with the sensitivity analysis of four additional scenarios which were selected based on different batch capacities and raw material supply percentages. This resulted in a supply chain management problem where optimization techniques can be implemented to decide the best scenario to manufacture biodiesel. For example, a new problem can be formulated to determine the conditions, in terms of capacity of batch plants and amount of raw material supply for the continuous plant, such that the total manufacturing cost can be minimized.

In Chapter 3, different optimal control problems were proposed for biodiesel production, however, these problems were specific to the batch reactor operation. In that sense, new optimal control problems can also be proposed for other units of operation. For example, in the batch distillation column considered in the separation process of glycerol, an operating policy can be implemented in order to maximize the distillate (e.g. the amount of glycerol) in a given time. The recovered glycerol can be sold and used for other purposes. This optimization problem can benefit biodiesel production since manufacturing costs become sufficiently competitive as the glycerol credits are also considered in the economic analysis. Another problem that can be studied, based on the supply chain management, is the minimization of the delivery time

so the overall production profit can be improved. In this case, instead of focusing on the minimization of reaction time in the batch reactor, other process conditions can be optimized such as distillation time in the different distillation columns of the plant.

One of the major contributions of this work was to develop an approach to model and characterize uncertainties in biodiesel production. As proposed in Chapter 4, the methods used in this thesis for modeling time-dependent uncertainties using Ito processes, and incorporating them into time-dependent decision making can be used as a premise for developing dynamic models with uncertainties and optimal policies for other batch processes. These approaches enable us to obtain a more realistic representation of the process and a control profile that improves the batch performance. Therefore, another relevant application of batch production under uncertainty is algae-based biodiesel production. As it has been found, biodiesel production has received a lot of criticism by the experts of food industry since its production, especially from vegetable oils, can lead to food crisis and price instability of the concerned food crops. Algae-based biodiesel have received considerable attention in the last 5 years due to its non-edible nature. Its growing interest is reflected in the higher yield per hectare over conventional oil crops since algae can grow in bioreactors or open ponds. In addition, the cultivation period is between 5 to 7 days compared to several months in case of soybean crops. The oil productivity of many microalgae is greater than the oil productivity of the best oil crops, and algae can grow in flue gas environment giving opportunities in consuming greenhouse gas as a feedstock (127). Same as biodiesel production from soybean oil, triglycerides obtained from algae have inherent uncertainties in

the initial composition and the variation of the algae species can lead to different oil content affecting the yield of the transesterification reaction. Although algae-based biodiesel represents a lot of potential in the market, its production cost is the biggest obstacle in commercialization.

Consideration of other sources of uncertainty is a possible extension of this research. As it was mentioned in this thesis, there are other parameters that can be considered uncertain in batch reactors, such as kinetic parameters. The kinetic model characterized the chemical reactions and their time scales. The exact kinetic model is rarely developed, in fact, it is assumed to be available. When the reaction is developed, there are inherent uncertainties in the calculation of kinetic parameters due to the empirical constants derived from experiments or the lack of information. For instance, in complex reactions a satisfactory kinetic model is not available to develop an optimum operating policy (128). Some of the parameters that describe the kinetic of a reaction and that can be uncertain are: the activation energy (i.e. Ea) and the frequency factor (i.e. A). These values play an important role since they define the course of chemical reaction by determining the probability of occurrence of the reaction, its velocity, dependence on temperature, and the catalytic effects. The initial composition uncertainties considered in this work along with the kinetic parameter uncertainty are good examples of static uncertainties. Moreover, since they affect some process parameters that change with time (e.g. concentration of reactants) they lead to time-dependent uncertainties. Therefore, stochastic processes and Ito calculus can also be used to model these uncertainties.

Another recommendation for future research is related to the experimental work. As shown in this thesis, different simulation programs as well as numerical methods were employed to find solutions for the optimal control problems. However, the models presented here are reduced versions of the reality, that is, a limited number of external influences such as the variability in feedstock composition were included. From the industrial point of view, a model fitting task is complicated since the process is subjected to data that is usually noisy and has other disturbances. Therefore, it will be very interesting to observe how closely the optimal temperature profile found in this thesis will lead to the predicted optimal concentration of biodiesel, reaction time, and profit values, when applied in the industry. In other words, how closely the simulation results mimic the experimental world.

Another idea for future research is the improvement of the properties of biodiesel so the quantity of commercial blends, currently used in the market, can be increased. Biodiesel can be blended and used in many different concentrations: B2, B5, B20, and B100. B2 corresponds to 2% of biodiesel and 98% of petroleum diesel while B100 is pure biodiesel. However, the ASTM develops specifications for commercial diesel fuel. These specifications allow biodiesel concentration of up to 5% (i.e. low level) that will allow safe operation in any compression-ignition engine, although B20% represents a good balance of cost, emissions, and cold weather performance. Unfortunately, in the case of B100 there still are concerns about performance. This biodiesel blend is less common than B5 or B20 due to a lack of regulatory incentives and

pricing. As a result not all diesel engine manufactures cover biodiesel use.

Finally, the most interesting recommendation for potential extension of further research in regards to the sustainability of bioenergy production for the planet. In this research, biodiesel production was studied at the plant level, but the implication of having this production from the ecosystem point of view was not considered. Biodiesel production is a great example of what sustainable development has done during the last decade since it is a result of the efforts that focus on green energy. Figure 52 (129) presents the extension of the framework from process design, to industrial ecology leading to socio-ecosystem sustainability. At the center of this framework is the green industry engineered with clean production, clean processes, green energy and eco-friendly management in which biodiesel production can be placed. Thus, the goal of sustainable development is looking for policies that enhance human well-being while protecting the planet. To achieve this goal, efforts at various levels should be implemented. However, as the world continues growing in terms of population with improving living standards, the long term environmental protection will be difficult. Optimal control theory can be used to derive policy guidelines and can provide enough tools to be able to observe how biodiesel production affects human interactions. In a broad sense, it is important to study the sustainability when bioenergy, in this case biodiesel production, is in the mix.
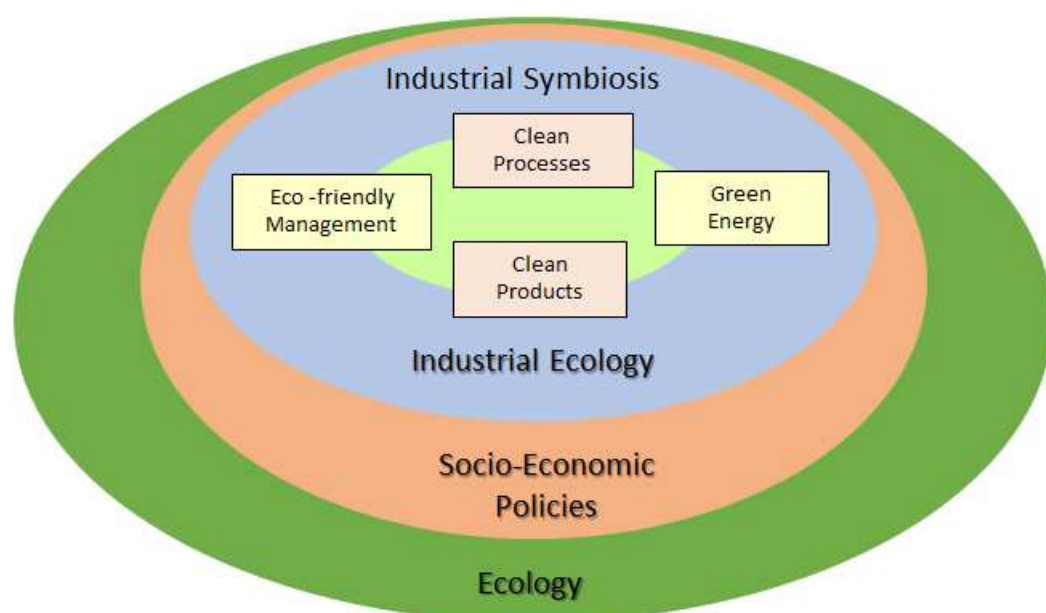
Figure 52. Sustainability of planet when bioenergy is in the mix

REFERENCES

CITED LITERATURE

[1] Cao, W., Han, H., and Zhang, J.: Preparation if biodielsel from soybean oil using supercritical methanol and co-solvent. Fuel, 84:347–357, 2005.

[2] Panwar, N., Kaushik, S., and Kothari, S.: Role of renewable energy sources in environmental protection. Renewable and Sustainable Energy Reviews, 15:1513–1524, 2011.

[3] Tyner, W., Dooley, F., and Viteri, D.: Alternative pathways for fulfilling the rfs mandate. Am.J. Agr. Econ, 93:465–472, 2011.

[4] Stast, S.: A reference guide to import soybean facts and figures. $http : //www.soystats.com/2011/Default - frames.htm$, June 2011.

[5] Administration, U. E.: Monthly biodiesel production survey. $http : //www.eia.gov/biofuels/biodiesel/production/March$, March 2013.

[6] Tapasvi, D., Wiesinborn, D., and Gustafson, C.: Process model for biodiesel production from various feedstocks. In Proceedings of the North Central ASAE/CSAE Conference, Winnipeg, MB., 2004.

[7] Friedrich, M. and Perne, R.: Design and control of batch reactors -an industrial viewpoint- . Computers chem. Eng., 19:S357–S368, 1995.

[8] Korovessi, E. and Linninger, A.: Batch processes. Boca Raton, FL, Taylor and Francis, 2005.

[9] Benavides, P., Diwekar, U., and Salazar, J.: Economic comparison of continuous and batch biodiesel production using soybean oil. Environmental Progress & Sustainable Energy, 32:11–24, 2013.

[10] Benavides, P. and Diwekar, U.: Optimal control of biodiesel production in a batch reactor part i: Deterministic control. Fuel, 9:218–226, 2012.

[11] Benavides, P. and Diwekar, U.: Optimal control of biodiesel production in a batch reactor part ii: Stochastic control. Fuel, 94:218–226, 2012.

[12] Benavides, P. and Diwekar, U.: Studying various optimal control problems in biodiesel production in a batch reactor under uncertainty. Fuel, 103:585–592, 2013.

[13] Shay, E.: Diesel fuel from vegetables oils: status and opportunities. Biomass Bioenerg., 7:227–242, 1993.

[14] Ryan, T., Dodge, L., and Callahan, T.: The effects of vegetable oil properties on ingection and combustion in two different diesel engines. J. AM Oil Chem.Soc., 61:1610–1619, 1984.

[15] Sheehan, J., Camobreco, V., Duffield, J., Graboski, M., and Shapouri, H.: An overview of biodiesel and petroleum diesel life cycles. Nrel/tp-580-24772, National Renewable Energy Labs, 1998.

[16] Wu, F., Wang, J., Chen, W., and Shui, S.: A study on emission performance of a diesel engine fueled with five typical methyl ester biodiesel. Atmos. Environ., 43:1481–1485, 2009.

[17] Gerpen, J., Shanks, B., Prusko, R., Clements, D., and Knothe, G.: Biodiesel handling and use guide. Nrel/tp-540-43672, National Renewable Energy Labs, 2009.

[18] Fukuda, H., Kondo, A., and Noda, H.: Review. biodiesel fuel production by transesterification of oils. Journal of Bioscience and Bioengineering, 92:405–416, 2001.

[19] Srivastava, A. and Prasad, R.: Triglecerides-based diesel fuels. Renew. Sust. Energ. Rev., 4:111–133, 2000.

[20] Varese, R. and Varese, M.: Methyl ester biodiesel: opportinity or necessary? Inform, 7:816–824, 1996.

[21] Yamane, K., Ueta, A., and Shimamoto, Y.: Influence of physical and chemical properties of biodiesel fuel on injection, combustion and exhaust emission characteristics in a di-ci engine. In Proceedings of 5th Int'l Sump. on Diagnostics and Modeling of Combustion in Internal Combustion Engines, pages 402–409, Nagoya, 2001.

[22] Dennis, Y., Xuan, W., and Leung, M.: A review on biodiesel production using catalyzed transesterification. Applied Energy, 83:1083–1095, 2010.

[23] Wang, Y. and Gu, B.: Mechanism and application of biodiesel preparation by transesterification. Adv. Fine Pet, 11:5–21, 2010.

[24] Lai, H., Wan, X., and Jiang, M.: Advance in production technology of biodiesel. Chem. Bioeng., 27:11, 2010.

[25] Peng, B., Shu, Q., Wang, G., and Wang, J.: Kinetics of esterification for acid-catalyzed preparation of biodiesel chemical reaction. Eng. Technol., 25:250, 2009.

[26] Lam, M., Lee, K., and Mohame, A.: Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. Biotechnology Advances, 28:500–518, 2010.

[27] Chen, Y., Wang, D., and Wang, B.: Study on preparation process of biodiesel from waste. Pet. Technol Appl., 26:415, 2008.

[28] Zhang, Y., Dube, M., McLean, D., and Kates, M.: Biodiesel production from waste cooking oil: 2. economic assesment and sensivility analysis. Bioresour. Technol., 90:229–240, 2003.

[29] Ren, T., Li, P., Sun, Y., and Qiao, Q.: Wan nor nadyaini wan omar, nor aishah saidina. Amin. Ind. Catal., 18:19, 2010.

[30] Liu, X. and H, H.: Transesterification of soybean oil to biodiesel using sro as a solid base catalyst. Catal. Commun., 8:1107–1111, 2006.

[31] Wan Nor Nadyaini Wan Omar, N. A. S. A.: Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. Biomass & Bioenergy, 39:1329–1338, 2011.

[32] Wang, L. H.: Research progress of biodiesel preparation catalyzed by solid acids. Chem. Bioeng., 26:12, 2009.

[33] Peng., B.-X., Shu., Q., Wang., J.-F., Wang, G.-R., Wang, D.-Z., and Han., M.-H.: Biodiesel production from waste oil feedstocks by solid acid catalysis. Process Safety and Environmental Protection, 86:441–447, 2008.

[34] Zhang., K.-P. and L.-L., J.-Q.: Penicillium expansum lipase-catalyzed production of biodiesel in ionic liquids. Bioresource Technology, 102:2767–2772, 2011.

[35] Nan-Wei Li, M.-H. Z.: Highly efficient transformation of waste oil to biodiesel by immobilized lipase from penicillium expansum. Process Biochemistry, 44:685–688, 2009.

[36] Sun, T. D.: Prospective and impacts of whole cell-mediated alcoholysis of renewable oils for biodiesel production. Biofuel Bioprod. Biorefin., 3:633–639, 2009.

[37] H.J., R. and W., D.: Study on free lipase-catalyzed ethanolysis for biodiesel preparetion in an oil/water biphasic system. J. Am. Oil. Chem. Soc, 88:1551–1555, 2011.

[38] Anitescu, G. B.: Fluid properties needed in supercritical transesterification of triglyceride feedstocks to biodiesel fuels for efficient and clean combustion a review. The Journal of Supercritical Fluids, 63:133–149, 2012.

[39] Lee, K. T.: A review on supercritical fluids (scf) technology in sustainable biodiesel production: Potential and challenges. Renewable and Sustainable Energy Reviews, 15:2452–2456, 2011.

[40] Macaira, J.and Santana, A. and Francesc Recasens, M.: Biodiesel production using supercritical methanol/carbon dioxide mixtures in a continuous reactor. Fuel, 90:2280–2288, 2011.

[41] Ahmad, A., Mat Yasin, N., Derek, C., and Lim, J.: Microalgae as a sustainable energy source for biodiesel production: A review. Renewable and Sustainable Energy Reviews, 15:584–593, 2011.

[42] Ehimen, E. Z. and Carrington, G.: Renewability analysis of microalgae biodiesel using different transesterification processes. International Journal of Energy Environment and Economics, 20:135–156, 2012.

[43] Turton, R., Bailie, R., Whiting, W., and Shaeiwitz, J.: Analysis, Synthesis, and Design of Chemical Processes. Upper saddle River, NJ: Prentice Hall PTR, 1998.

[44] Wagialla, K. M., Rahman, M. E., and Elawad, E. A.: A comparative study batch and continuous refining of cottonseed oil in sudan. J. Amer. Oil Chem. Soc., 61:900–907, 1984.

[45] Gorsek, A. and Glavic, P.: Design of batch versus continuous processes. part i: Single-purpose equipment. Trans. IChemE., 75:709–717, 1997.

[46] Gorsek, A. and Glavic, P.: Design of batch versus continuous processes. part ii: Multi-purpose equipment. Trans. IChemE., 75:718–723, 1997.

[47] Fonseca, F., Vidal-Vieira, J., and Ravagnani, S.: Transesterification of vegetables oils: Simulating the replacement of batch reactors with continuous reactors. Bioresource Technology, 101:8151–8157, 2010.

[48] Myint, L. and El Halwagi, M.: Process analysis and optimization of biodiesel production from soybean oil. Clean Tech. Environ. Policy, 11:263–276, 2006.

[49] Haas, M., Mc. Aloon, A., Yee, W., and Foglia, T.: A process model to estimate biodiesel production costs. Bioresour. Technol., 97:671–678, 2006.

[50] Sakai, T. and Kawashima, A.: Economic assessment of batch biodiesel production processess using homogeneous and heterogeneous alkali catalysts. Bioresour. Technol., 100:3268–3276, 2009.

[51] West, A. H., Posarac, D., and Ellis, N.: Assessment of four biodiesel production processes using hysys plant. Bioresour. Technol., 99:6587–6601, 2008.

[52] Chung, S. and Farrey, M.: Biofuel supply chain challenges and analysis. Master's thesis, Massachusetts Institute of Technology, Boston, U.S., 2010.

[53] Biomass: National biofuels action plan. biomass research and development board. $http : //www1.eere.energy.gov/biomass/pdfs/nbap.pdf$, June 2008.

[54] Baneriee, A. and Noguer, J.: Biofuels supply chain characterizaritions. Master's thesis, Massachusetts Institute of Technology, Boston, U.S., 2007.

[55] (ERS), E. R. S.: Commodity costs and returns: U.s and regional cost and return data. $http : //www.ers.usda.gov/Data/CostsAndReturns/testpick.htm.$2011, June 2011.

[56] Marchetti, J.: The effect of economic variables over a biodiesel production plant. Energy conversion and management, 52:3227–3233, 2011.

[57] International buyers' guide. transporting u.s. soybean to export markets. u.s. $http : //ussec.org/ussoy/buyersguide.html$, November 2011.

[58] Index mundi. $www.indexmundi.com/commodities/?commodity = soybean − oil\&months = 60$, March 2013.

[59] Biodiesel.org: Soybean oil and meal economics. $www.Biodiesel.org$, June 2011.

[60] English, B., Jensen, K., and Menard, J.: Economic feasibility of producing biodiesel in tennessee. $http : www.biofuels.com/archive/TN_biodiesel.pdf.$, June 2011.

[61] Noureddini, H. and Zhu, D.: Kinetic of transesterification of soybean oil. J. Am. Oil. Chem. Soc., 74:1457–1463, 2007.

[62] Freedman, B., Pryde, E., and Mounts, T.: Variables affecting the yield of fatty esters from transesterified vegetables oils. J. Am. Oil. Chem. Soc., 61:1638–1643, 1984.

[63] Aspen technology, inc. 7.2, 2010.

[64] Diwekar, U.: Understanding batch distillation process principle with multibatchds. Computed Application in Engineering Education, 4:275–284, 1996.

[65] Biegler, L., Grossmann, I., and Weterberg, A.: Systematic methods of chemical process design. Upper saddle River, NJ., Prentice Hall PTR, 1997.

[66] Gerpen, J., Pruszko, R., Clements, D., and Shanks, B.: Building a successful biodiesel business: Technology Consideration, developing the business analytical methodologies, Biodiesel basics. 2006.

[67] Economic indicators.: Chemical engineering. $http://www.che.com$.2011, May 2011.

[68] Denbigh, K.: Optimal temperature sequences in reactors. Chem. Eng. Sci., 8:125–132, 1958.

[69] Cuthrell, J. and Biegler, L.: Simultaneous optimization and solution method for batch reactor control profiles. Comput. Chem. Eng., 13:49–62, 1989.

[70] Crescitelli, S. and Nicoletti, B.: Near optimal control of batch reactors. Comput. Chem. Eng., 28:463–471, 1973.

[71] Logsdon, J.: Efficient determination of optimal control profiles for differential algebraic systems. Doctoral dissertation, Carnegie Mellon University, 1990.

[72] Logsdon, J. and Biegler, L.: A relaxed reduced space sqp strategy for dynamic optimization problems. Comput. Chem. Eng., 17:367–372, 1993.

[73] Luus, R.: Optimal control of batch reactors by iterative dynamic programming. J. Proc. Control., 4:218–226, 1994.

[74] Srinivasan, B., Palankib, S., and Bonvin, D.: Dynamic optimization of batch processes: I. characterization of the nominal solution. Comp. Chem. Eng., 27:1–26, 2003.

[75] Ferella, F., Mazziotti, G.and De Michelis, I., Stanisci, V., and Veglio, F.: Optimization of the transesterification reaction in biodiesel production. Fuel, 89:36–42, 2010.

[76] Sahoo, P. and Das, L.: Process optimization for biodiesel for production from jatropha, karanja and polanga oils. Fuel, 88:1588–1594, 2009.

[77] Shashikant, V. and Hifjur, R.: Process optimization for biodiesel production from mahua (madhuca indica) oil using response surface methodology. Bioresource Tech., 97:379–384, 2006.

[78] Math, M., Sudheer, P., and Soma, V.: Optimization of biodiesel prodcution from oils and fats with high free acids. Indian J. Sci. Tech., 3:318–321, 2010.

[79] Mjalli, F., San, K., Yin, C., and Hussain, M.: Dynamic and control of biodiesel transesterification reactor. Chem. Eng. technol., 32:13–26, 2009.

[80] Masound, S. and Kravaris, C.: Optimal design and operation of batch reactors. 1. theoretical framework. Ing. Eng. Chem., 32:866–881, 1993.

[81] Bonvin, D.: Optimal operation of batch reactor - a personal view. J. Proc. Cont., 8:335–368, 1998.

[82] Aziz, N. and Mujtaba, L.: Optimal control of semi-batch reactors. Computer Aided Chemical Engineering, 9:609–614, 2001.

[83] Levenspiel, O.: Chemical Reaction Engineering. New York, NY., John Wiley & Sons, 1999.

[84] Frangrui, M. and Milford, H.: Biodiesel prodcution: review 1. Bioresour. Technol., 70:1–15, 1999.

[85] Mathews, J. and Fink, K.: Numerical methods using matlab. River, NJ., Prentice-Hall publication, 2004.

[86] Rico-Ramirez, V. and Diwekar, U.: Stochastic maximum principle for optimal control under uncertainty. Comput. Chem. Eng., 28:2845–2849, 2004.

[87] Biegler, L. and Grossmann, I.: Retrospective on optimization. Computers and Chemical Engineering, 28:1169–1192, 2004.

[88] Pontryagin, L.: Some mathematical problems arising in connection with the theory of automatoc control system. Session of the Academic Sciences of the USSR on Scientific Problems of Automatic Industry, pages 15–20, 1956.

[89] Pontryagin, L.: Basis problems of automatic regulation and control (in russia). zd-vo Akad Nauk SSSR, 1:110, 1956.

[90] Boltyanskii, V., Gamkrelidze, G., and Pontryagin, L.: On the theory of optimum processes. Izd-vo Akad Nau SSSR, 1957.

[91] Diwekar, U.: Introduction to Applied Optimization. Kluwer Academic Publishers, Dordrecht, 2003.

[92] Diwekar, U.: Batch distillation: simulation, optimal design and control. Washington, D.C., Taylor and Fracis, 1995, 2003.

[93] Diwekar, U.: Unified approach to solving optimal design and control problems in batch distillation. Amer. Inst. Chem. Eng. J., 38:1551–1563, 1992.

[94] Kerkhof, L. H. and Vissers, J. M.: On the profit of optimum control in batch distillation. Chem. Eng. Sci., 33:961–970, 1978.

[95] Reporter, C. M.: Icis chemical business. $http : //www.icis.com/Articles/2011/06/09/9468135/usda − maintains − record − corn − crop − projection − for − 2011.html$, May 2011.

[96] Eevera, T., Rajendran, K., and Saradha, S.: Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions. Renew. Energ., 34:762–765, 2009.

[97] Ierapetritou, M. and Li, Z.: Modeling and managing uncertainty in process planning and scheduling. in w. chaovalitwongse, optimization and logistics challenges in the enterprise. $http : //sol.rutgers.edu$, 2009.

[98] Bierge, J.: Stochastic programming: optimizing the uncertain. Technical report, University of Michigan, Industrial and operations engineering, 1992.

[99] Ulas, S. and Diwekar, U.: Thermodynamic uncertainties in batch processing and optimal control. Comput. Chem. Eng., 28:2245–2258, 2004.

[100] Fotopoulos, J., Georgakis, C., and Stenger Jr., H.: Uncertainty issues in the modeling and optimization of batch reactor with tendency models. Chem. Eng. Sci., 49:5533–5547, 1994.

[101] Leung, V. P. and Padmanabhan, L.: Stochastic optimal control theory and its application to control of batch reactor with unknown parameters and process noise. Chem. Eng. Journal, 7:201–212, 1974.

[102] Ruppen, D., Benthack, C., and Bonvin, D.: Optimization of batch reactor operation under parametric uncertainty-computational aspects. J. Proc. Cont., 5:235–240, 1995.

[103] Morari, M.: Flexibility and resiliency of process systems. Comp. chem. Eng., 7:423–437, 1983.

[104] Terwiesch, P., Agarwal, M., and Rippin, D.: Batch unit optimization with imperfect modeling, a survey. J. Proc. Cont., 4:238–258, 1994.

[105] Srinivasan, B., Bonvin, D., Visser, E., and Palanki, S.: Dynamic optimization of batch processes ii. role of measurements in handing uncertainty. Comp. Chem. Eng., 27:27–44, 2002.

[106] Dixit, A. and Pindyck, R.: Investment under uncertainty. Princeton, New Jersey, Princeton University Press, 1994.

[107] Diwekar, U. and Rubin, E.: Stochastic modeling of chemical processes. Comput. Chem. Eng., 15:105–114, 1991.

[108] Iman, R. and Conover, W.: Small-sample sensitivity analysis techniques for computer models, with an application to risk assessment. Commun. Stat., Part A: Theory Methods, 17:1749–1842, 1984.

[109] Dantzig, G. and Glynn, P.: Parallel processors for planning under uncertainty. Ann. Oper. Res., 22:1–21, 1990.

[110] Kalagnanam, J. and Diwekar, U.: An efficient sampling technique for off-line quality control. Technometrics, 39(3):308–319, 1997.

[111] Kloeden, P. and Planten, E.: Numerical solution of stochastic differential equations. Heidelberg, Germany, 1992.

[112] Ulas, S., Diwekar, U., and Rico-Ramirez, V.: Stochastic optimal control in batch distillation: a real options theory approach. In Proceedings of INFORMS/CUSTOM symposium on managing risk in an uncertain world, Chicago, 2003.

[113] Ulas, S., Diwekar, U., and Stadtherr, M.: Uncertainty in paramenter estimation and optimal control in batch distillation. Comput. Chem. Eng., 28:1805–1814, 2005.

[114] Knothe, G.: Designer biodiesel: optimizing fatty ester composition to improve fuel properties. Energy Fuel Properties, 22:1358–1364, 2008.

[115] Linstromberg, W.: Organic chemistry. Lexington, MA, 1970.

[116] Abbasi, S. and Diwekar, U.: Characterization and stochastic modeling of uncertainties in the biodiesel production. Clean techn Environ Policy, 2013.

[117] Diwekar, U. and Rubin, E.: Technical reference manual for stochastic simulation in aspen. In Proceedings of U.S Department of Energy, Morgantown Energy Research Center, W.V, Center for Energy and Environmental Studies, Carnegie Mellon University, Pittsburg, 1989.

[118] Leao, R., Oliveira, F., and Hamacher, S.: Dealing with uncertainties in the biodiesel supply chain based on small farmers: A robust approach. In Presented at Rio oil & Gas Expo and Conference, Brazil, 2010.

[119] Meyer, S.: Us biofuels analisys under uncertainty and volatility in the biofuels industry: Fapri stochastic modelling. In Presented at Biofuels, food and feed tradeoffs, Farm Foundation, 2007.

[120] Schadeand, B. and Wiesenthal, T.: Biofuels: a model based assessment under uncertainty applying the monte carlo method. J. Policy Model, 2010.

[121] Cott, B. and Macchietto, S.: Temperature control of exothermic batch reactors using generic model control. Ind. Eng. Chem. Res., 28:1171–1184, 1989.

[122] Louleh, Z., Cabassud, M., and Marie-Ve Aronique, Lann, L.: A new strategy for temperature control of batch reactors: experimental application. Chemical Engineering Journal, 78:11–20, 1999.

[123] Aziz, N. and Mujtaba, I.: Optimal operation policies in batch reactors. Chem. Eng. J., 85:313–325, 2002.

[124] Bouhenchira, H., Cabassudb, M., and Le Lannc, M.: Predictive functional control for the temperature control of a chemical batch reactor. Computers and Chemical Engineering, 30:1141–1154, 2006.

[125] Hoffman, Z.: Simulation and economic evaluation of coal gasification with sets reforming process for power production. Master's thesis, Louisiana State University, Baton Rouge, 2005.

[126] Schmidt, L.: The Engineering of Chemical Reactions. Oxford university pressl, New York, 2005.

[127] Janaun, J. and Naoko, E.: Perspectives on biodiesel as a sustainable fuel. Renewable and Sustainable Energy Reviews, 14:1312–1320, 2010.

[128] Tomazi, K.: Optimization of batch reactions in series with uncertainty. Annals Opera. Research, 132:189–206, 2004.

[129] Shastri, Y.: Sustainable system management. Master's thesis, University of Illinois at Chicago, Chicago, U.S., 2007.

[130] Timmerhaus, K., Peters, M., and West, R.: Plant design and economics for chemical engineers. Mc Graw Hill, New York, 2003.

APPENDICES

Appendix A

BIODIESEL ECONOMIC ASSESSMENT

As mentioned in Chapter 2, there are many elements that influence the cost of manufacturing of specific products. The technical decisions regarding the operation and selection of raw material, among others, can play an important role in the estimation of the total manufacturing cost. The following tables present a list of important costs involved in the economic assessment to produce biodiesel. As mentioned before, the total manufacturing cost is divided into three categories, direct, fixed and general expenses. The direct costs involve the cost of raw material, waste treatment, utilities, and operating labor. These values are shown in Table XXIV for the annual production of biodiesel. This table is comparing each cost of one continuous plant with three batch plants. The cost of utilities involves the electricity, steam and cooling tower water consumption. The cooling water can be supplied from a central facility such as a cooling tower while the steam can be produced by the evaporation at 10barg and 184°C. On the other hand, operation labor requirements depend on the number of process units and whether the process is continuous or batch these values change. In Timmerhaus et al. (130) gives a typical labor requirements based on the units used in the process.

Table XXV illustrates the Equipment used in both continuous and batch plant and their respective costs. The design and costs calculation of reactors, decanters, heat exchangers, and coolers were based on the work by Hoffman (125) while distillation columns calculation was

Appendix A (Continued)

TABLE XXIV

ANNUAL COSTS FOR THE ANNUAL PRODUCTION OF BIODIESEL FROM SOYBEAN

Description	Annual cost (US millions\$/yr) Continuos model	Annual cost (US millions\$/yr) Batch model
Direct manufacturing cost		
Raw materials		
Soybean oil (Triol)	28.139	26.867
Methanol	1.637	1.637
Hydrochloric acid (HCl)	0.010	0.010
Sodium hydroxide (NaOH)	0.145	0.145
Water	4.49e-4	4.51e-4
subtotal raw material	29.932	28.661
Utilities		
Electricity	1.49e-3	5.13e-4
Steam (10 barg, 184^0C)	0.374	0.133
Cooling tower water (80^0F to 100^0F)	1.08e-2	5.02e-3
subtotal utilities	0.387	0.139
Others		
Wastewater treatment	0.018	0.013
Operation Labor	0.319	0.957
Direct supervisory and clerical labor	0.057	0.172

Appendix A (Continued)

presented in (130). It was assumed that 12% of the total equipment cost went to pumps, vessels and piping. Once the equipment cost was computed, the *FCI* (fixed capital investment) was calculated. The results are shown for the case of continuous and one batch plant in Table XXVI. Table XXVII presents the batch scheduling for each plant different scenario studied in the sensitivity analysis, this is the result of variation in the percentages of production capacity and supply of raw material.

Appendix A (Continued)

TABLE XXV

EQUIPMENT COSTS (MILLIONS $)

Type	Description	Continuous (one plant)	Batch
Reactor	Transesterification	0.074	0.049
Storage tank (oil)	Storage of feedstock	0.198	-
Decanters			
Decanter 1	Separation glycerol/Oil	0.061	0.032
Decanter 2	Separation triol/biodiesel	0.043	0.029
Decanter 3	Biodiesel wash tank	0.026	0.017
Heat Exchangers	Reactor preheater	0.011	0.004
	GLYDIST1 tower preheater	0.003	1.61e-4
	METDIST tower preheater	0.005	0.002
	Water washing preheater	0.002	0.001
	Total HEX	0.02	0.006
Coolers	Decanter 1 cooler	0.026	0.009
	Decanter 2 cooler	0.037	0.005
	Total coolers	0.064	0.014
Columns	Glycerol/Methanol separator (GLYDIST)	0.110	0.013
	Methanol/Biodiesel separator (METDIST)	0.015	0.010
	Total Columns	0.125	0.023
Pumps, vessels, piping		0.073	0.020
Purchased Equipment		0.685	0.190

Appendix A (Continued)

TABLE XXVI

ESTIMATION OF FIXED CAPITAL INVESTMENT (FCI) (MILLIONS $)

Fixed capital Investment	Basis (% of purchased Equipment)	Cost Continuous	Cost Batch (one plant)
Direct Costs			
Purchased Equipment	100%	0.685	0.190
Purchased Equipment Installation	47%	0.322	0.089
Instrumentation and Control	36%	0.247	0.068
Piping	68%	0.466	0.129
Electrical system	11%	0.075	0.021
Buildings	18%	0.123	0.034
Yard improvements	10%	0.068	0.019
Services facilities	70%	0.479	0.133
Total direct plant cost	360%	2.465	0.684
Indirect Costs			
Engineering and supervision	33%	0.226	0.063
Construction expenses	41%	0.281	0.078
Legal expenses	4%	0.027	0.008
Contractor's fee	22%	0.151	0.042
Contingency	44%	0.301	0.084
Total indirect plant cost	144%	0.986	0.273
Fixed capital investment (*FCI*)	504%	3.451	0.957
Working capital (15% of total capital investment)	89%	0.609	0.169
Total Capital investment		4.061	1.126

Appendix A (Continued)

TABLE XXVII

BATCH SCHEDULING IN DIFFERENT SCENARIOS

Case	State	Production capacity	Batch/days
	IA	25	6
1	IL	50	12
	MO	25	6
	IA	40	10
2	IL	20	5
	MO	40	9
	IA	50	12
3	IL	20	5
	MO	30	7
	IA	40	10
4	IL	10	2
	MO	50	12
	IA	35	9
Base Case	IL	35	8
	MO	30	7

Appendix B

CALCULATION OF THE DERIVATIVE OF THE HAMILTONIAN: DETERMINISTIC CASE

As it was mentioned before, the maximum principle is used in optimal control theory to find the best possible control of a dynamic system. This approach states that the Hamiltonian must be maximized over the control variable, in other words, it applies the optimality conduction dH/dT < tolerance. In the next part, the derivative of the Hamiltonian is calculated in order to determine the optimal temperature trajectory for this problem.

The Hamiltonian for the six components is presented as:

$$H = z_1 F_1 + z_2 F_2 + z_3 F_3 + z_4 F_4 + z_5 F_5 + z_6 F_6 \tag{B.1}$$

This problem requires the use of the total derivative, which states that: *if a continuous function z=f(x,y) of several variables (e.g. t, x, y, etc.) is derived with respect to one of its input variables, e.g., t; then the derivative can be expressed in terms of a series of partial derivatives.* As a result, the rate change of 'z' with respect to t' can be calculated as:

Appendix B (Continued)

$$\frac{dz}{dt} = \frac{\partial z}{\partial x}\left(\frac{dx}{dt}\right) + \frac{\partial z}{\partial y}\left(\frac{dy}{dt}\right) \tag{B.2}$$

If we apply the total derivative concept to Equation B.1 shown in the previous paragraph, then the derivative of the Hamiltonian can be calculated by Equation B.3:

$$\frac{dH}{dT} = \sum_{i=1}^{6} \frac{\partial H}{\partial C_i}\theta_i + \sum_{i=1}^{6} \frac{H}{z_i}\phi_i \tag{B.3}$$

Where θ_i and ϕ_i are represented by equation (A.2.4) and (A.2.5).

$$\theta_i = \frac{dC_i}{dT} \tag{B.4}$$

$$\phi_i = \frac{dz_i}{dT} \tag{B.5}$$

Then, to calculate the values of θ_i and ϕ_i, we consider the following property, respectively:

$$\frac{d}{dT}\left(\frac{dC_i}{dt}\right) = \frac{d}{dt}\left(\frac{dC_i}{dT}\right) = \frac{d\theta_i}{dt} \tag{B.6}$$

Appendix B (Continued)

$$\frac{d}{dT}\left(\frac{dz_i}{dt}\right) = \frac{d}{dt}\left(\frac{dz_i}{dT}\right) = \frac{d\phi_i}{dt} \tag{B.7}$$

Where, the differential equations for θ_i and ϕ_i are given as:

$$\frac{d\theta_i}{dt} = f\left(C_i, \theta_i, T\right) \tag{B.8}$$

$$\frac{d\phi_i}{dt} = f\left(C_i, \theta_i, z_i, \phi_i, T\right) \tag{B.9}$$

As an example, the differential equation for θ_{TG} and ϕ_{TG} (Triglycerides) are shown in Equation B.10 and A2.11:

$$\frac{d\theta_{TG}}{dt} = -\frac{dk_1}{dT}C_{TG}C_A - k_1\theta_{TG}C_A - k_1 C_{TG}\theta_A + \frac{dk_2}{dT}C_{DG}C_E + k_2\theta_{DG}C_E + k_2 C_{DG}C_{\theta_E} \tag{B.10}$$

$$\begin{aligned}
\frac{d\phi_{TG}}{dt} = \quad & \theta_{TG}k_1 C_A + z_1\frac{dk_1}{dT}C_A + z_1 k_1\theta_A - \theta_{DG}k_1 C_A - z_2\frac{dk_1}{dT}C_A - z_2 k_1\theta_A \\
& -\theta_E k_1 C_A - z_4\frac{dk_1}{dT}C_A - z_4 k_1\theta_A + \theta_A k_1 C_A + z_5\frac{k_1}{dT}C_A + z_5 k_1\theta_A \tag{B.11}
\end{aligned}$$

Appendix B (Continued)

Finally, a numerical method such as RKF is used to integrate the system of equations represented by Equation B.8, with initial conditions: $\theta\ (t_0) = [0;\ 0;\ 0;\ 0;\ 0;\ 0]$. On the other hand, to compute ϕ_i, backward integration and using again RKF method is also used to solve the system of equation represented by Equation B.9, but in this case, the is boundary condition are expressed as: $\phi\ (t_f) = [0;\ 0;\ 0;\ 0;\ 0;\ 0]$.

Appendix C

CALCULATION OF THE DERIVATIVE OF THE HAMILTONIAN: STOCHASTIC CASE

In this section, an analytical approach is presented in order to calculate the derivative of the Hamiltonian to determine the optimal temperature trajectory. A similar approach was presented in Appendix 2. Applying the stochastic maximum principle presented in Chapter 5:

The Hamiltonian:

$$H = z_1F_1 + z_2F_2 + z_3F_3 + z_4F_4 + z_5F_5 + z_6F_6 + \frac{g_{TG}^2}{2}\omega_1 + \frac{g_{DG}^2}{2}\omega_2 + \frac{g_{MG}^2}{2}\omega_3 + \frac{g_E^2}{2}\omega_4 + \frac{g_A^2}{2}\omega_5 + \frac{g_{GL}^2}{2}\omega_6$$

$$(C.1)$$

where the adjoint equations are compute using Eq.4.19 and Eq.4.20, for instance, the adjoint equation for triglycerides (i.e. z_1) is represented by Equation (A3.2) and the adjoint equation due to the randomness (ω_i) by Equation C.3:

$$\frac{z_1}{dt} = z_1k_1C_A - z_2k_1C_A - z_4k_1C_A + z_5k_1C_A - \frac{1}{2}\left((0)\omega_1 + (0)\omega_2 + (0)\omega_3 + (0)\omega_4 + (0)\omega_5 + (0)\omega_6\right)$$

$$(C.2)$$

Appendix C (Continued)

$$\frac{\omega_1}{dt} = 2\omega_1 k_1 C_A - 2\omega_2 k_1 C_A - 2\omega_4 k_1 C_A + 2\omega_5 k_1 C_A - z_1(0) - z_2(0) - z_3(0)$$

$$-z_4(0) - z_5(0) - z_5(0) - z_6(0) - \frac{1}{2}\left((0)\omega_1 + (0)\omega_2 + (0)\omega_3 + (0)\omega_4 + (0)\omega_5 + (0)\omega_6\right) \quad \text{(C.3)}$$

With the following boundary conditions:

$$z_i(t_f) = [0; 0; 0; 1; 0; 0] \quad \omega_i(t_f) = [0; 0; 0; 0; 0; 0]$$

Applying the total derivative on Equation C.1, we can calculate analytically the derivative of the Hamiltonian as:

$$\frac{H}{dT} = \sum_{i=1}^{6} \frac{\partial H}{\partial C_i}\left(\frac{dC_i}{dT}\right) + \sum_{i=1}^{6} \frac{\partial H}{\partial z_i}\left(\frac{dz_i}{dT}\right) + \sum_{i=1}^{6} \frac{\partial H}{\partial \omega_i}\left(\frac{d\omega_i}{dT}\right) \quad \text{(C.4)}$$

Considering the following expressions:

$$\theta_i = \frac{dC_i}{dT} \quad \text{(C.5)}$$

$$\phi_i = \frac{dz_i}{dT} \quad \text{(C.6)}$$

Appendix C (Continued)

$$\varphi_i = \frac{d\omega_i}{dT} \tag{C.7}$$

Substituting Equation C.5, Equation C.6 and Equation C.7 into Equation C.4 results in:

$$\frac{H}{dT} = \sum_{i=1}^{6} \frac{\partial H}{\partial C_i} \theta_i + \sum_{i=1}^{6} \frac{\partial H}{\partial z_i} \phi_i + \sum_{i=1}^{6} \frac{\partial H}{\partial \omega_i} \varphi_i \tag{C.8}$$

Applying the following property for each component:

$$\frac{d}{dT}\left(\frac{dC_i}{dt}\right) = \frac{d}{dt}\left(\frac{dC_i}{dT}\right) = \frac{d\theta_i}{dt} \tag{C.9}$$

$$\frac{d}{dT}\left(\frac{dz_i}{dt}\right) = \frac{d}{dt}\left(\frac{dz_i}{dT}\right) = \frac{d\phi_i}{dt} \tag{C.10}$$

$$\frac{d}{dT}\left(\frac{d\omega_i}{dt}\right) = \frac{d}{dt}\left(\frac{d\omega_i}{dT}\right) = \frac{d\varphi_i}{dt} \tag{C.11}$$

With the following boundary conditions:

$\theta(t_0) = [0; 0; 0; 0; 0; 0]$

$\phi(t_f) = [0; 0; 0; 0; 0; 0]$

$\varphi(t_f) = [0; 0; 0; 0; 0; 0]$

Appendix C (Continued)

Finally, six differential Equation C.9, Equation C.10, and Equation C.11 are solve using a numerical method, such as Runge Kutta Fehlberg. This method uses forward integration for Equation C.9 and backward integration for Equation C.10 and Equation C.11.

VITA

Pahola Thathiana Benavides Gallego

Title: Optimal Control of Batch Production of Biodiesel Fuel under Uncertainty

Education:

- **Ph.D. in Industrial Engineering and Operation Research:** University of Illinois at Chicago (2010-2013)

- **B.Tech. in Chemical Engineering:** National University of Colombia, Manizales-Caldas, Colombia (2002-2007)

Professional Experience:

- **Graduate research assistant, Chicago, IL**. Industrial Engineering Department. University of Illinois at Chicago. (January 2010 - present)

- **Visitor scholar**. Bioengineering Department. University of Illinois at Chicago. (August 2009 - December 2009)

- **Production coordinator**. Jabonerias Hada S.A. (soap factory). Manizales, Colombia. (August 2007 May 2008)

- **Teaching assistant**. National University of Colombia. Manizales, Colombia. (February 2006 July 2006)

Internship Experience:

- **Industrial Licorera de Caldas(Liquor factory)**Manizales, Colombia. (February 2007 - July 2007)

Professional Affiliations:

- American Institute of Chemical Engineers (AIChE): May 2010-Present

- Institute for Operations Research and the Management Sciences (INFORMS): September 2012-Present

- Institute for Sustainability: 2012-Present

Awards:

- Honorable mention recipient for the 2013 Sustainable Engineering Forum Student Paper Award. AIChE: November 2013.

- Graduate Sustainability Award. UIC student research forum. University of Illinois at Chicago: April 2013

- The Chicago Consular Corps Scholarship. University of Illinois at Chicago:November 2012

Invited Talks:

- Benavides, P.: Optimal Control Problems in Biodiesel Production under Uncertainty. At *Biocore Research group*,Sophia-Antipolis, France, May 2012.

Publications:

Journal Articles: Published

- Benavides, P.; Salazar, J.; Diwekar, U.: Economic Comparison of Continuous and Batch Biodiesel Production using soybean oil. Environmental Progress and sustainable Energy, 32(2013)11-24.

- Benavides, P.; Diwekar, U.: Studying various optimal control problems in biodiesel production in a batch reactor under uncertainty. Fuel,103(2013)585-592.

- Benavides, P.; Diwekar, U.: Optimal Control of Biodiesel Production in a Batch Reactor Part I: Deterministic Control.Fuel, 94 (2012) 211-217.

- Benavides, P.; Diwekar, U.: Optimal Control of Biodiesel Production in a Batch Reactor Part II: Stochastic Control. Fuel, 94 (2012)218-226

Conference/Proceedings:

- Benavides, P.; Diwekar, U., and Cabezas, H.: Controllability of Complex Networks for Sustainable System Dynamics. In *UIC Student Research Forum*, Chicago, IL, April, 2013.

- Benavides, P.; Salazar, J.; Diwekar, U.: Economic Comparison of Continuous and Batch Biodiesel Production using soybean oil. In *AIChE Midwest Regional Conference*, Chicago, IL, January, 2013.

- Benavides, P.; Diwekar, U.; and Cabezas, H.: Role of Controllability for Long Term Sustainability. In *AIChE Annual Meeting*, Pittsburgh, PA, November, 2012.

- Benavides, P.; Diwekar, U.: Studying Various Optimal Control Problems in Biodiesel Production in a Batch Reactor under Uncertainty. In *AIChE Annual Meeting*, Pittsburgh, PA, November, 2012.

- Benavides, P.; Diwekar, U.: Studying Various Optimal Control Problems in Biodiesel Production in a Batch Reactor under Uncertainty. In *INFORMS Annual Meeting*, Phoenix, AR, November, 2012.

- Benavides, P.; Diwekar, U.: Studying Various Optimal Control Problems in Biodiesel Production in a Batch Reactor. In *UIC Student Research Forum*, Chicago, IL, April, 2012.

- Benavides, P.; Salazar, J.; and Diwekar, U.: . Comparing Continuous and Batch Process Design under Uncertainty for Biodiesel Production. In *AIChE Annual Meeting*, Minneapolis, MN, October, 2011.

- Benavides, P.; Diwekar, U. : Studying Various Optimal Control Problems in Biodiesel production in Batch Reactor. In *AIChE Annual Meeting*, Minneapolis, MN, October, 2011.

- Benavides, P.; Diwekar, U.: Optimal control of Biodiesel production in a batch reactor in the face of Feed variability. In *AIChE Annual Meeting*, Salt Lake City, UT, November, 2010.

- Benavides, P.; Diwekar, U: Optimal control of Biodiesel production in a batch reactor in the face of Feed variability. In *AIChE Midwest Regional Conference*, Chicago, IL, September 2010.

Computer Skills:

- Programming skills: MATLAB, GAMS,FORTRAN,ASPEN, NETLOGO,MultiBatchDS
- Operating systems: Windows 2000/XP/7.