SIMULTANEOUS DESIGN, SCHEDULING AND OPERATION

THROUGH PROCESS INTEGRATION

A Dissertation

by

EID M. AL MUTAIRI

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

DOCTOR OF PHILOSPHY

August 2008

Major Subject: Chemical Engineering

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ABSTRACT

Simultaneous Design, Scheduling and Operation Through Process Integration.

(August 2008)

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Processing facilities are normally designed with sufficient flexibility to handle nominal variations. When the process features planned changes in feedstock and products, scheduling is often used to optimize process operation. The objective of this dissertation is to develop a new approach to design and scheduling with economic, environmental, heat integration and inherently safer design objectives. Specifically, this work introduces a systematic framework and the associated mathematical formulation for simultaneous process design and scheduling while simultaneously addressing economic, environmental, heat integration and inherently safer design objectives. Therefore, more than one type of proper tradeoffs are established between these objectives. The environmental issues pertaining to the parameterized process retrofitting, scheduling, and operation strategies are simultaneously considered along with the environmental

impact of these changes. Similarly, the design synthesis of heat-exchange networks (HENs) is addressed in the context of optimizing energy consumption under scheduling scenarios. Finally, the goal of inherently safer design is simultaneously considered with the expected schedules of the process. Several optimization formulations are developed for the projected schedules while allowing design modifications and retrofitting changes. The modifications and changes include new environmental management units, synthesis of flexible and optimal HENs, and design of an inherently safer process. Process models with the appropriate level of relevant details are included in the formulations. A discretization approach has been adopted to allow for a multiperiod optimization formulation over a given time horizon. The resulting framework identifies opportunities for synergism between the economic, environmental, heat integration and inherently safer design objectives. It also determines points of diminishing return beyond which tradeoffs between the above mentioned objectives are established. The devised procedure is illustrated with case studies.

DEDICATION

To my father Shaikh Musaad Al-Assami

To my mother

To my wife

To my son Musaad

To my daughter Arwa

To my brothers and sisters

ACKNOWLEDGEMENTS

First and foremost, all praise to Almighty Allah, the merciful and the most gracious who gave me the courage, support and patience without which I could not have finished this work. His help manifested greatly in all stages of my study and research towards completion of my Ph.D. Thanks Allah for giving me the ability and resources to get this far and achieve my goals.

I would like to express my profound gratitude and unbounded thanks to my advisor and friend, Dr. Mahmud M. El-Halwagi for his tremendous support, guidance, education, discussions and many more aspects that added a lot to my research and personal experiences. There have been so many times when he has inspired me to see things form more than one angle and helped me discover paths through roadblocks. Working with Dr. El-Halwagi motivates me always to conduct a research and at same time linking it with industry and real world.

I would like also to thank my graduate advisory committee members; Dr. M. Sam Mannan, Dr. Juergen Hahn and Dr. Sergiy Butenko for serving in my committee, for their time and for their helpful comments. Having had the pleasure of taking classes or interacting with them in Process System Engineering group or other meetings, it has been a privilege to learn from and get to know each of them.

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

LIST OF TABLES

NOMENCLATURE

Indices

i_u	Input stream to process unit
i_v	Input stream to environmental management unit
j_u	Output stream from process unit
j_v	Output stream from environmental management unit
m	Pinch regime (above or below)
P	Product
p_{i_u} or p_{j_u}	Scenario for hot input or hot output stream
q	Material
r_{i_u} or r_{j_u}	Scenario for cold input or cold output stream
t	Time
u	Process unit
v	Environmental management unit
vc	Cooling utility
w	Waste stream
y	Heating utility
z	Interval in temperature interval diagram

Sets

EMU	Environmental management units
CP	Cold streams
CU	Cooling utilities
HP	Hot streams
HU	Heating utilities
INPUT	Input streams
OUTPUT	Output streams
P	Product amount
PERIODS	Operating periods
Q	Materials
SN	Subnetwork
U	Process units
WASTES	Environmental discharges for the process

Parameters

d_u^{min}	Minimum design variable
d_u^{max}	Maximum design variable
$Load^{env}$	Maximum load released of a waste to environment
$P_{p,t}^{Demand}$	Demand of product p at t^{th} period
o_u^{min}	Minimum operating variable

o_u^{max}	Maximum operating variable
Z^{env}	Maximum allowable release of a waste to environment

Variables

$C_{p,t}^{product}$	Unit selling price of product p during period t
d	Design variable
$F_{i_u,t}$	Flowrate for the $i_u{}^{th}$ input to the process unit
$F_{i_v,t}$	Mixed flow rate to EMUs
$G_{j_u,t}$	Flowrate for the $j_u{}^{th}$ output from the process unit
g_{j_u,i_v}	Flowrate assigned from source j_u to destination i_v during period t
h	Heat capacity
$Net\_Gen_{u,q,t}$	Generation of material q
$p_{j_u,p,t}$	Flowrate assigned from j_u to the pth product stream
p	Operating variable
POC_t	Plant operating cost during period t
$r_{j_v,i_u,t}$	Flowrate recycled back to the process to the $i_u{}^{th}$ input of the uth unit
TAC^{EMU}	Total annualized cost of the environmental management system
W_w	Flowrate of the wth waste stream
$w_{j_v,w,t}$	Flowrate assigned to the wth waste stream

$W_{w,t}$	Flowrate of the wth waste stream during the tth period
$X_{i_u,q,t}$	Composition of material q in the input stream i_u to the process unit
$Y_{j_u,q,t}$	Composition of material q in output stream j_u^{th}
$Z_{w,q}$	Composition of the qth pollutant in the wth waste stream
$C_{p,t}^{product}$	Unit selling price of product p during period t

Binary variables

$E_{i,j,m}$	Binary variable for existence of a match between process hot and cold streams
$I_{g,p_g,t}^{cold}$	Binary variable for existence of a scenario for cold streams
$I_{h,p_h,t}^{hot}$	Binary variable for existence of a scenario for hot streams
I_v	Binary integer variable designating the presence or absence of the vth EMU

Greek

ΔT_m	Minimum heat exchange driving force
$\delta_{i,z}$	Load of a hot stream or a hot utility in specific temperature interval

CHAPTER I

INTRODUCTION AND BACKGROUND

1.1 Scheduling of chemical processes

Scheduling is a critical issue in process operations and is crucial for improving production performance.[1] Scheduling of any process typically involves handling production, management of transitions, and accommodating inventory constraints, while meeting demands of final products with specified due dates. The problem deals with sequencing of products for each unit, product quantities and optimal beginning and end of production and storage tasks.[2, 3]

Scheduling can be planned for short or long term. Short-term production scheduling usually deals with a general problem of different sets of due dates of the products demand. The objective of short-term scheduling is to determine the optimal production plan utilizing the available resources over a given time horizon while satisfying the production requirements at due dates and/or at the end of the time horizon.[3-5]

_____

This dissertation follows the style of *Industrial & Engineering Chemistry Research*.

Short-term scheduling enhances the process flexibility and production efficiency due to change of market demands. Profits can be increased inevitably when conducting scheduling with short time horizons to minimize the losses of sales and waste of resources. Short-term scheduling is characterized with its distinct feature of considering the activities necessary to produce desired times, while satisfying a large number of time and relationship constraints among activities and resources. The scheduling problems in general can be modeled using continuous or discrete time models.[6, 7, 8]

Discrete time models are common in scheduling problems. They are based on two features. First, the scheduling horizon is divided into a finite number of time intervals with predefined duration. Second, the events are allowed to happen only at the boundaries of the discrete intervals. Hence, the complexity of the problem is reduced and the solution becomes less cumbersome.[9]

1.2 Scheduling and planning

Planning in the process industry is used to create production, distribution, sales and inventory plans based on customer and market information while observing all relevant constraints. There is no clear definition of the borderline between planning and scheduling problems. However, to distinguish between these two is rather an artificial approach. In reality the borderlines between scheduling and planning are vague. There

are strong overlaps between them. Looking to the two definitions from different perspectives by summarizing a few aspects and objectives of planning and scheduling would help draw a sharper borderline between the scheduling and planning. In planning, material flow and balance equations connecting sources and sinks are considered. Time-indexed models using a relative coarse discretization of time, e.g. a year, quarters, months or weeks are usually accurate enough.

On the other hand, the focus on time in scheduling problem is more detailed and may require continuous time formulations. Furthermore, one faces rather (conflicting) goals than objectives: the optimal use of resources, minimal makespan, minimal operating cost or maximum profit versus more qualitative goals such as a reliability (meet demand in time, proper quality, etc.) and robustness. Such qualitative goals are difficult for quantitative characterization.

Another important distinct difference is that the scheduling problems are concerned with renewable resources (manpower, energy), while planning problems handle non-renewable resources (raw material, capital). Moreover, renewable resources may be discrete, i.e., consumed at a constant level throughout the processing of the product, or continuous, in which the demand for the resource varies with the processing time.[10, 11]

Furthermore, planning is usually driven by economics and it covers long-term time horizon. On the other hand, scheduling is typically driven by feasibility and focuses on

short-term time horizon. *Both planning and scheduling are integrated when there are long-term goals such as the establishment of effective environmental impact reduction system for a certain process.*

1.3 Scheduling problems in oil refineries

Most scheduling problems found in industrial environments can be regarded as large scale and cumbersome optimization problem. For instance, scheduling in oil refineries is nonlinear with many decisions that identified at a glance the MINLP problem. The scheduling of oil refineries consists of a detailed crude oil processing schedule, process unit schedule and blending and shipping schedule. The purpose of the scheduling is to transform the production plan into a schedule useful for all operations within a time horizon of a few days.

Refinery scheduling is a critical link between refinery planning processes and refinery operations execution processes. The improvement of downstream supply change would add few cents per barrel. Nowadays, the focus of optimizing refinery operation and scheduling is based upon the demand side instead of optimization based on feedstock and supply which was the traditional way. Effective refinery scheduling presented in literature range from linear programs (LP) to mixed-integer nonlinear programs (MINLP) where the latter adds more complexity to the optimization problem.[12-14]

The optimized refinery scheduling can be integrated with other applications such as refinery planning, oil movement system, supply chain execution system, asset management system, etc. An integrated refinery scheduling solution would use the data for scheduling like demand forecast, deals from traders, production and planning capacity, maintenance and shutdowns, and status of scheduling progress.[15, 16]

1.4 Simultaneous design, operation and scheduling

The operational flexibility inherent in chemical processes is what makes them attractive in situations where product demands and formulations change rapidly, or where small production runs do not warrant the construction of dedicated lines or plants. However, the same special characteristics introduce extra degrees of complexity in the design of chemical processes. In particular, the chemical process or plant operation can be manipulated based on the demands and supply issues which entail certain design requirements during the operation scheduling.

In many cases, scheduling strategies are not incorporated or integrated very well, which may lead to over-design or under-design. This implies launching of retrofitting projects in order to comply with new design and operational changes. It is important and vital to insure that any resource is incorporated in the design and can be used as efficiently as

possible. This is achieved via detailed considerations of plant scheduling during the design stage.

Simultaneous design and scheduling considers a further level of integration where decisions on the configuration and design of units must be coupled with scheduling decisions. The main challenge is how to develop design and operation models of chemical plants which are rich in alternatives and that in a realistic way be coupled to scheduling models.[1]

Considering design, synthesis, and scheduling simultaneously increases the efficiency of the process as well as avoiding economic losses in fixed or operating costs. It also confirms compliance with environmental regulations and takes care of needed design issues ahead of time which avoids losses of huge spending due to necessity to comply with environmental red lines.[17, 18] A design procedure for chemical processes cannot be claimed to be complete unless it can properly account for the effect of various scheduling policies on the capacity utilization. Thus, it is clear that if increased efficiency of operation is anticipated at the stage of synthesis and sizing, cheaper and more efficient designs can be obtained. This refers to, as mentioned above, simultaneous design and scheduling. This is indeed quite a difficult problem.[19, 20]

In simultaneous design and operation, decisions are made concerning: (1) design of the plant, such as the size/processing rate for the equipments, and (2) scheduling of the plant,

such as, (a) tasks to execute, where to execute them, how much material to process, and when to start and finish them, (b) storage profiles of all materials involved, and (c) short-term intervals of the time horizon under investigation.[21, 22]

Many open literature [23, 19, 20, 24-26, 27, 28, 17] stated that there is scarcity in works related to simultaneous design and scheduling of continuous plants. *Most of work which was done in this area focuses on batch plants. This brings the need to investigate more on integrating design and scheduling for continuous processes.*

The simultaneous design, operation and scheduling is an effective approach to increase the profits and lower costs of any process. Considering scheduling and operational changes in design stage will enhance the comprehensive modeling of chemical processes and provide integrated process design.

1.5 Selected literature review for simultaneous design and scheduling

Few research efforts have addressed the problem of considering scheduling aspects while scheduling the problem developing the design. Birewar and Grossmann (1989) incorporated constraints that account for scheduling effects in the optimal design. The problem that was addressed by Birewar and Grossmann was a plant with defined stages and units, production rates, time horizon, processing times and size factors. It was

required to find sizes of the units, the production scheduling and possible use of intermediate storages. The objective function was minimization of the investment cost of the plant. They got various plant configurations and production scheduling based on different storage policies like unlimited intermediate storage (IS) or zero wait (ZW).[19]

Birewar and Grossmann in a later contribution (1990) shed more light on simultaneous synthesis, design and scheduling where they developed MINLP models to solve the problem.[20] More recently, Lin and Floudas (2001) developed MINLP model utilizing continuous time formulation to solve the problem of simultaneous synthesis, design and scheduling. The problem is solved where the following were given: production recipes, available process units, storage policy, production requirement and the time horizon under consideration. It was required to determine the optimal configuration of the plant, amount of material processed and the processing time for various processes. The objective was to minimize the capital cost or to maximize the overall profit. Lin and Floudas developed a mathematical model for integrated synthesis, design and scheduling and solved it for various case studies.[17]

1.6 Process integration

Process integration is a framework of design methodologies which emphasize the unity of the process. The main categories of process integration are mass integration and

energy integration. Mass integration is a systematic methodology that provides a fundamental understanding of the global flow of mass within the process. It has been developed and applied to identify global insights, synthesize strategies, and address the root causes of the environmental and mass processing problems at the heart of the process.[29]

On the other hand, energy integration deals with all forms of energy such as heating, cooling, power generation/consumption, pressurization, and fuel. Increasing heat recovery in chemical processes is of big importance when integrating heat in the process. Heat exchanger networks, HENs, are of significant importance because of their role in recovering heat in the process. In most chemical processes, it is necessary to synthesize cost-effective HENs that can transfer heat among hot and cold streams. For a given system, the synthesis of HENs entails answering several questions including:

- Which heating/cooling utilities should be employed?

- What is the optimal heat load to be removed/added by each utility?

- How should the hot and cold streams be matched?

- What is the optimal system configuration?

1.7 Scope and objectives

The scope of this dissertation is to address the problem of simultaneous scheduling, design, and operation through the process integration. A key theme is to incorporate process schedules early enough at the design stage. In this work, various economic, environmental, safety, and energy objectives are reconciled. This work is aimed at illustrating how the scheduling and design objectives are considered simultaneously over a certain time horizon. Specifically, the following are the main objectives of the dissertation:

1. To reconcile the economic and environmental objectives simultaneously with the design and scheduling of the process.

2. To reduce the environmental impact through simultaneous design, scheduling and operation.

3. To integrate the demands of heating and cooling utilities with the expected schedules and design aspects of the process. The design of hear-exchange networks (HENs) is considered at early design stages while accounting for the scheduling and operation of the process.

4. To establish the proper tradeoff between the inherently safer design and other process objectives. The scheduling is considered as well as a safety metric during the design phase.

The environmental impact reduction through simultaneous design, scheduling and is discussed in Chapter III while Chapter IV discusses incorporation of scheduling considerations in the retrofitting design of heat exchanger networks. Simultaneous approach considering the inherently safer design and process scheduling is covered in Chapter V. Conclusions and recommendations are presented in Chapter VI.

CHAPTER II

PROBLEM STATEMENT

The overall theme of this dissertation is concerned with the development of design and operation tools for maximizing the gross profit of the processing facilities. The design and operation are considered simultaneously to get advantage of the trading-off of competing design and operational objectives. This can be achieved via operation and production scheduling as well as process integration of the process. In addition to economic aspects, the following objectives are addressed:

1. Environmental impact reduction

2. Heat integration and retrofitting of heat exchanger network design

3. Inherently safer design

The problem statement is given as follows:

Given a continuous process with:

- A set of unit operations U= {u|u= 1, 2… N_u}. Each process unit, u, has a set of input streams $INPUT_u$ = $\{i_u \mid i_u = 1,2...,N_u^{in}\}$ and a set of output streams $OUTPUT_u$ = $\{j_u \mid j_u = 1,2...,N_u^{out}\}$. An input stream, i_u, has a flowrate, F_{i_u}, the composition of component q , $X_{i_u,q}$, and a temperature, $T_{i_u}^{in}$, while an output

stream , j_u, has a flowrate, G_{j_u}, the composition of component q, $Y_{j_u,q}$ and a temperature, $T_{j_u}^{out}$.

- The input or output process streams that need to cooled are defined as hot streams and given by the set HP={y|y= 1,2,…, N_{HP}}. On the other hand, the input or output process streams that need to heated are defined as cold streams and given by the set CP={v|v= 1,2,…, N_{CP}}. Every hot or cold stream has a supply and target temperatures, i.e., T^s and T^{tg} respectively.

- The process also has set of utility hot streams, HU={y|y= 1,…, N_{HU}}, and set of utility cold streams, CU={v|v= 1,…, N_{CU}}. The hot and cold utilities are used to provide the necessary heating and cooling requirements after heat integration of the process that is conducted simultaneously with the process operation and production scheduling.

- A given decision-making time horizon ($time_h$). Within this horizon, the variations in the market conditions are anticipated and expressed in terms of time-dependent changes in quantities and prices of supply (e.g., feedstocks, utilities, etc.) and demand (e.g., products and byproducts).

The aim of this dissertation is to develop systematic procedures for design and scheduling that address the following objectives:

- Environmental impact reduction through simultaneous design, scheduling and operation

- Incorporation of scheduling considerations in the retrofitting design of heat exchanger networks

- Simultaneous approach considering the inherently safer design and process scheduling

Chapters III, IV and V address these objectives, present the specific problem statements, and discuss the approaches and mathematical formulations. Case studies on oil refineries for every topic are solved to demonstrate the applicability of the devised procedures.

CHAPTER III

ENVIRONMENTAL-IMPACT REDUCTION

THROUGH SIMULTANEOUS DESIGN, SCHEDULING, AND

OPERATION

3.1 Introduction

As a result of changing market demands, feedstock characteristics, and economic factors, many industrial facilities develop operational schemes along with design flexibilities that enable a cost-effective operation while complying with the various constraints. Several approaches are typically adopted to handle the potential variations for the process. It is instructive to review some of the common problems and approaches in process design and operation. The primary design problem is the nominal grassroots design problem (Fig. 3.1) which deals with a given base case of steady-state input and expects the plant to deliver a steady-state output. Given that process inputs are likely to change, it is important to account for such variations. If the process design is not flexible enough to accommodate such changes, then the process outputs will not meet the desired specifications (defined by lower and upper bounds) no matter what control schemes are used. This is the case of an inflexible design (Fig. 3.2). On the other hand, when

appropriate flexibility analysis and strategies[30] are included in the design, a properly-controlled process performs within the desired output bounds (Fig. 3.3).
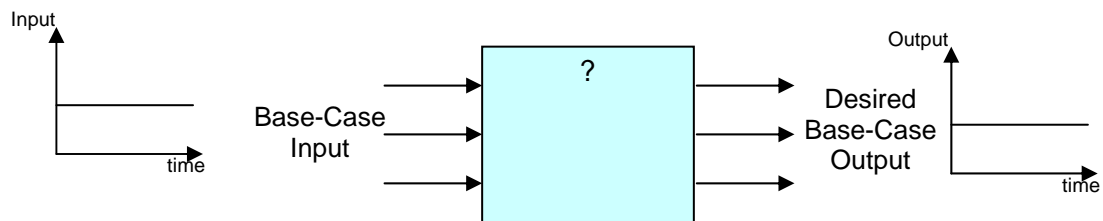
Figure 3.1. Nominal (base-case) grassroots design
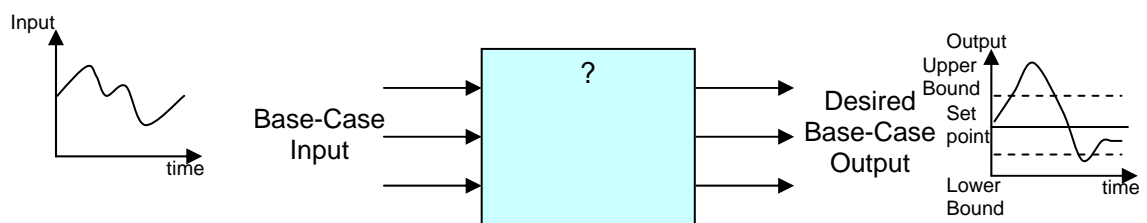
Figure 3.2. Inflexible design (even with proper process control)
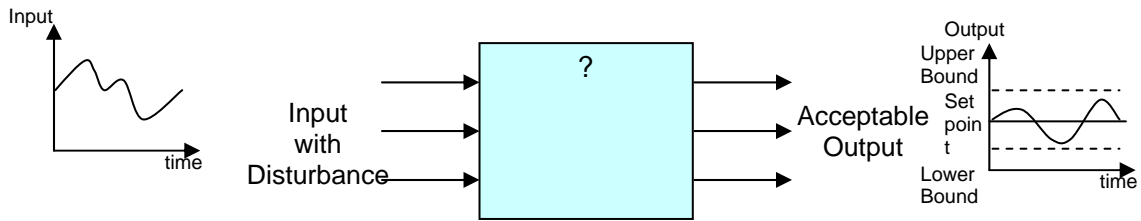
Figure 3.3. Including flexibility in design (with proper process control and operation)

For an existing design, the base-case input may change to a new (or future) base case. Accordingly, there will be a new base case for the output. Revising the design of the existing plant to take the new base-case input and deliver the new base-case output is the problem of nominal design retrofitting. Modifications of the existing design may include expanding capacities of units, adding/replacing units, rerouting streams, altering design and/or operating variables, etc. Fig. 3.4 is a schematic representation of the retrofitting problem.
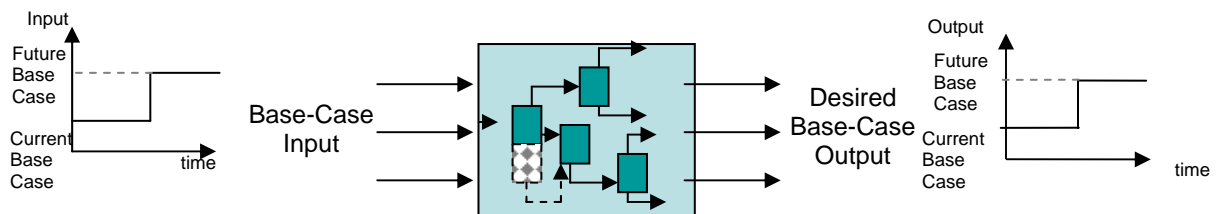
Figure 3.4. Base-case design retrofitting

Scheduling[1] is a critical issue in process operations and is crucial for improving production performance for a given process design. Scheduling of any process typically involves handling production, changes in feedstocks, management of transitions, and accommodating inventory constraints, while meeting demands of final products with specified due dates. The problem deals with sequencing of products on each unit, product quantities, optimal beginning and end of production and storage tasks.[2, 3] Fig. 3.5 is a schematic representation of scheduling. The scheduling can be short or long term. Short-term production scheduling is dealing with a general problem of different sets of due dates of the products demand. The objective of short-term scheduling is to determine the optimal production plan utilizing the available resources over a given time horizon while satisfying the production requirements at due dates and/or at the end of the time horizon.[3-5, 31]
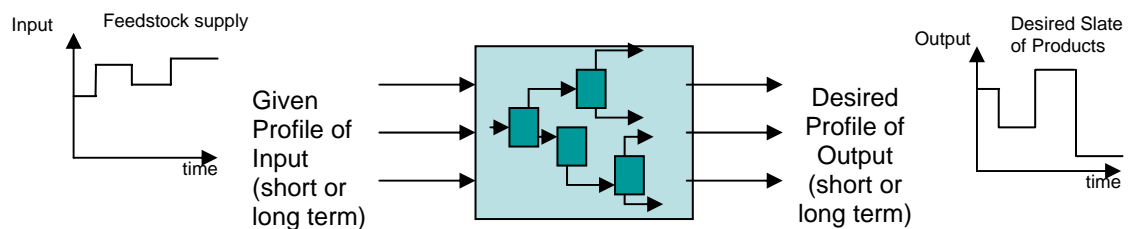
Figure 3.5. Process scheduling

Short-term scheduling enables the process to be more responsive to changes in market demands and, therefore, leads to enhanced profits. Mathematical programming techniques have been used to systematize scheduling decisions.[6-8, 17-22] Short-term scheduling studies are useful during the design phase of the process (based on anticipated market changes) and subsequently during actual operation (based on actual short-term market needs). Fig. 3.6 gives an overview of a typical design cycle. It starts by process synthesis and analysis for the generation and selection of a nominal case design followed by flexibility analysis and an initial process schedule based on anticipated process changes. Then, the control system is designed and implemented. Next, based on actual variations in input data or desired output, process scheduling and operating schemes are developed.

3.2 Handling environmental issues during design and scheduling

As a result of changes in process inputs and/or schedules or as new environmental regulations are enacted, design modifications are usually needed to render the process in environmental compliance. The conventional approach in handling the environmental issues during process design and scheduling has been primarily sequential in nature. Fig. 3.7 is a sequential approach which starts by determining a desired production schedule based on market demands. While the original set of production schedules were achievable using the nominal case design and satisfying environmental regulations,

significant changes in process schedules may lead to design infeasibility and/or environmental incompliance. This may be attributed to the possibility of economically-driven schedules (beyond the initially-anticipated schedules) that do not account for environmental performance.
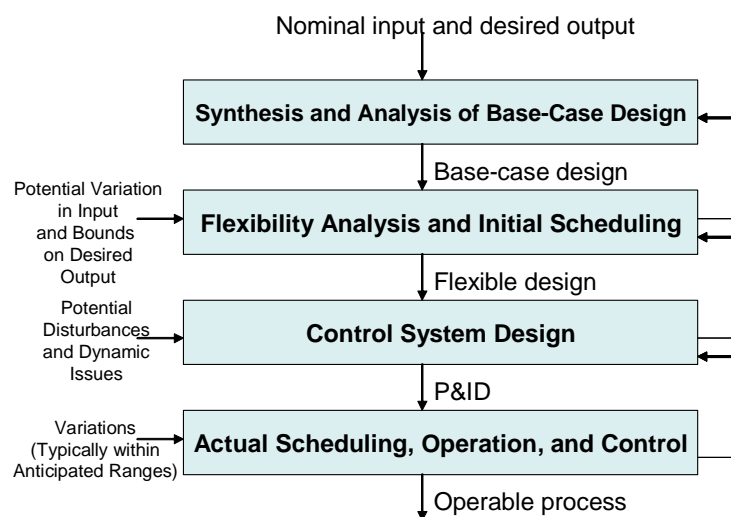
Figure 3.6. A typical design cycle

Another possibility is that new environmental regulations are enacted after the nominal-case design has been implemented. In either case, there is typically the need to retrofit the design or alter the desired schedules to insure environmental compliance. If design modifications are allowed, then a design cycle is initiated to focus on process activities such as process integration, debottlenecking[32], pollution prevention[33], pollution control,

etc. The objective of such design changes is to meet the desired production schedule and the environmental regulations. If no design modifications are permitted (e.g., for budgeting reasons), then the desired production schedules are not met and alternate schedules are developed to operate within the constraints of the current design and the environmental regulations.

New market demands/changes

Development of New Scheduling Schemes of Products to Meet Market Demands

Desired process schedules

Desired Schedules Met with Current Design?   Yes   **Environmental Regulations Met with Current Design?**   Yes

No   No   New schedules of products for environmentally-acceptable operable process

Design Changes Allowed?   Yes

No

Development of Alternate Scheduling Schemes of Products Subject to Current Design and Environmental Regulations (does not meet market demands)

Proceed to a new **design cycle** (debottlenecking, pollution prevention, pollution control, etc.) **to meet desired schedule of products and environmental regulations**

New schedules **(do not match desired scheduling of products but meet environmental regulations)**

Figure 3.7. Sequential design and scheduling with environmental constraints

It is important to note that in the aforementioned sequential arrangement, if there are violations in design constraints and/or environmental regulations, then the following approaches are used:

- Modify the design to meet the desired schedules and/or the environmental regulations (associated with the process performing to meet the desired schedules). This is the case of "scheduling dominates."

- Modify the production schedules to operate within the limitations of the current process design. This is the case of "design dominates."

- Modify the production schedules to operate within environmental compliance. This is the case of "environment dominates."

Each of the three aforementioned cases subjects two objectives to a third objective. While this sequential approach leads to processes that work, the question is whether such solutions are always optimal? The answer is no. For instance, consider the case of "scheduling dominates." Since the determined scheduling scheme is based on economic factors pertaining to cost (e.g., raw materials, processing) and value (e.g., product sales), it is possible to cause certain environmental violations which will require a design modification whose cost exceeds the value of implementing that particular schedule. This can lead to sub-optimal solutions. Therefore, we propose that the design retrofitting for environmental compliance be carried out *simultaneously* with the determination of anticipated schedules. This establishes two types of proper tradeoffs (a) between design and scheduling and (b) between economic and environmental objectives.

3.3 Problem statement

The problem to be addressed by this work is stated as follows: Given a continuous process with:

- A set of unit operations U= {u|u= 1,2, …, N_u}. Each process unit, u, has a set of input streams $INPUT_u$ = $\{i_u \mid i_u = 1,2...,N_u^{in}\}$ and a set of output streams $OUTPUT_u$ = $\{j_u \mid j_u = 1,2...,N_u^{out}\}$. An input stream, i_u, has a flowrate, F_{i_u}, and the composition of component q , $X_{i_u,q}$, while an output stream , j_u, has a flowrate, G_{j_u}, and the composition of component q, $Y_{j_u,q}$.

- A set of environmental discharges for the process: WASTES = {w|w is a waste stream leaving the process and is subject to environmental regulations}.

- A set of environmental regulations governing the composition and/or load of the pollutants leaving the plant, i.e.

$$Z_{w,q} \le Z_{w,q}^{env} \tag{3.1}$$

and

$$W_w Z_{w,q} \le Load_{w_u q}^{env} \tag{3.2}$$

where $Z_{w,q}$ is the composition of the qth pollutant in the wth waste stream and Z_w is the flowrate of the wth waste stream.

- A given decision-making time horizon (t_h). Within this horizon, the variations in the market conditions are anticipated and expressed in terms of time-dependent

changes in quantities and prices of supply (e.g., feedstocks, utilities, etc.) and demand (e.g., products and byproducts).

Available for consideration is a set of candidate environmental technologies (environmental management units: "EMUs"): EMU=$\{v|v= N_u+1, N_u +2, …, N_u + N_v\}$ that may be added to the process to reduce environmental impact and comply with environmental regulations of the process. It is desired to develop a systematic procedure that can determine production schedules, process modifications, and EMUs selection and design so as to maximize the process profit.

3.4 Approach and mathematical formulation

To simplify the problem, the following assumptions are introduced:

- The decision-making time horizon is discretized into N_t periods leading to a set of operating periods: PERIODS = $\{t|t= 1,2, …,N_t\}$. Within each time period, the process operates in steady-state mode. Also, it is only allowed to have intra-period integration (i.e., no streams are stored, integrated, and exchanged over more than one period). In selecting the number and duration of the periods, one has to strike proper balance between capturing the market variations, significance to the process, and computational efforts.

- Process modifications will be limited to two alternatives:

a) Manipulation of certain design and operating variables for each unit within permissible ranges, i.e.,

$$d_u^{\min} \leq d_u \leq d_u^{\max} \qquad (3.3)$$

and

$$o_u^{\min} \leq o_u \leq o_u^{\max} \quad \forall u . \qquad (3.4)$$

This assumption implies that the design of the current process is flexible enough to produce any of the anticipated production schedules and that there is no economic incentive to add a process unit or reroute process streams.

b) Addition of new EMUs (whose number, design, and placement will be determined as part of the solution procedure).

3.4.1 Structural representation

In order to embed potential configurations of interest, a source-sink structural representation of the problem is adopted.[31] Outputs from process units are split into fractions and assigned to inputs of the EMUs. Each EMU discharges several outputs. An output from the EMU is split and distributed into fractions; some of which are discharged as wastes while the others return back to the process to be assigned to process inputs. The flows from process units to EMUs and from EMUs to wastes and back to the process are unknown and to be determined as part of the solution. Fig. 3.8 provides a schematic of the structural representation.
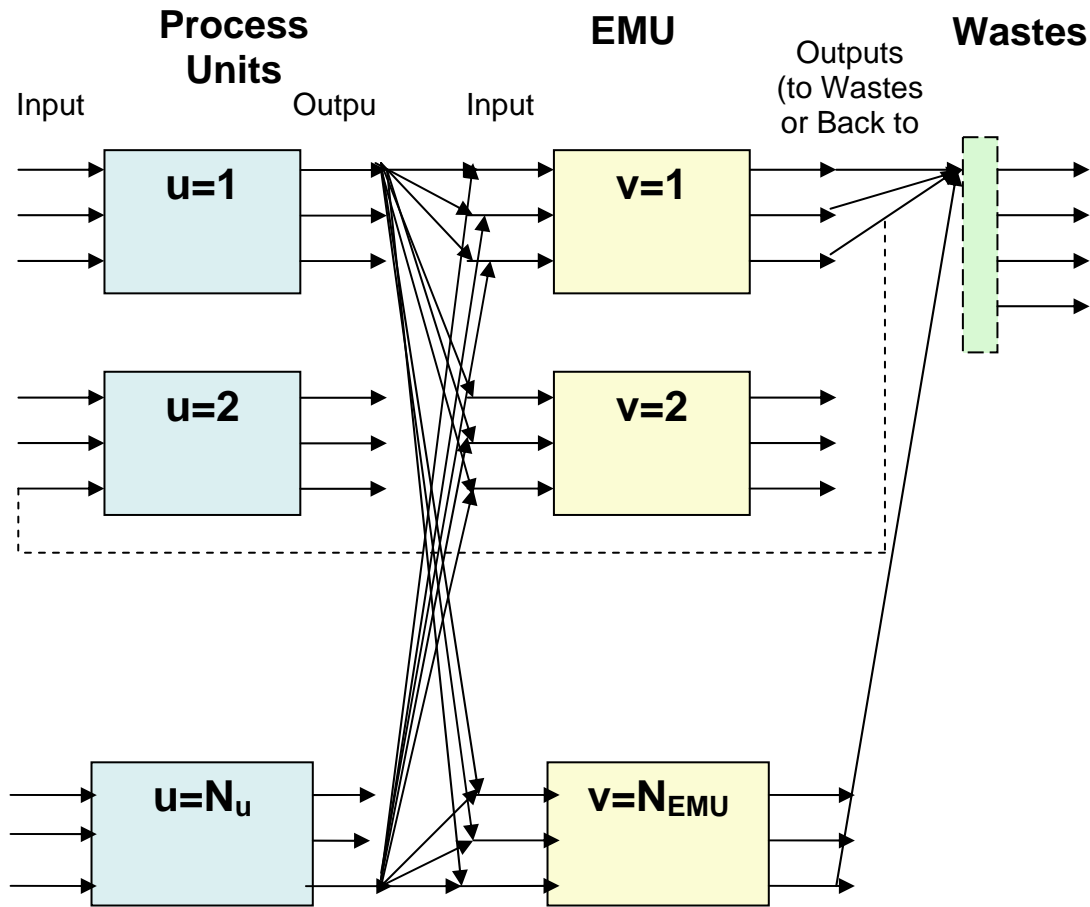
Figure 3.8. Structural representation of the problem

Now, we proceed with the modeling aspects. The mass balance equation for unit u during period t is given by:

$$\sum_{j_u} G_{j_u,t} = \sum_{i_u} F_{i_u,t} \qquad\qquad \forall u,t \qquad\qquad (3.5)$$

and the qth component balance for unit u during period t is expressed as:

$$\sum_{j_u} G_{j_u,t} * Y_{j_u,q,t} = \sum_{i_u}\left(F_{i_u,t} * X_{i_u,q,t} + Net\_Gen_{u,q,t}\right) \qquad \forall q,u,t \tag{3.6}$$

where the additional index, t, in the flowrates and compositions refers to the time period over which these flowrates and compositions are considered. Additionally, the performance model for unit u at period t is expressed as by a set of algebraic equations represented by:

$$(G_{j_u,t}, Y_{j_u,q,t} : j_u = 1,2,...,N_u^{out} \text{and} q) = f_u(F_{i_u,t}, X_{i_u,q,t} : i_u = 1,2,...,N_u^{in} \text{and} q, d_{u,t}, o_{u,t}) \tag{3.7}$$

Let the flowrate assigned from source j_u to destination i_v during period t be referred to as g_{j_u,i_v}. The flowrate from the j_u^{th} source goes to other units, to EMUs, and to final product streams. Therefore, the material balance for the splitting of source j_u is given by:

$$G_{j_u,t} = \sum_u \sum_{i_u} g_{j_u,i_u,t+} \sum_v \sum_{i_v} g_{j_u,i_v,t+} \sum_p P_{j_u,p,t} \qquad \forall u,j_u,t \tag{3.8}$$

where $p_{j_u,p,t}$ is the flowrate assigned from j_u to the pth product stream. The flowrate of the pth product in period t is described by:

$$P_{p,t} = \sum_u \sum_j P_{j_u,p,t} \qquad \forall p,t \tag{3.9}$$

Then, for the mixing of the split flowrate before the i_v^{th} input to the vth EMU, the material balance and the qth component balance during period t are given by:

$$F_{i_v,t} = \sum_u \sum_{j_u} g_{j_u,i_b} \qquad \forall v,i_v,t \tag{3.10}$$

$$F_{i_v,t} * X_{i_v,q,t} = \sum_u \sum_{j_u} g_{j_u,i_b} * Y_{j_u,q,t} \qquad \forall v,i_v,q,t \tag{3.11}$$

The mass balance equation for EMU, v, during period t is given by:

$$\sum_{j_v} G_{j_v,t} = \sum_{i_v} F_{i_v,t} \qquad\qquad \forall v,t \qquad\qquad (3.12)$$

The qth component balance for EMU,v, during period t is expressed as:

$$\sum_{j_u} G_{j_u,t} * Y_{j_v,q,t} = \sum_{i_v}\left(F_{i_v,t} * X_{i_v,q,t} + \text{Net\_Gen}_{v,q,t}\right) \qquad \forall q,v,t \qquad (3.13)$$

and the unit performance equation for the vth EMU is expressed as:

$$(G_{j_v,t}, Y_{j_v,q,t} : j_v = 1,2,..., N_v^{out} \text{ and } q = 1,2,...N_{Components})$$

$$= f_v(F_{i_v,t}, X_{i_v,q,t} : i_v = 1,2,..., N_v^{in} \text{ and } q = 1,2,...N_{Components}, d_{v,t}, o_{v,t})$$

$$\forall v, i_v, q, t \qquad\qquad (3.14)$$

There are N_w waste streams leaving the process. Each output stream, j_v, from an EMU unit is split into several flowrates; some are assigned to waste outlets and some are recycled back to the process to enter process units. The flowrate assigned to the wth waste stream is referred to as $w_{j_v,w,t}$ and the flowrate recycled back to the process to the i_u^{th} input of the uth unit is described by $r_{j_v,i_u,t}$. Therefore, the material balance for the splitting of the j_v^{th} stream is given by:

$$G_{j_v,t} = \sum_w w_{j_v,w,t} + \sum_u \sum_{i_u} r_{j_v,i_u,t} \qquad\qquad \forall v, j_v, t \qquad\qquad (3.15)$$

The flowrate of the wth waste stream during the tth period is given by:

$$W_{w,t} = \sum_v \sum_{j_v} w_{j_v,w,t} \qquad\qquad \forall w,t \qquad\qquad (3.16)$$

and the qth component material balance for the wth waste stream is given by:

$$W_{w,t} * Z_{w,q,t} = \sum_v \sum_{j_v} w_{j_v,w,t} * Y_{j_v,q,t} \qquad\qquad \forall w,q,t \qquad\qquad (3.17)$$

The environmental regulations for the wth waste stream and the qth pollutant are described by:

$$Z_{w,q,t} \leq Z^{env}_{w,q,t} \qquad\qquad (3.18)$$

 and

$$W_{w,t} * Z_{w,q,t} \leq Load^{env}_{w,q,t} \qquad\qquad (3.19)$$

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

$$d_u^{min} \leq d_{u,t} \leq d_u^{max}, \qquad\qquad (3.20)$$

$$d_v^{min} \leq d_{v,t} \leq d_v^{max} \qquad\qquad (3.21)$$

$$o_u^{min} \leq o_{u,t} \leq o_u^{max} \qquad\qquad (3.22)$$

and

$$o_v^{min} \leq o_{v,t} \leq o_v^{max} \qquad\qquad (3.23)$$

The product demand and composition constraints are expressed as:

$$P_{p,t} \leq P^{Demand}_{p,t} \qquad\qquad (3.24)$$

The flowrate and composition constraints for the i_u^{th} input to the process unit are given by:

$$F_{i_u}^{min} \leq F_{i_u,t} \leq F_{i_v}^{max} \qquad\qquad (3.25)$$

and

$$X_{i_u,q}^{min} \leq X_{i_u,q,t} \leq X_{i_u,q}^{max} \qquad\qquad (3.26)$$

The flowrate and composition constraints for the i_vth input to the vth EMU are given by:

$$F_{i_v}^{\min} \leq F_{i_v,t} \leq F_{i_v}^{\max} \tag{3.27}$$

$$X_{i_v,q}^{\min} \leq X_{i_v,q,t} \leq X_{i_v,q}^{\max} \tag{3.28}$$

The objective function is given by:

Maximize gross profit $= \sum_t \sum_p C_{p,t}^{product} * P_{p,t} - \sum_t POC_t - TAC^{EMU}$ (3.29)

where $C_{p,t}^{product}$ is the unit selling price of product p during period t, POC_t represents the plant operating cost (e.g., feedstocks, utilities, etc.) during period t, and the term TAC^{EMU} is the total annualized cost of the environmental management system which is defined as the sum of the annualized fixed costs (AFC) and the environmental annual operating cost (EOC) and is expressed as:

$$TAC^{EMU} = \sum_v I_v * AFC_v + \sum_t \sum_v EOC_{v,t} \tag{3.30}$$

where I_v is a binary integer variable designating the presence or absence of the vth EMU and is determined through the following constraint:

$$\sum_{i_v} F_{i_v,t} \leq F_v^U * I_v \qquad\qquad \forall t \tag{3.31}$$

Where F_v^U is an upper bound on the allowable flowrate to unit v. When the flowrate entering unit v is positive, the value of I_v is forced to be one. Otherwise, it takes the value of zero.

The foregoing expressions constitute the mathematical program for the problem. It is a mixed-integer nonlinear program (MINLP) which can be solved to identify the optimal scheduling, process modifications, and selection as well as design of the EMUs.

3.5 Case study: simultaneous design and scheduling in refineries with NOx regulations

Scheduling is an important activity in refineries. Most of the research contributions in refinery scheduling have focused on responding to market demands to maximize profit.[34-38] For instance, in the US, the demand for gasoline usually increases during summer while the demand for diesel typically increases in winter. Various process units (e.g., the fluid catalytic cracker FCC) are operated differently along with pooling and blending to obtain the desired products. It is worth noting as the refinery is operated differently, its environmental emissions will also change. Here, we expand the scope of scheduling to include the need for compliance with environmental regulations including NOx emissions. We also allow for the addition of NOx removal units as needed. There are several technologies that can reduce NOx emissions. Selective catalytic reduction units (SCR) units may be installed in oil refineries in order to assure that NOx is within the acceptable environmental range. NOx emissions fluctuate depending on the mode of operation, product demands or crude properties. Therefore, the design and operation of the SCR is tied to scheduling decisions and vice versa. In this case study, there is an

anticipated profile for market demands. The objective is to determine the optimal refinery scheduling along with any process modifications and the number and design and the EMUs (SCR in this case).

First, the process has been simulated using ASPEN Plus to develop a base-case model for the refinery. The FCC unit has also been modeled based on the work on Bamufleh (2000)[39] which characterizes the amount of produced gasoline through the following function:

$$Gasoline = a(\frac{H}{C+S} + \log f_c T) + b(M_{eff}) + c(N_B) + d(C/O) + e(T) + f(Conversion)$$

(3.32)

where C/O is the catalyst to oil ratio and T is the temperature of the FCC. Depending on the operation of the regenerator, the value of C/O, and the FCC operating temperature, the extent of NOx emission varies. Therefore, there is a tradeoff between gasoline production and the design and operation of the SCR unit(s) and the process modifications for the refinery. Initial efforts have been made to pose the problem as an MINLP based on the aforementioned mathematical formulation.

For the FCC/SCR case where the increases in gasoline demand which increases inevitable the NOx emissions, there are two options here:

1- Operating with highest load for current SCR and loosing the market opportunity.

2- Installing new SCR to handle the NOx emissions increase.

The novel approach developed in our work will enable us to allow competence of both options. Solving the MINLP problem using Lingo give results in Table 3.1 which clarifies that the optimum solution is the first option which is operating the current SCR to its maximum capacity. The first option (optimal solution) hereby provides a savings of about $6300/day or $2 millions annually.

Table 3.1. FCC/SCR Case Study for Two Periods

Conditions	Case1: Period I Optimum Soln.	Case 2: Period II Soln. 1	Case 3: Period II Soln. 2 (optimal)
Feed(lb/hr)	658814	750000	750000
Feed(BBl)	50000	56920	56920
NOx Load (lb/hr)	24	46	30
Gasoline (BBl)	24117	27455	25677
Gasoline Sales ($/d)	69215	78795	73692
NOx cost($/d)	2597	4879	3760
New SCR ($/d)	-	10360	-
Total NOx cost ($/d)	2597	15238	3760
Profit ($/d)	66618	63557	69932

3.6 Conclusions

A systematic framework and the associated mathematical formulation for process design and scheduling has been developed considering simultaneously the economic and environmental objectives. The environmental issues pertaining to the parameterized process retrofitting, scheduling, and operation strategies have been integrated with the environmental impact of these changes. Specifically, this work introduces a new approach for the reconciliation of scheduling, design, and environmental objectives. Two types of proper tradeoffs have been methodically established (a) between design and scheduling and (b) between economic and environmental objectives. The environmental issues pertaining to the parameterized process retrofitting, scheduling, and operation strategies are simultaneously considered along with the environmental impact of these changes. A multi-period MINLP optimization formulation is developed for the case of project schedule while allowing design retrofitting changes that include new environmental units and modification of design and operating conditions in the process (without new process units). Initial efforts have been discussed for a case study on scheduling a refinery for various product demands while considering NOx emissions and the possibility of adding new NOx reduction technologies.

CHAPTER IV

INCORPORATION OF SCHEDULING CONSIDERATIONS IN THE RETROFITTING DESIGN OF HEAT EXCHANGE NETWORKS

4.1 Introduction

With changing market conditions and demands, various industries must develop design and operating strategies that enable the cost-effective operation of the process while addressing several key objectives. Production schedules should be determined so as to increase revenue, enhance efficiency, and conserve natural resources. Proper heat integration in chemical plant is one of the essential strategies for an efficient operation and can lead to considerable cost savings. Over the past 30 years, significant research contributions have been made in developing design techniques for the synthesis of heat exchange networks (HENs). Much of this work has focused on heat integration as the overarching goals with objectives such as minimizing heating and cooling utilities and total annualized cost of the network. On the other hand, much less work has been done in the area of reconciling heat integration with other process objectives. In an attempt to exploit the interactions between the process operating conditions (stream temperatures and flowrates) and the heat recovery network, Papoulias and Grossmann (1983) developed a strategy for simultaneous optimization of the process and heat integration based on mixed integer linear programming (MILP).[40] This approach allows the

flowrates to vary as part of optimizing the process and the associated network of heat exchangers. In order to avoid nonlinear terms in the formulation, fixed temperature intervals are defined. Duran and Grossmann (1986)[41] introduced a mathematical approach for the optimization of heat exchange networks where the supply and target temperatures are allowed to vary. Mathematical constraints are introduced to account for the unknown temperature and to locate candidate and true pinch points, thereby ensuring that the final flowsheet will feature the minimum utility target. According to this approach, bounds on the energy requirements of the process are explicitly included within the synthesis problem; however, the structure and overall cost of the heat recovery system are not traded off with process costs. Grossmann et al. (1998) developed another method for the simultaneous optimization of flowsheet and heat integration. It is based on introducing integer variables that give a general formulation for heat loads and composite curves.[42] Yee and Grossmann (1990) proposed a structural optimization model, where process alternatives are optimized simultaneously with the heat exchanger network that accommodates the heating and cooling requirements of the process streams.[43] They introduced a superstructure representation which included many possible flowsheet alternatives. However, the number of variables and constraints that are needed to produce the required mathematical representations may be large. Thus, simplifying assumptions may be required.

The aforementioned techniques were developed to address base-case designs. As mentioned earlier, scheduling is a critical issue in process operations and is crucial for

improving production performance for a given process design. Scheduling of any process typically involves handling production, changes in feedstocks, management of transitions, and accommodating inventory constraints, while meeting demands of final products with specified due dates.[1] The problem deals with sequencing of products on each unit, product quantities, optimal beginning and end of production and storage tasks.[2, 3] Fig. 4.1 is a schematic representation of scheduling. Scheduling can be short or long term. Short-term production scheduling deals with general problems of different sets of due dates of the products demand. The objective of short-term scheduling is to determine the optimal production plan utilizing the available resources over a given time horizon while satisfying the production requirements at due dates and/or at the end of the time horizon.[4, 31]
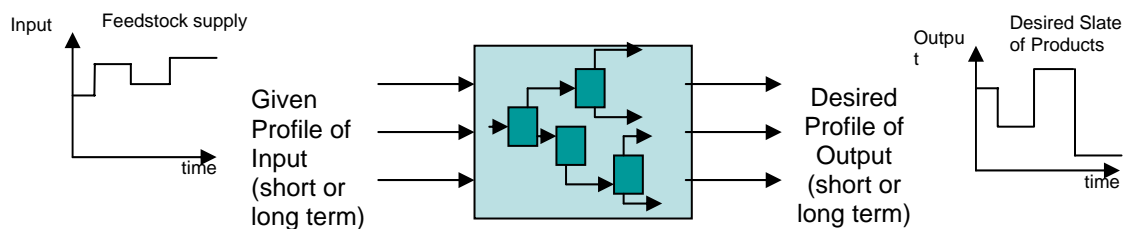
Figure 4.1. Process scheduling

Short-term scheduling enables the process to be more responsive to changes in market demands and, therefore, leads to enhanced profits. Mathematical programming techniques have been used to systematize scheduling decisions.[6, 7, 17, 18, 28, 44] Short-term scheduling studies are useful during the design phase of the process (based on anticipated market changes) and subsequently during actual operation (based on actual short-term market needs).

Fig. 4.2 gives an overview of a typical design cycle. It starts by process synthesis and analysis for the generation and selection of a nominal case design followed by base-case process integration including the network synthesis of heat exchangers. Then, the control system is designed and implemented. Next, based on actual variations in input data or desired output, process scheduling and operating schemes are developed.

Nominal input and desired output

| **Synthesis and Analysis of Base-Case Design** |

Base-case design

| **Base-Case HEN Synthesis and Design** |

Flexible design

Potential Disturbances and Dynamic Issues → | **Control System Design** |

P&ID

Variations (Typically within Anticipated Ranges) → | **Actual Scheduling, Operation, and Control** |

Operable process
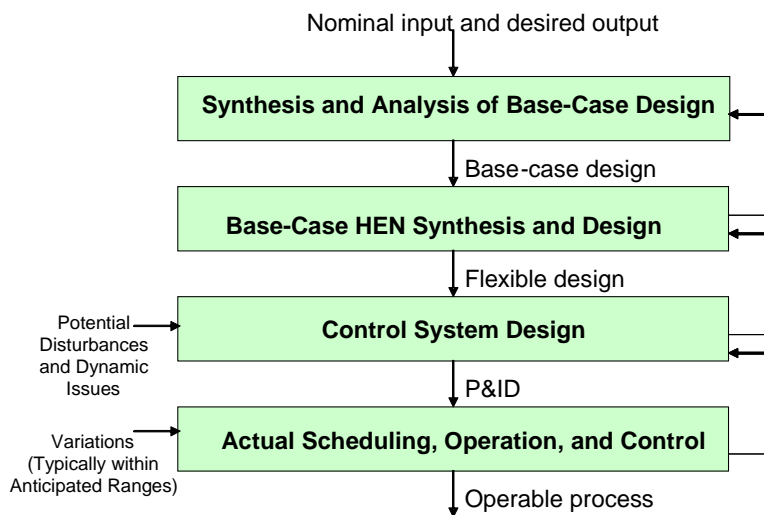
Figure 4.2. A typical design cycle accounting for HEN

Process scheduling is modified from a period to another based on market demand and/or feedstock supply fluctuations in economics and quantity/quality. For processes involving operational changes based on market-driven schedules, heat integration is typically included in the base-case design according to the nominal input data. As the process schedules are developed to accommodate market changes, there are two key limitations for the designed HEN:

1. Flexibility: The base-case HEN may not be flexible enough to accommodate the desired changes for the scheduled operations.

2. Optimality: When HENs are designed without considering the potential schedules, the network will be limited by the base-case design and may prevent

the implementation of optimal schedules based on size and connectivity of the exchangers. Additionally, the base-case design is unlikely to capture the necessary tradeoffs between the economic aspects of the proposed schedules and the energy implications.

To overcome these limitations, this paper introduces two contributions:

1. Accounting for expected schedules in the base-case design

2. Incorporation of a flexible HEN synthesis into the design while considering expected schedules

The proposed approach establishes tradeoffs between design, economic aspects of scheduling, and net savings from heat integration. The proposed approach also synergizes and incorporates scheduling aspects of the process into the design of the HEN. Several challenges arise in implementing the approach. These include:

    a. How to integrate the HEN design, operation and scheduling?

    b. How to include process variations in the synthesis of the HEN?

    c. How to insure the flexibility of devised design to function over anticipated process schedules?

A systematic procedure is developed along with the optimization formulations. Several new concepts are introduced to enhance the solvability and solution quality of the optimization formulation.

4.2 Problem statement

The problem to be addressed by this work is that given a continuous process with:

- A set of unit operations U= {u|u= 1,2, …, N_u}. Each process unit, u, has a set of input streams $INPUT_u$ = $\{i_u \mid i_u = 1,2..., N_u^{in}\}$ and a set of output streams $OUTPUT_u$ = $\{j_u \mid j_u = 1,2..., N_u^{out}\}$. An input stream, i_u, has a flowrate, F_{i_u}, the composition of component q , $X_{i_u,q}$, and a temperature, T_{i_u}, while an output stream , j_u, has a flowrate, G_{j_u}, the composition of component q, $Y_{j_u,q}$ and a temperature, T_{j_u}.

- The input or output process streams that need to be cooled are defined as hot streams and given by the set HP={y|y= 1,2,…, N_{HP}}. On the other hand, the input or output process streams that need to be heated are defined as cold streams and given by the set CP={v|v= 1,2,…, N_{CP}}. Every hot or cold stream has a supply and target temperatures, i.e., T^s and T^{tg} for hot streams and, t^s and t^{tg} for cold streams.

- The process also has set of utility hot streams, HU={y|y= 1,…, N_{HU}}, and set of utility cold streams, CU={v|v= 1,…, N_{CU}}. The hot and cold utilities are used to provide the necessary heating and cooling requirements after heat integration of the process that is conducted simultaneously with the process operation and production scheduling. Flowrates and inlet and outlet temperatures of the process hot and cold streams are to be optimized.

- A given decision-making time horizon ($time_h$). Within this horizon, the variations in the market conditions are anticipated and expressed in terms of time-dependent changes in quantities and prices of supply (e.g., feedstocks, utilities, etc.) and demand (e.g., products and byproducts).

It is desired to develop a systematic procedure that can determine optimal process design that accounts for expected scheduling and heat integration. Additionally, a flexible HEN is to be synthesized to operate over the range of expected schedules.

Fig. 4.3 illustrates the problem in a graphical form where the process units, process streams, subsets of hot and cold streams and HENs are shown.
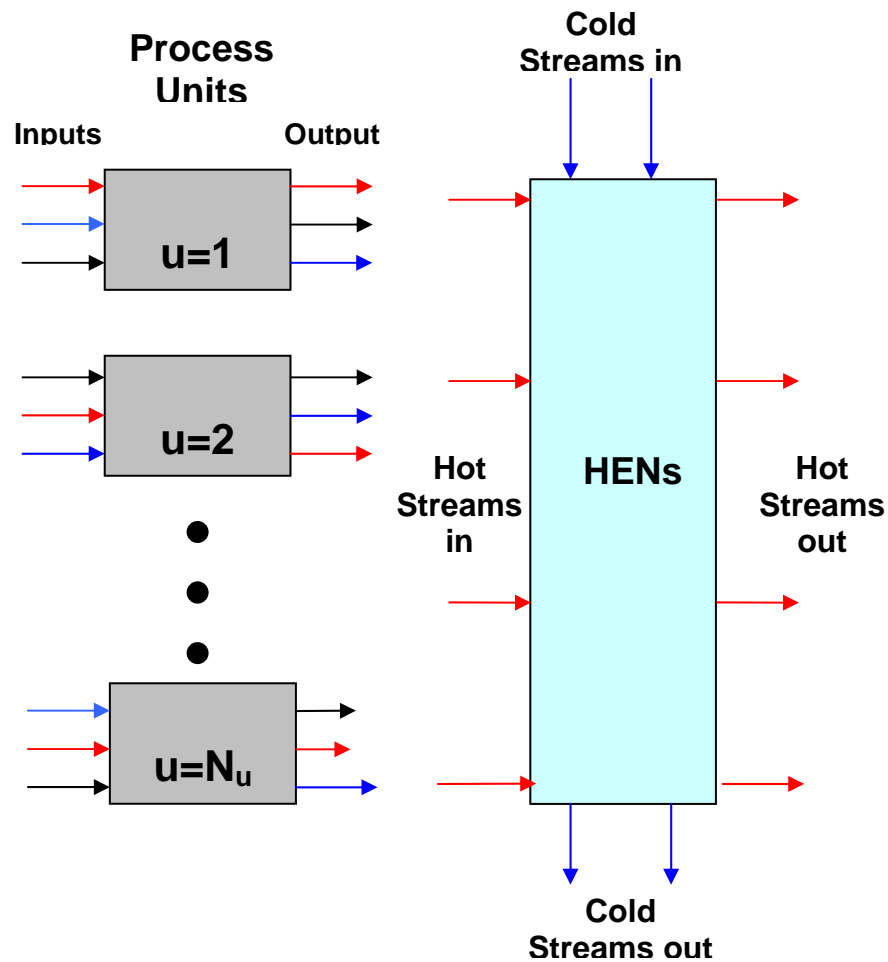
Figure 4.3. Diagram for the process and HENs

4.3 Problem complexity and proposed approach

There are several complicating factors in addressing the abovementioned problem. The following is a discussion of these complications and the approaches proposed to overcome them:

- **Reconciling design and scheduling:** As a result of changes in process inputs and/or schedules or as new regulations are enacted, design modifications are usually needed to render the process in feasible operation. The conventional approach in handling the changes in the process operation during process design and scheduling has been primarily sequential in nature. While the original set of production schedules were achievable using the nominal case design and satisfying the process conditions, significant changes in process schedules may lead to design infeasibility. In such case, there is typically the need to retrofit the design or alter the desired schedules to insure feasible operation and compliance with any new regulations. We propose including the set of expected schedules into the design during the base-case design. If design modifications are allowed, then a design cycle is initiated to focus on process activities such as process integration (e.g. heat integration), debottlenecking, pollution prevention, pollution control, etc. If no design modifications are permitted (e.g., for budgeting reasons), then the desired production schedules are not met and alternate schedules are developed to operate within the constraints of the current design.[45]

- **Process modification and HEN synthesis:** Since process modification is to be carried out simultaneously with heat integration, there is a challenge in the synthesis of the HEN. Unknown flowrates and temperatures render conventional base-case HEN synthesis techniques inapplicable. Approaches allowing for

variable temperatures and flows (e.g., floating pinch method[41, 43, 46]) result in MINLPs that are difficult to solve with no guarantee for global solution or even convergence. *Hence, we introduce the new concept of process substreams obtained by discretizing hot and cold streams into substreams. This concept transforms the MINLP formulation into a mixed-integer linear programming (MILP) formulation.*

- **HEN flexibility over expected schedule:** Base-case HEN may not be able to accommodate schedule-driven changes. Hence, we propose to synthesize the HEN to account for various expected scheduling scenarios. The challenge is to synthesize a single configuration accommodating all expected changes. Hence, we identify a number of expected scheduling scenarios and refer to each one as a period. Then, a multiperiod HEN synthesis problem is solved to generate a single network configuration that accommodates all expected schedules.

The above challenges and associated approaches to overcome them are systematically addressed as shown in the procedure flowchart (Fig. 4.4). First, the relevant input data and constraints are gathered and a number of excepted scheduling scenarios are identified. Accordingly, the process model is developed with the proper level of details to account for the process performance in terms of the design and operating decision variables. Next, a nonlinear programming (NLP) formulation is developed to incorporate the expected scheduling scenarios into the design. Meanwhile, an MILP formulation is

developed to determine the minimum heating and cooling utility targets for the HEN. The two formulations are integrated to allow the simultaneous optimization of the process design and the HEN while accounting for the expected scheduling scenarios. Because of the targeting nature of the HEN model, it is not complicated by introducing the network configuration and stream matches problems.
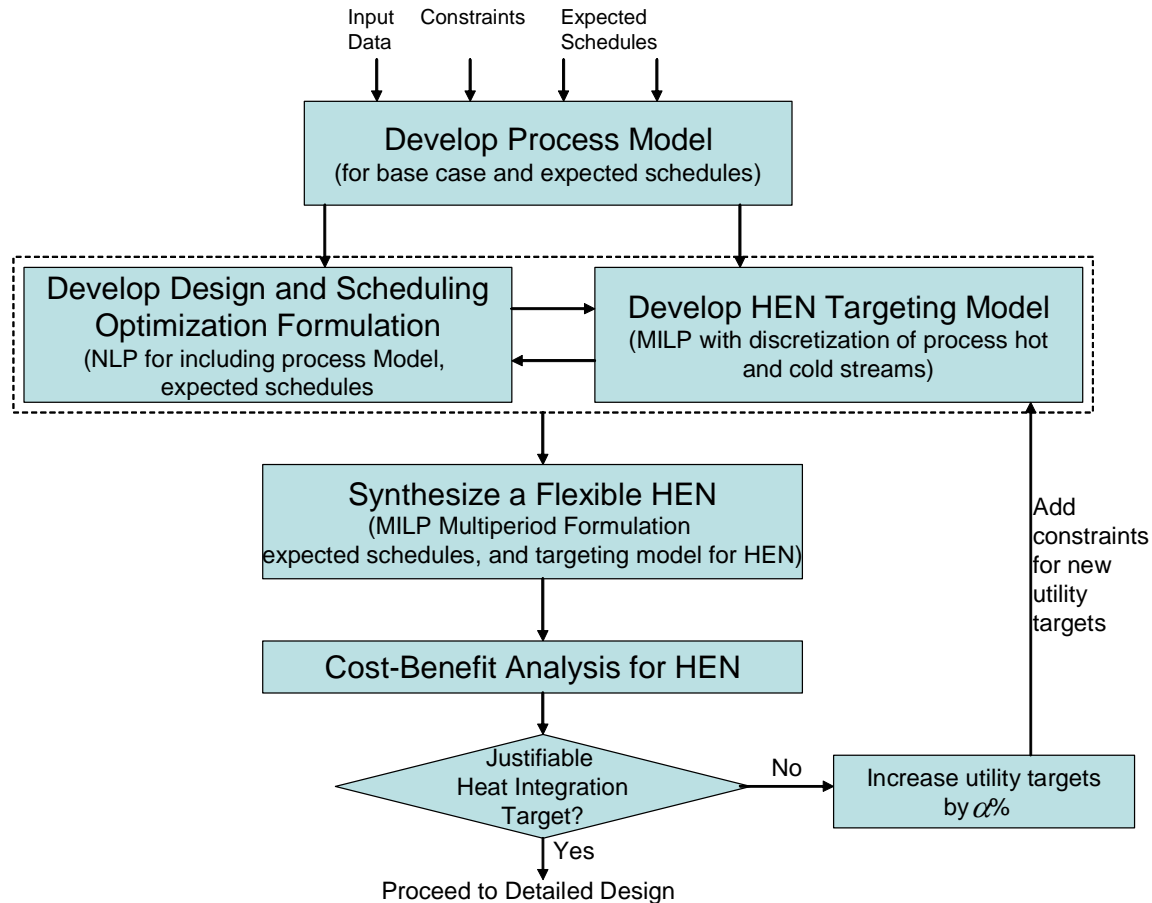
Figure 4.4. Flowchart of simultaneous heat integration and scheduling approach

Once the targeting step is undertaken, an MILP multiperiod HEN formulation is developed to determine the configuration of the flexible network that can address all the variations associated with the expected scenarios. Next, a cost-benefit analysis is undertaken to examine whether or not the heat integration network should reach the maximum level of stream integration and minimum consumption of heating and cooling utilities. If yes, the designer proceeds to detailed design. If not, then the extent of heat integration is reduced by increasing the utilities by an iterative increase ($\alpha\%$). The new utility targets are added to the constraints and the procedure is repeated until the proper tradeoff between heat integration and process design and scheduling is achieved.

4.4 Mathematical formulation

To simplify the problem, the following assumptions are introduced:

- The decision-making time horizon is discretized into N_t periods leading to a set of operating periods: PERIODS = $\{t|t= 1,2, …,N_t\}$. Within each time period, the process operates in steady-state mode. Also, it is only allowed to have intra-period integration (i.e., no streams are stored, integrated, and exchanged over more than one period). In selecting the number and duration of the periods, one has to strike proper balance between capturing the market variations, significance to the process, and computational efforts.

- Process units' modifications are conducted by manipulating certain design and operating variables for each unit within permissible ranges, i.e.,

$$d_u^{min} \leq d_u \leq d_u^{max} \quad \forall u \in U \tag{4.1}$$

and

$$o_u^{min} \leq o_u \leq o_u^{max} \quad \forall u \in U . \tag{4.2}$$

which implies that the design of the current process is flexible enough to produce any of the anticipated production schedules and that there is no economic incentive to add a process unit or reroute process streams.

The mathematical formulation is divided into three key steps as was described in Fig. 4.4. They are detailed in the following sections:

4.4.1 Design and scheduling model

In this section, design and scheduling models of the process are illustrated. The mass balance equation for unit u during period t is given by:

$$\sum_{j_u} G_{j_u,t} = \sum_{i_u} F_{i_u,t} \qquad \forall u,t \tag{4.3}$$

and the qth component balance for unit u during period t is expressed as:

$$\sum_{j_u} G_{j_u,t} * Y_{j_u,q,t} = \sum_{i_u} \left(F_{i_u,t} * X_{i_u,q,t} + Net\_Gen_{u,q,t} \right) \qquad \forall q,u,t \tag{4.4}$$

The energy balance is given by:

$$\sum_{j_u} G_{j_u,t} * h_{j_u} = \sum_{i_u} F_{i_u,t} * h_{i_u} \qquad\qquad \forall u,t \qquad\qquad (4.5)$$

where the additional index, t, in the flowrates, compositions and temperatures refers to the time period over which these flowrates, compositions and temperatures are considered.

Additionally, the performance model for unit u at period t is expressed as by a set of algebraic equations represented by:

$$(G_{j_u,t}, Y_{j_u,q,t}, T_{j_u}^{out} : j_u = 1,2,..., \text{OUTPUT}_u, q \in Q \text{ and } t \in \text{PERIODS})$$

$$= f_u(F_{i_u,t}, X_{i_u,q,t}, T_{i_u}^{in} : i_u = 1,2,..., \text{INPUT}_u, q \in Q \text{ and } t \in \text{PERIODS}, d_{u,t}, o_{u,t}) \qquad (4.6)$$

The flowrate, composition and temperature constraints for the i_u^{th} input to the process units and for the j_u^{th} output from the process unit are given by:

$$F_{i_u}^{min} \leq F_{i_u,t} \leq F_{i_v}^{max} \qquad\qquad\qquad (4.7)$$

$$F_{j_u}^{min} \leq F_{j_u,t} \leq F_{j_u}^{max} \qquad\qquad\qquad (4.8)$$

$$X_{i_u,q}^{min} \leq X_{i_u,q,t} \leq X_{i_u,q}^{max} \qquad\qquad\qquad (4.9)$$

$$X_{j_u,q}^{min} \leq X_{j_u,q,t} \leq X_{j_u,q}^{max} \qquad\qquad\qquad (4.10)$$

$$T_{i_u}^{min} \leq T_{i_u,t} \leq T_{i_u}^{max} \qquad\qquad\qquad (4.11)$$

and

$$T_{j_u}^{min} \leq T_{j_u,t} \leq T_{j_u}^{max} \qquad\qquad\qquad (4.12)$$

4.4.2. HEN targeting model with discretization of process hot and cold streams

Because of the changing temperatures and flowrates, the targeting model for identifying minimum heating and cooling utilities of the HEN becomes an MINLP. As mentioned before, there are convergence problems coupled with the nonconvexity of the nonlinear terms leading which make it difficult to achieve the global solution. Therefore, we introduce a new targeting formulation which results in an MILP that readily converges to the global solution. The temperature interval diagram (TID) is used for the devised mathematical program of the variable temperature and flow HEN. Both supply and target temperatures are discretized in the feasible range where the mathematical programming will insure the choice of the supply and target temperatures linked to the optimal simultaneous scheduling and heat integration.

As explained before, the process has a set of CP cold streams and HP hot streams as indicated above as well as CU referring to cooling utilities and HU referring to hot utilities. The following indices are used: h for a process hot stream, g for a cold process stream, y for an external heating utility, v for external cooling utility, and z for temperature intervals. The hot and cold temperatures are separated by a minimum driving force, ΔT_m.

In order to avoid the nonlinearities and complexities associated with the unknown supply and target temperatures, a discretization technique is used along with the use of integer cut. The basic idea is that each supply and target temperature is discretized into a

number of scenarios spanning the feasibility range of the temperature. For instance, for the hot stream h in period t, a number $N_{h,t}$ of discretized streams are created. The index p_h is used for the various discretizations of hot stream h in period t. Each discretization is assigned the full flowrate of the hth stream (i.e., $F_{h,p_h,t} = F_{h,t}$). Eventually, only one of the discretizations will be selected. For each p_h, a supply and a target temperatures are selected. These supply and target temperatures are designated by $T^s_{h,p_h,t}$ and, $T^t_{h,p_h,t}$, respectively. Their values are selected while satisfying the following constraints on the permissible range for each supply and target temperature:

$$T_h^{s,\min} \leq T^s_{h,p_h,t} \leq T_h^{s,\max} \qquad\qquad \forall\, h, p_h \qquad\qquad (4.13)$$

$$T_h^{t,\min} \leq T^t_{h,p_h,t} \leq T_h^{t,\max} \qquad\qquad \forall\, h, p_h \qquad\qquad (4.14)$$

A similar discretization scheme is created for the process cold streams, i.e.

$$t_g^{s,\min} \leq t^s_{g,p_g,t} \leq t_g^{s,\max} \qquad\qquad \forall\, g, p_g \qquad\qquad (4.15)$$

$$t_g^{s,\min} \leq t^s_{g,p_g,t} \leq t_g^{s,\max} \qquad\qquad \forall\, g, p_g \qquad\qquad (4.16)$$

Figure 4.5 shows the temperature interval diagram (TID) for the discretized streams. For the zth interval on the TID, the exchangeable load of the $p_h{}^{th}$ or $p_g{}^{th}$ scenarios of the hot and the cold streams passing through the zth interval are defined as:

$$HH_{z,h,p_h,t} = F_{h,t}C_{p,t}(T_{z-1,t} - T_{z,t}) \qquad\qquad \forall\, h, p_h \qquad\qquad (4.17)$$

and

$$HC_{z,g,p_g,t} = f_{g,t}C_{p,t}(t_{z-1,t} - t_{z,t}) \qquad\qquad \forall\, g, p_g \qquad\qquad (4.18)$$

where T_{z-1} and T_z are the hot-scale temperatures at the top and the bottom lines defining the zth interval and t_{z-1} and t_z are the corresponding cold scales.

Next, for each discretization of the process hot and cold streams, a binary integer variable is introduced. These binary variables are referred to as $I_{h,p_h,t}^{hot}$ and $I_{g,p_g,t}^{cold}$ for the hot and the cold discretization, respectively. The binary variable is assigned a value of one when the discretization exists and zero when it does not, i.e.
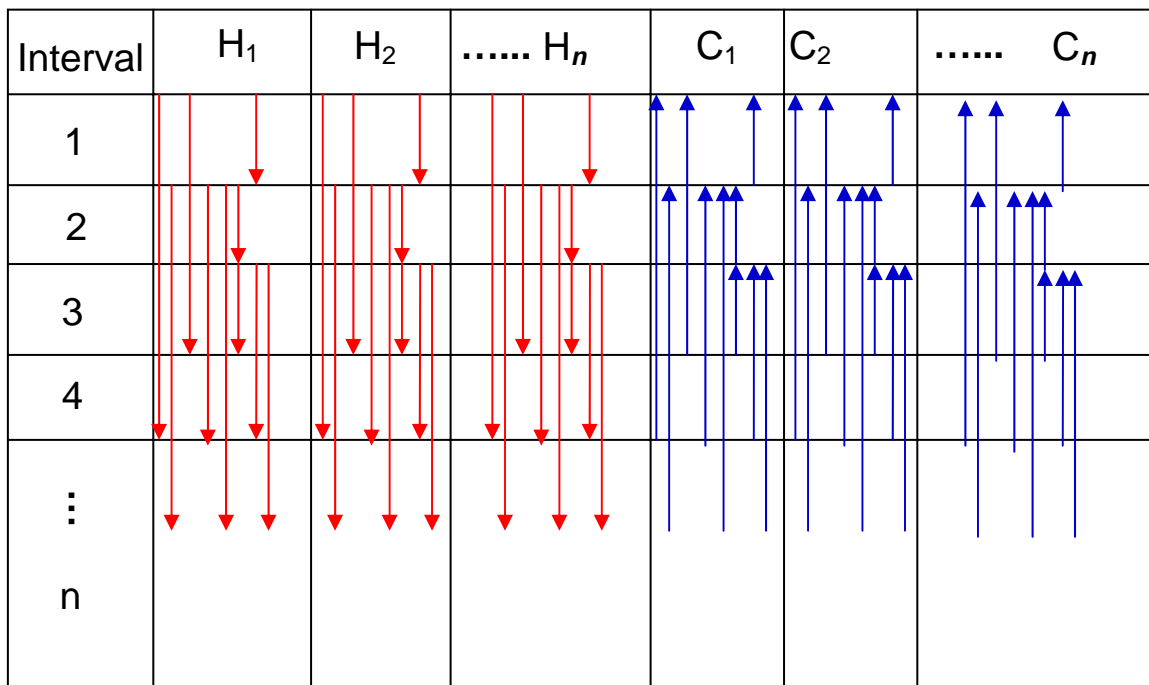
Figure 4.5. TID diagram for discretized supply and target temperatures

$$F_{h,p_h,t} \leq I^{hot}_{h,p_h,t} * U \tag{4.19}$$

where U is a large enough number (upper bound on the flowrate). Similarly, for the cold streams:

$$f_{g,p_g,t} \leq I^{cold}_{g,p_g,t} * U \tag{4.20}$$

To ensure that only one discretization exists for each hot and cold stream, binary integer variables are introduced and defined by the following constraints:

$$\sum_{p_h} I^{hot}_{h,p_h,t} = 1 \qquad\qquad \forall h \tag{4.21}$$

$$\sum_{p_g} I^{cold}_{g,p_g,t} = 1 \qquad\qquad \forall g \tag{4.22}$$

By summing up the heating loads and cooling capacities, we get:

$$HH^{total}_{z,t} = \sum_h \sum_{p_h} HH_{z,h,p_h,t} \qquad\qquad \forall z \tag{4.23}$$

$$HC^{total}_{z,t} = \sum_g \sum_{p_g} HC_{z,g,p_g,t} \qquad\qquad \forall z \tag{4.24}$$

Now, the heating and cooling utilities are incorporated in the model. For temperature interval z, the heat load of the yth heating utility is given by:

$$HHU_{y,z,t} = FU_{y,t} Cp_y (T_{z-1,t} - T_{z,t}) \tag{4.25}$$

where FU_y is the flowrate of the yth heating utility. The sum of all heating loads of the heating utilities in interval is expressed as:

$$HHU_{z,t}^{total} = \sum_y HHU_{y,z,t} \tag{4.26}$$

The total heating loads of the yth utility in HEN may be evaluated by summing up the individual heat loads over intervals:

$$QH_{y,t} = \sum_z HH_{y,z,t} \tag{4.27}$$

Similarly the cooling capacity of the vth cooling utility in the zth interval is calculated as follows:

$$HCU_{v,z,t} = fU_{v,t} Cp_v (t_{z-1,t} - t_{z,t}) \tag{4.28}$$

where $fU_{v,t}$ is the flowrate of the vth cooling utility. The sum of all cooling capacities of the cooling utility is expressed as:

$$HCU_{z,t}^{total} = \sum_v HCU_{v,z,t} \tag{4.29}$$

The total cooling capacity of the uth utility in the HEN may be evaluated by summing up the individual cooling loads over intervals:

$$QC_{v,t} = \sum_z HC_{v,z,t} \tag{4.30}$$

For the zth temperature interval, one can write the following heat balance equation;

$$HH_{z,t}^{total} - HC_{z,t}^{total} = HHU_{z,t}^{total} - HCU_{z,t}^{total} + r_{z-1,t} - r_{z,t} \tag{4.31}$$

where:

$$r_{0,t} = r_{int,t} = 0$$

$$r_{z,t} \geq 0, z = 1, 2, ..., n_{\text{int}} - 1$$

$$FU_{y,t} \geq 0$$

$$FU_{v,t} \geq 0 \tag{4.32}$$

The flowrate assigned from j_u to the pth product stream is $p_{j_u,p,t}$. The flowrate of the pth product in period t is described by:

$$P_{p,t} = \sum_u \sum_j p_{j_u,p,t} \qquad\qquad \forall p,t \tag{4.33}$$

The design and operating constraints for the process units are:

$$d_u^{\min} \leq d_{u,t} \leq d_u^{\max} \tag{4.34}$$

and

$$o_u^{\min} \leq o_{u,t} \leq o_u^{\max} \tag{4.35}$$

The product demand and composition constraints are expressed as:

$$P_{p,t} \leq P_{p,t}^{Demand} \tag{4.36}$$

The HEN targeting formulation can now be coupled with the previously-developed model for design and scheduling. The objective function of maximizing the gross profit of the process is given by:

Maximize Gross Profit =

$$\sum_t \sum_p C_{p,t}^{product} * P_{p,t} - \sum_t POC_t - \sum_t \sum_z \left(C_{hot.t} * HHU_z^{total} - C_{cold,t} * HCU_z^{total} \right) \qquad (4.37)$$

where $C_{p,t}^{product}$ is the unit selling price of product p during period t, POC_t represents the

plant operating cost (e.g., feedstocks, utilities, etc.) during period t, $C_{hot.t}$ is the price of

the heating utility and $C_{cold,t}$ is the price of cooling utility during period t.

The foregoing model constitutes the optimization program for the problem. If the

process model is linear, then the combined formulation for the design, scheduling and

HEN targeting is a mixed-integer linear program (MILP). Otherwise, it becomes a

mixed-integer nonlinear program (MINLP). The solution identifies the optimal

scheduling, process modifications, and the optimum target of heating and cooling

utilities. Next, the HEN configuration has to be synthesized to be flexible enough to

accommodate the changes associated with the anticipated schedules. This is shown in the

next section.

4.4.3 Synthesis of flexible HEN (MILP)

In order to have a uniform design for all periods, the following is a methodical way for

matching the streams and designing the HEN. It is based on the work of El-Halwagi and

Manousiouthakis[47] which is developed for MEN substreams and work of Papoulias and

Grossmann (1989) for a base-case HEN.[40] However, the formulation is extended in this

work to account for the multiperiod flexibility. Mathematical programming is used to

formulate the matching and confirm that matching is working for all periods a long the time horizon (time$_h$). The program follows the pinch rule where no heat is exchanged across the pinch. So the problem can be discomposed into two subnetworks, one above the pinch and one below the pinch. The subnetworks will be denoted as an index, m, is defined as *1* for above pinch and *2* for below pinch. The objective function is to minimize number of heat exchangers.

$$\min \sum_{m=1,2} \sum_{i \in HP} \sum_{j=CP} E_{i,j,m} \tag{4.38}$$

s.t.

Heat balance for hot stream around the temperature intervals:

$$\delta_{i,z,t} - \delta_{i,z-1} + \sum_{j \in CP} Q_{i,j,z,t} = Q_{i,z,t}^{H} \qquad i \in HP, z \in SN_m, m = 1,2 \tag{4.39}$$

Heat balance for each cold stream around the temperature intervals:

$$\sum_{i \in HP} Q_{i,j,z,t} = Q_{j,z,t}^{C} \qquad j \in CP, z \in SN_m, m = 1,2 \tag{4.40}$$

Matching of loads:

$$\sum_{z \in SN_m} Q_{i,j,z,t} - U_{i,j,z,t} E_{i,j,m} \leq 0 \qquad i \in HP, j \in CP, m = 1,2 \tag{4.41}$$

Non-negative residuals:

$$\delta_{i,z,t} \geq 0 \qquad i \in HP, z \in SN_m, m = 1,2 \tag{4.42}$$

Non-negative loads:

$$Q_{i,j,z,t} \geq 0 \qquad i \in HP, j \in CP, z \in SN_m, m = 1,2 \tag{4.43}$$

Binary integer variables for matching streams:

$$E_{i,j,m} = 0/1 \qquad i \in HP, j \in CP, m = 1,2 \tag{4.44}$$

The solution of this mathematical program identifies the proper matches for minimum number of heat exchangers. The identified network configuration is flexible enough to accommodate the potential variations associated with the anticipated schedule. The result of the foregoing procedure is the determination of the design modification that incorporates process schedules and maximum extent of heat integration. If the objective is not to reach maximum extent of heat integration, then one can slightly modify the above procedure to establish a tradeoff between the extent of heat integration and overall cost. This is accomplished by iteratively increasing the extent of heating and cooling utilities (starting with the previously determined targets), synthesizing the flexible HEN, evaluating its cost, and conducting a cost-benefit analysis to select the final configuration.

4.5 Case study: fluid catalytic cracking, operation, scheduling, and HEN design

Scheduling is an important activity in refineries. Most of the research contributions in refinery scheduling have focused on responding to market demands to maximize profit. For instance, in the US, the demand for gasoline usually increases during summer while the demand for diesel typically increases in winter. Various process units (e.g., the fluid catalytic cracker FCC) are operated differently along with pooling and blending to obtain the desired products. Usually the changes implemented on the operation of the refinery due to different demand will not affect heat exchanger network which is

designed for high heating utilities and cooling capacities. A trade-off between the heat exchanger network expenses and the profits anticipated can be established beforehand so that the design of HEN is based on the optimal tradeoff between the scheduling of production all over the time horizon for all periods.

In this case study, the heating utility for the feed which affects the operation of the process, hence the yield, is considered for design. On the other hand, the scheduling of production to satisfy the market demand is considered too. Two periods are studied which represents two level of productions and based on that it will compete simultaneously with the HEN design.

Fig. 4.6 illustrates a schematic figure for HEN in typical FCC unit. There are many parameters that can be studies in HEN that affects the production, hence the performance of FCC unit. One important parameter is the feed preheating temperature which refers to the temperature of the feed supplied to the riser.
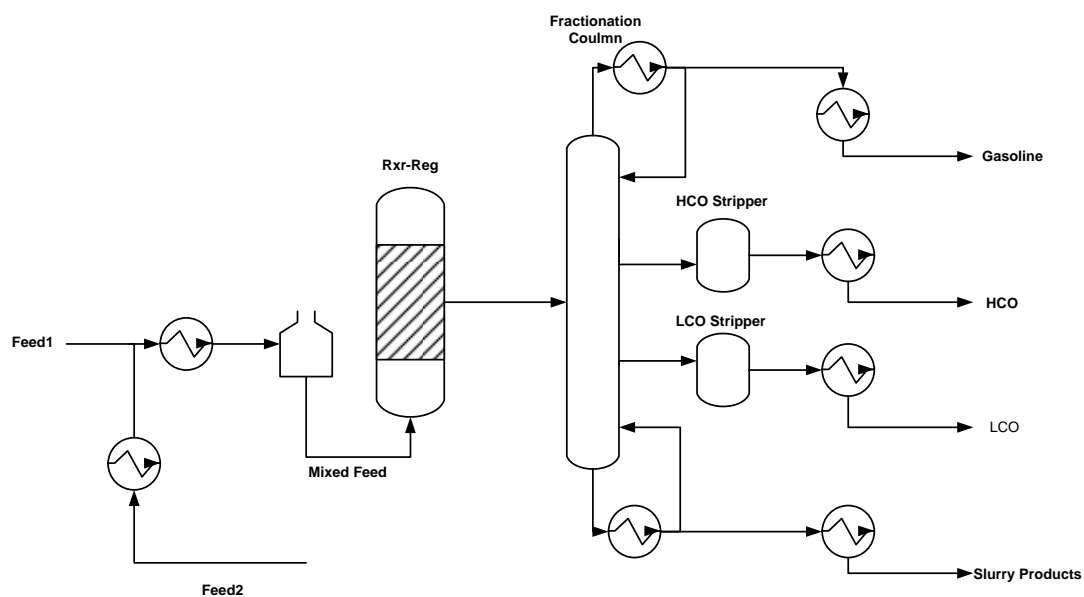
Figure 4.6. HEN of FCC unit (base case)

In a heat-balanced commercial operation, increasing the temperature of the feed to a cracking reactor reduces the heat that must be supplied by combustion of the coked catalyst in the regenerator. Feedstock preheating is usually supplied by heat exchange with hot product streams, a feed preheater, or both. When feed rate, recycle rate, and reactor temperature are held constant as feed preheat is increased, the following changes in operation result:

1. The catalyst/oil ratio (catalyst circulation rate) is decreased to hold the reactor temperature constant.

2. Conversion and all conversion-related yields, including coke, decline owing to the decrease in catalyst/oil ration and severity.

3.   The regenerator temperature will usually increase. Although the total heat released in the regenerator and the amount of air required by the regenerator is reduced by the lower coke yield, the lower catalyst circulation usually over-rides this effect and results in an increase in regenerator temperature.

4.   As a result of the lower catalyst circulation rate, residence time in the stripper and overall stripper efficiency are increased, liquid recovery is increased, and a corresponding decrease in coke usually results.

Advantages is usually taken of these feed preheat effects, including the reduced air requirement, by increasing the total feed rate until coke production again requires all of the available air.[48]

The performance equations predicting the yields of various components of FCC are taken from literature.[39, 49] For instance the gasoline yield correlation is:

$$Gasoline = a(\frac{H}{C+S} + \log f_c T) + b(M_{eff}) + c(N_B) + d(C/O) + e(T) + f(Conversion) \quad (4.45)$$

The other components yields are as follows:

$$LCO = 59.73 - 0.55(Conversion)$$
$$HCO = 100 - LCO - Conversion$$

(4.46)

Table 4.1 shows tabulated values for hot and cold streams flows and temperatures in a base case unit.[50] This base case optimal HEN design is conducted using process integration tools. The minimum requirements for the cooling and heating utilities are:

Q_H^{min} =11.11 MW

Q_C^{min} =57.75 MW

with utilities TAC of $2.73 MM.

Now, the tradeoff between the production and HEN design can be shown when increasing the production due to changes in market demands for gasoline where we can keep same T_{feed} and have the production increase or manipulating the feed preheating temperature to give the proper tradeoff between scheduling of the production and HEN configuration.

Table 4.1. FCC-HEN Base Case [50]

Stream	FCp(MW/ºC)	T^s(ºC)	T^t(ºC)	ΔH(MW)
H1	0.184839	343	281	11.46
H2	0.1819355	343	281	11.28
H3	0.3445	281	232	16.88
H4	0.0082	343	121	1.82
H5	0.0057	263	49	1.23
H6	0.0195238	202	97	2.05
H7	0.0256	97	49	1.23
H8	0.0662295	254	193	4.04
H9	0.0571	193	179	0.8
H10	0.056569	179	77	5.77
H11	0.125	163	157	0.75
H12	0.13	157	49	14.04
H13	0.3563	111	60	18.17
H14	0.2283	60	37	5.25
C1	0.124565	182	274	11.46
C2	0.0757047	125	274	11.28
C3	0.2365	274	360	20.34
C4	0.082	51	76	2.05
C5	0.0824	76	125	4.04

For an increase in the feed to 50000BPD for fixed temperatures and flow case, we get an annual profit of $16.39 MM while if we allow the tradeoff between the heat integration of FCC as well as the production scheduling then we can get the optimal solution of profit of $17.20 MM (Table 4.2). Although, there is a decrease in the gasoline production in the optimal case, we still can earn more profit by minimizing the utility consumption.

Table 4.2. Results for FCC-HEN/SCH Case Study

Value	Base Case Period I	New Case Period II	New Case Period II (Optimal)
Feed (BPD)	35000	50000	50000
Gasoline Pdn (BPD)	31859	45456	45277
Q_H^{min} (MW)	11.116	15.88	10.81
Q_c^{min} (MW)	57.754	66.214	66.058
Preheated Feed Temperature (ºC)	360	360	345
Gasoline Profit Annual ($MM)	16.59	23.70	23.61
Utilities Annual Cost ($MM)	2.71	3.67	2.76
Annual Profit ($MM)	11.32	16.39	17.20

4.6 Conclusions

A novel methodology for simultaneous process scheduling and heat integration has been introduced. This approach includes design modifications, heat integration, and anticipated schedules. First, a formulation has been developed to account for the anticipated schedules and heat integration during the design phase. Because of the complexity of the formulation for heat integration with varying flows and temperatures, a new targeting approach has been introduced. It is based on discretizing hot and cold streams into substreams then using integer cuts to select the optimal temperatures and flows. Then, a multiperiod formulation has been developed to insure flexibility of the designed HEN. This approach determines the optimal production while considering heat integration of the process. Trade-off between the two competing objectives has been established in this approach. Finally, a case study of FCC-HEN is solved to illustrate the applicability of the new approach.

CHAPTER V

AN OPTIMIZATION APPROACH TO THE INTEGRATION OF INHERENTLY-SAFER DESIGN AND PROCESS SCHEDULING

5.1 Introduction

The fluctuations in market demands for various products and availability of raw materials require adaptation in production schemes. Process scheduling is one of the most effective approaches to adjusting the type and quantity of products in response to the changes in market conditions. For instance, oil refineries must continuously adjust the product slate to account for seasonal changes in product demand (e.g., gasoline, diesel, heating oils, etc.). Therefore, it is beneficial to include process scheduling expectations during the design and retrofitting activities. In addition to the technical, economic, and environmental objectives of design, it is necessary to consider process safety metrics for appropriate management of hazards. Unfortunately in some occurrences, lack of knowledge, technology, or implementation of process safety has led to tragic incidents. Examples are the Flixborough incident with 28 fatalities[51], the Bhopal incident with more than 2,000 fatalities[51], the Pasadena-Texas explosion with 23 fatalities[51], and the more recent Texas City-refinery explosion which cost the lives of 15 people are several examples of incident. In addition to multiple fatalities and injuries, the loss resulted includes capital loss, lawsuits, decreased stock price, ruined image/brand,

etc.

In order to understand what had happened, what to learn from those incidents and how to improve ours, it is very important to comprehend the term hazard. Adapted from the Center for Chemical Process Safety (CCPS), hazard is defined as physical or chemical characteristic that has the potential for causing harm to people, the environment, or property.[52] It is an intrinsic and the basic properties of the material, cannot be eliminated, and can be released under a certain condition. For example, under the right condition, 10,000 lbs of propane holds the same amount of energy which could be released by 28 tons of TNT. Those energies are inherent to the propane, and cannot be eliminated or changed. The release of that energy will lead to an incident.

There are various ways of accounting for process safety in design. While it may be impossible to completely eliminating risk, the knowledge to find the better methodology and strategy in managing risks becomes prominent. One of the strategies is the application of inherently safer design concept and combines it with process design and optimization during the early stages of design where the degree of freedom in process modification is still high [53]. While integrating inherently safer design into process design and optimization was attempted without considering abrupt changes that may occur due to different demand rates for production and or new regulations imposed, process scheduling is not considered simultaneously in that approach.[54]

 The objective of this chapter is to introduce a procedure for the integration of inherently safer design techniques with process scheduling. Expected variations in production scheduling are included early enough in the design phase. Additionally, safety metrics are used in screening and selecting design alternatives. Safety level is measured by quantifying the hazards belong to the process using the Dow Fire and Explosion Index (F&EI) methodology. The linkage between each of the optimization results and its associated safety level will provide better visualization regarding safe the processes are during the process changes or modification. This will add knowledge to the related engineers and decision makers to when dealing with process scheduling. The following sections provide an overview of two important subjects: (a) inherently safer design, and (b) Dow Fire and Explosion Index.

5.2 Inherently safer design

The term "Inherently Safer Design" started appearing in safety discussion after Trevor Kletz introduced this concept as an identifiable element of process safety in one of his most famous phrases "What You Don't Have Can't Leak". Inherently safer design infers the elimination of hazards as much as possible out of a chemical or physical process permanently as opposed to using layers of protection. There are four primary principles of inherently safer design concept proposed by Kletz (1991)[55]:

1. Intensification – to reduce the inventories of hazardous materials as more inventory of hazardous chemicals mean more hazards.

2. Substitution – to use less hazardous materials in the process.

3. Attenuation – to operate a process at less dangerous process conditions (pressure, temperature, flow rate, etc).

4. Limitation of effects – to design the process according to the hazards offered by the process in order to reduce the effects of the hazards.

While the concept will result in lower hazards and lower requirement for providing layers of protection, the concept also affects the production rate. Therefore, it is a challenge for engineers to establish tradeoffs between the technical and economic objectives of the design and inherent safety considerations.[56]

5.3 Dow's fire and explosion index (F&EI)

The Dow Fire and Explosion Index (F&EI) is the most widely used hazard index and has been revised six times since 1967. The latest edition (7th edition), which was published in 1994, is employed in this research. AIChE (1994) describes F&EI as the quantitative measurements which are based on historical data, energy potential of the materials under evaluation, and the extent to which loss prevention practices are currently applied.[57] F&EI is valuable as a guide to decide whether it is necessary for process designers to

consider other less hazardous materials and/or other process routes.[58] Moreover, F&EI helps engineers to be aware of the hazards in each process unit while making important decisions in reducing the severity and/or the probability of the potential incident.

F&EI relates process hazards to process information (i.e., process conditions, materials, type of equipment, and other characteristics of the process) in terms of "penalties". Not every penalty is applicable to the process under evaluation thus that careful judgment should be made and a discussion with expert is recommended in order to obtain the right index. F&EI is based on the "worst case" which means only the most hazardous material in the evaluated process are assessed at a time in a specific operational state (i.e., start up, shut down, and normal operation). For example, when a process unit has hazards posed by three different flammable liquids, F&EI evaluation must be determined based on all flammable liquids. Then, the higher F&EI between the three evaluations is used as the worst case and considered as the hazards of the process. This is due to the fact that the while the worst case might not be the first event during the incident, any initiating event could provides condition where the worst case could happen. This concept helps the designers and decision makers to prepare for the worst case.[59]

The details of procedures, guidelines, and equations to determine the penalties and the method is provided in *Dow's Fire and Explosion Hazard Classification Guide* 7th Edition which was published in 1994 by American Institute of Chemical engineers (AIChE).

F&EI calculation is composed of steps as illustrated in Fig. 5.1 and the following documents are required[57]:

1.   Plot of the plant/process and/or process flow sheet

2.   Replacement cost data for the installed process equipment under study

3.   Fire and Explosion Index Hazard Classification Guide, 7th Edition

4.   Fire and Explosion Index, Loss Control Credit Factors, Process Unit Analysis Summary, and Manufacturing Unit Risk Analysis Summary Form.

The method starts with the selection the process unit to be evaluated. The process unit that could pose a significant impact in a potential incident should be overlooked. Therefore, these important factors must be considered when selecting the process units under evaluation (AIChE, 1994):

- Chemical energy potential (Material factor).

- Quantity of hazardous material.

- Business interruption and capital density (dollars per ft^2).

- Operating pressure and temperature.

- History of fire and explosion incident related to the same type of process unit.

- The importance of the process unit to the whole process.
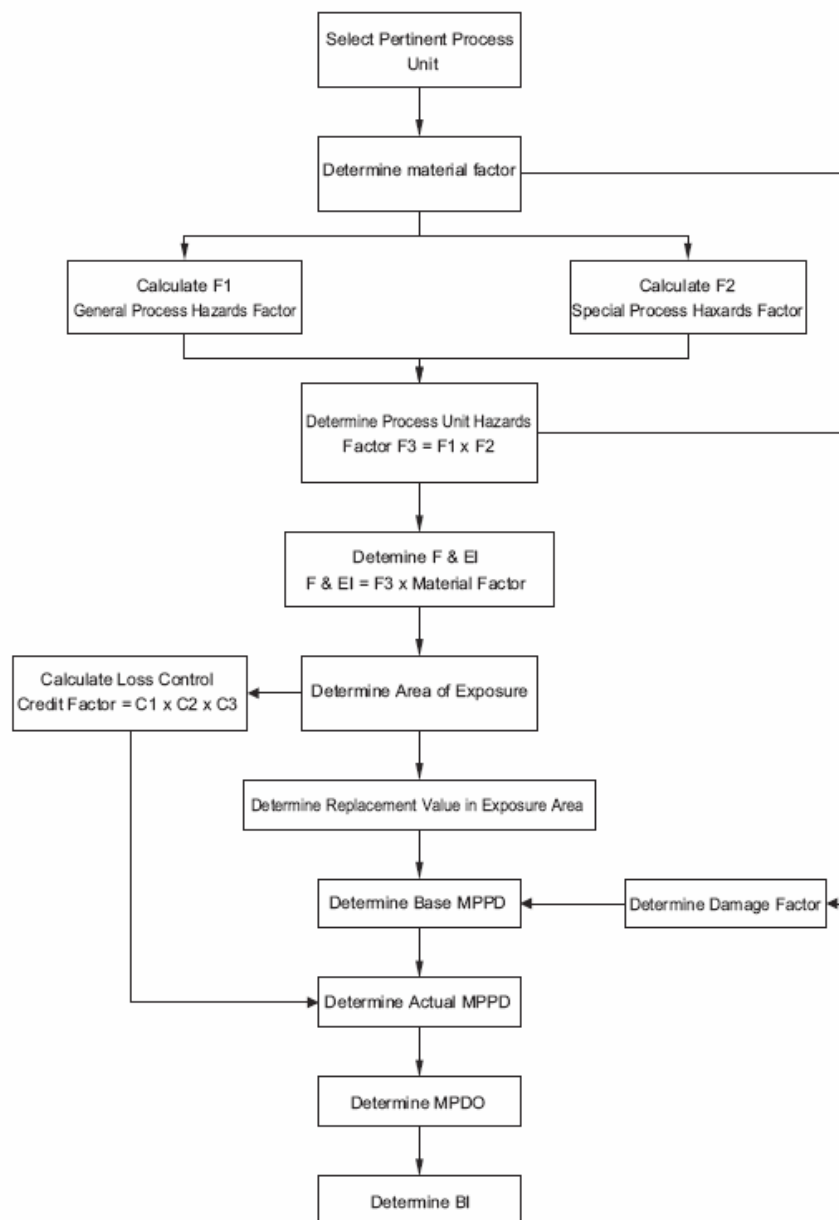
Figure 5.1. Dow's fire and explosion index calculation procedure [57]

The F&EI has two major components, Process Unit Hazards Factor (F_3) and Material

Factor (MF). F3 consists of General Process Hazards (F1) and Special Process Hazards

(F2).[57] Definitions of these terms are as follows:

- Material factor is the intrinsic rate of potential energy release caused by fire or explosion produced by combustion or chemical reaction F_3 consists of General Process Hazards (F_1) and Special Process Hazards (F_2).

- General process hazard items have historically played an important role in determining the magnitude of potential incidents, and are applicable to most process conditions.

- Special process hazards are the factors that play an important role in increasing the probability of a potential incident and comprise of the specific process condition that historically contribute to the major causes of fire and explosion incidents.

The F&EI is determined by the Equations (5.1) and (5.2)[57]:

$$F_3 = F_1 \times F_2 \tag{5.1}$$

$$F \& EI = MF \times F_3 \tag{5.2}$$

While it may be impossible to completely eliminating risk, the knowledge to find the better methodology and strategy in managing risks becomes prominent. One of the strategies is the application of inherently safer design concept and combine it with process design and optimization during the early stages of design where the degree of

freedom in process modification is still high.[60] While integrating inherently safer design into process design and optimization was attempted without considering abrupt changes that may occur due to different demand rates for production and or new regulations imposed, process scheduling is not considered simultaneously in that approach.

Currently optimization is performed as an attempt to enhance the process design and the operating conditions of equipment to achieve the largest production, the greatest profit, minimum production cost, the least energy usage, etc. Safety studies are usually performed after process design and optimization and are usually conducted in an iterative procedure. Since there is typically not a single "correct" or "safe" solution, there is a need to establish "tradeoffs" especially when cost benefit analysis is involved along with safety. The objective of safety studies is to reduce the frequency and the magnitude of hazardous events as long as economically practicable. All design engineers must be aware of those hazards and make sure that the design is at an acceptable risk level. Safety is a focal point of any process design that must be balanced with many other factors such as economics, practicality, and technology, market, etc.[61] Safety must be integrated in all aspects of design starting from conceptual to detailed design. Therefore, safety must be integrated into the overall design procedure and presented alongside with other objectives and constraints.

Suardin et al. (2007) integrated inherently safer design concept into process design and optimization using well-accepted hazard identification method. The integration was

conducted at the early design stages where it is most effective since there are a lot of degrees of freedom for making changes. With this integration, illustrated that safety parameters have active role and give strong feedback to the basic process design strategy.[60]

In an attempt to exploit the interactions between the process operation and the process proper safety metrics should be established in mathematical form to be optimized within the production and the process operation scheduling. Suardin et al. (2007) had implemented F&EI metrics to optimize the inherently safer designs. However, no attempt is done on the tradeoff between the scheduling of the process and its inherently safer design simultaneously.[60]

As stated earlier in this chapter that the objective of this work is to introduce a procedure for the integration of inherently safer design techniques with environmental objectives and process scheduling. Expected variations in production scheduling are included early enough in the design phase. Additionally, safety metrics are used in screening and selecting design alternatives. Safety level is measured by quantifying the hazards of the process using the Dow F&EI. An optimization approach is developed to account for potential design and scheduling options while incorporating safety and environmental objectives. The proposed approach will optimize the process by establishing a pareto curve that demonstrates the tradeoff between the inherently safer design and various production and operation scheduling.

5.4 Problem statement

The problem to be addressed by this work is stated as follows: Given a continuous process with:

- A set of unit operations U= {u|u= 1, 2, …, N_u}. Each process unit, u, has a set of input streams $INPUT_u = \{i_u \mid i_u = 1,2..., N_u^{in}\}$ and a set of output streams $OUTPUT_u = \{j_u \mid j_u = 1,2..., N_u^{out}\}$. An input stream, i_u, has a flowrate, F_{i_u}, and the composition of component q , $X_{i_u,q}$, while an output stream , j_u, has a flowrate, G_{j_u}, and the composition of component q, $Y_{j_u,q}$.

- A set of environmental discharges for the process: WASTES = {w|w is a waste stream leaving the process and is subject to environmental regulations}.

- A set of environmental regulations governing the composition and/or load of the pollutants leaving the plant, i.e.

$$Z_{w,q} \leq Z_{w,q}^{env} \tag{5.3}$$

and

$$W_w Z_{w,q} \leq Load_{w_u q}^{env} \tag{5.4}$$

where $Z_{w,q}$ is the composition of the qth pollutant in the wth waste stream and Z_w is the flowrate of the wth waste stream.

- A set of candidate environmental technologies (environmental management units: "EMUs"): EMU={v|v= N_u+1, N_u +2, …, N_u + N_v} that may be added to

the process to reduce environmental impact and comply with environmental regulations of the process.

- Safety metrics that is used to evaluate various design options to control the wastes to comply with the environmental regulations. The safety metrics designate each EMU options with respect to safety by safety index. The value of the safety index provides the design another dimension to consider simultaneously with the scheduling of process operation, choice of EMU and process safety. F&EI is used to quantify the safety metrics of the process where the expected schedules have designated values of F&EI based on operation mode and design of the process.

- A given decision-making time horizon (t_h). Within this horizon, the variations in the market conditions are anticipated and expressed in terms of time-dependent changes in quantities and prices of supply (e.g., feedstocks, utilities, etc.) and demand (e.g., products and byproducts).

It is desired to develop a systematic procedure that can determine production schedules, process modifications, and EMUs selection and design so as to maximize the process profit. On the other hand, this procedure goes along simultaneously with consideration of changes in process safety. The final decisions related to process scheduling, design, process modifications, EMUs selection and design is linked with inherently safer design simultaneously to have the proper tradeoff between all multiobjectives mentioned above.

5.5 Approach

To simplify the problem, the following assumptions are introduced:

- The decision-making time horizon is discretized into N_t periods leading to a set of operating periods: PERIODS = $\{t|t= 1,2, \ldots,N_t\}$. Within each time period, the process operates in steady-state mode. Also, it is only allowed to have intra-period integration (i.e., no streams are stored, integrated, and exchanged over more than one period). In selecting the number and duration of the periods, one has to strike proper balance between capturing the market variations, significance to the process, and computational efforts.

- Process modifications will be limited to two alternatives:

  a) Manipulation of certain design and operating variables for each unit within permissible ranges, i.e.,

  $$d_u^{\min} \leq d_u \leq d_u^{\max} \tag{5.5}$$

  and

  $$o_u^{\min} \leq o_u \leq o_u^{\max} \quad \forall u . \tag{5.6}$$

This assumption implies that the design of the current process is flexible enough to produce any of the anticipated production schedules and that there is no economic incentive to add a process unit or reroute process streams.

b) Addition of new EMUs (whose number, design, and placement will be determined as part of the solution procedure).

5.5.1 Structural representation

In order to embed potential configurations of interest, a source-sink structural representation of the problem is adopted. Outputs from process units are split into fractions and assigned to inputs of the EMUs. Each EMU discharges several outputs. An output from the EMU is split and distributed into fractions; some of which are discharged as wastes while the others return back to the process to be assigned to process inputs. The flows from process units to EMUs and from EMUs to wastes and back to the process are unknown and to be determined as part of the solution. Fig. 5.2 provides a schematic of the structural representation.
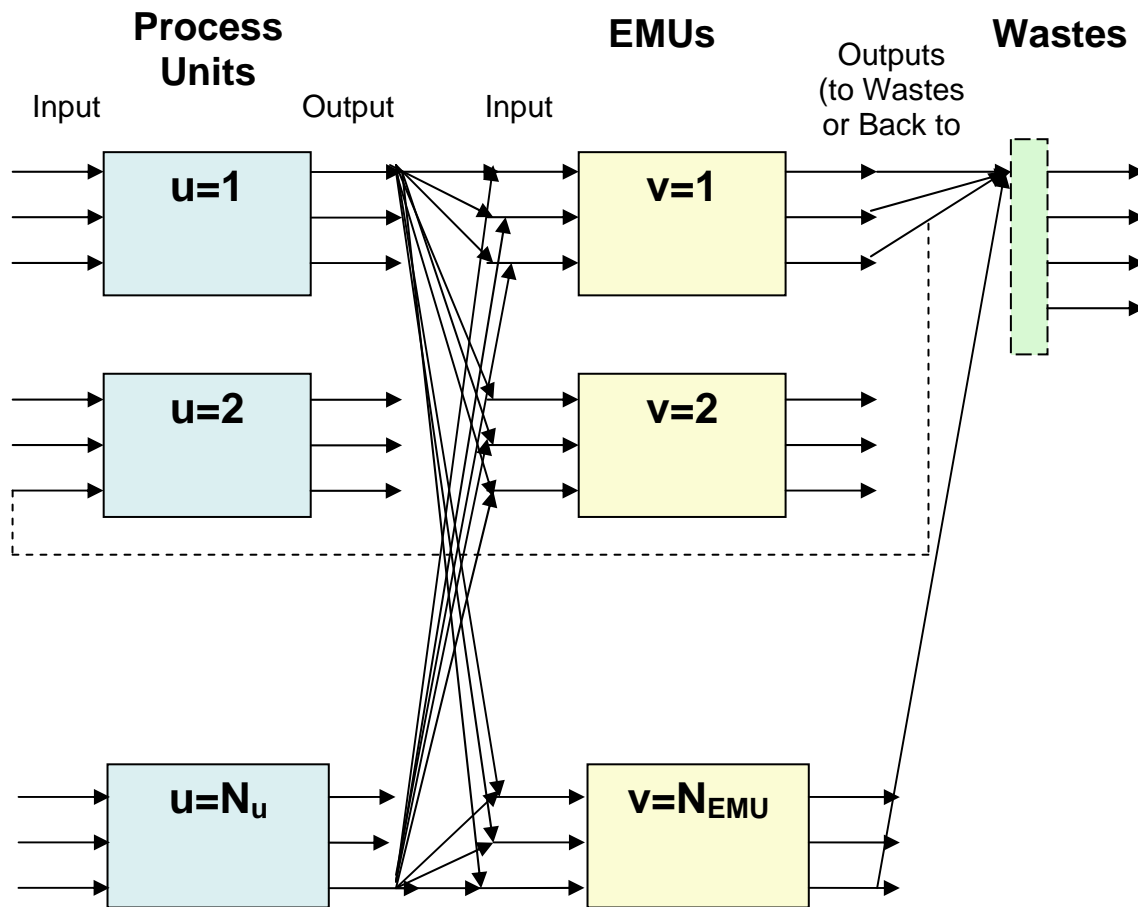
Figure 5.2. Structural representation of the problem

Now, we proceed with the modeling aspects. The mass balance equation for unit u during period t is given by:

$$\sum_{j_u} G_{j_u,t} = \sum_{i_u} F_{i_u,t} \qquad \forall u,t \qquad (5.7)$$

and the qth component balance for unit u during period t is expressed as:

$$\sum_{j_u} G_{j_u,t} * Y_{j_u,q,t} = \sum_{i_u} \left(F_{i_u,t} * X_{i_u,q,t} + \text{Net\_Gen}_{u,q,t} \right) \qquad \forall q,u,t \tag{5.8}$$

where the additional index, t, in the flowrates and compositions refers to the time period over which these flowrates and compositions are considered. Additionally, the performance model for unit u at period t is expressed as by a set of algebraic equations represented by:

$$(G_{j_u,t}, Y_{j_u,q,t} : j_u = 1,2,...,N_u^{out} \text{and} q) = f_u(F_{i_u,t}, X_{i_u,q,t} : i_u = 1,2,...,N_u^{in} \text{and} q, d_{u,t}, o_{u,t}) \tag{5.9}$$

Let the flowrate assigned from source j_u to destination i_v during period t be referred to as g_{j_u,i_v}. The flowrate from the j_u^{th} source goes to other units, to EMUs, and to final product streams. Therefore, the material balance for the splitting of source j_u is given by:

$$G_{j_u,t} = \sum_u \sum_{i_u} g_{j_u,i_u,t+} \sum_v \sum_{i_v} g_{j_u,i_v,t+} \sum_p P_{j_u,p,t} \qquad \forall u,j_u,t \tag{5.10}$$

where $p_{j_u,p,t}$ is the flowrate assigned from j_u to the pth product stream.

The flowrate of the pth product in period t is described by:

$$P_{p,t} = \sum_u \sum_j p_{j_u,p,t} \qquad \forall p,t \tag{5.11}$$

Then, for the mixing of the split flowrate before the i_v^{th} input to the vth EMU, the material balance and the qth component balance during period t are given by:

$$F_{i_v,t} = \sum_u \sum_{j_u} g_{j_u,i_b} \qquad \forall v,i_v,t \tag{5.12}$$

$$F_{i_v,t} * X_{i_v,q,t} = \sum_u \sum_{j_u} g_{j_u,i_b} * Y_{j_u,q,t} \qquad \forall v,i_v,q,t \tag{5.13}$$

The mass balance equation for EMU, v, during period t is given by:

$$\sum_{j_v} G_{j_v,t} = \sum_{i_v} F_{i_v,t} \qquad \forall v,t \qquad\qquad (5.14)$$

The qth component balance for EMU,v, during period t is expressed as:

$$\sum_{j_u} G_{j_u,t} * Y_{j_v,q,t} = \sum_{i_v} \left(F_{i_v,t} * X_{i_v,q,t} + Net\_Gen_{v,q,t} \right) \qquad \forall q,v,t \qquad (5.15)$$

and the unit performance equation for the vth EMU is expressed as:

$$(G_{j_v,t}, Y_{j_v,q,t} : j_v = 1,2,..., N_v^{out} \text{ and } q = 1,2,...N_{Components})$$

$$= f_v (F_{i_v,t}, X_{i_v,q,t} : i_v = 1,2,..., N_v^{in} \text{ and } q = 1,2,...N_{Components}, d_{v,t}, o_{v,t}) \qquad \forall v,i_v,q,t \qquad (5.16)$$

There are N_w waste streams leaving the process. Each output stream, j_v, from an EMU unit is split into several flowrates; some are assigned to waste outlets and some are recycled back to the process to enter process units. The flowrate assigned to the wth waste stream is referred to as $w_{j_v,w,t}$ and the flowrate recycled back to the process to the i_u^{th} input of the uth unit is described by $r_{j_v,i_u,t}$. Therefore, the material balance for the splitting of the j_v^{th} stream is given by:

$$G_{j_v,t} = \sum_w w_{j_v,w,t} + \sum_u \sum_{i_u} r_{j_v,i_u,t} \qquad \forall v,j_v,t \qquad (5.17)$$

The flowrate of the wth waste stream during the tth period is given by:

$$W_{w,t} = \sum_v \sum_{j_v} w_{j_v,w,t} \qquad \forall w,t \qquad (5.18)$$

and the qth component material balance for the wth waste stream is given by:

$$W_{w,t} * Z_{w,q,t} = \sum_{v} \sum_{j_v} w_{j_v,w,t} * Y_{j_v,q,t} \qquad\qquad \forall w,q,t \qquad\qquad (5.19)$$

The environmental regulations for the wth waste stream and the qth pollutant are described by:

$$Z_{w,q,t} \leq Z^{env}_{w,q,t} \qquad\qquad (5.20)$$

and

$$W_{w,t} * Z_{w,q,t} \leq Load^{env}_{w,q,t} \qquad\qquad (5.21)$$

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

$$d_u^{min} \leq d_{u,t} \leq d_u^{max} \qquad\qquad (5.22)$$

$$d_v^{min} \leq d_{v,t} \leq d_v^{max} \qquad\qquad (5.23)$$

$$o_u^{min} \leq o_{u,t} \leq o_u^{max} \qquad\qquad (5.24)$$

and

$$o_v^{min} \leq o_{v,t} \leq o_v^{max} \qquad\qquad (5.25)$$

The product demand and composition constraints are expressed as:

$$P_{p,t} \leq P^{Demand}_{p,t} \qquad\qquad (5.26)$$

The flowrate and composition constraints for the i_u^{th} input to the process unit are given by:

$$F_{i_u}^{min} \leq F_{i_u,t} \leq F_{i_v}^{max} \qquad\qquad (5.27)$$

and

$$X^{\min}_{i_u,q} \leq X_{i_u,q,t} \leq X^{\max}_{i_u,q} \tag{5.28}$$

The flowrate and composition constraints for the $i_v{}^{th}$ input to the vth EMU are given by:

$$F^{\min}_{i_v} \leq F_{i_v,t} \leq F^{\max}_{i_v} \tag{5.29}$$

and

$$X^{\min}_{i_v,q} \leq X_{i_v,q,t} \leq X^{\max}_{i_v,q} \tag{5.30}$$

The objective function is given by:

$$\text{Maximize gross profit} = \sum_t \sum_p C^{product}_{p,t} * P_{p,t} - \sum_t POC_t - TAC^{EMU} \tag{5.31}$$

where $C^{product}_{p,t}$ is the unit selling price of product p during period t, POC_t represents the plant operating cost (e.g., feedstocks, utilities, etc.) during period t, and the term TAC^{EMU} is the total annualized cost of the environmental management system which is defined as the sum of the annualized fixed costs (AFC) and the environmental annual operating cost (EOC) and is expressed as:

$$TAC^{EMU} = \sum_v I_v * AFC_v + \sum_t \sum_v EOC_{v,t} \tag{5.32}$$

where I_v is a binary integer variable designating the presence or absence of the vth EMU and is determined through the following constraint:

$$\sum_{i_v} F_{i_v,t} \leq F^U_v * I_v \qquad \forall t \tag{5.33}$$

where F^U_v is an upper bound on the allowable flowrate to unit v. When the flowrate entering unit v is positive, the value of I_v is forced to be one. Otherwise, it takes the value of zero.

The foregoing expressions constitute the mathematical program for the problem. It is a mixed-integer nonlinear program (MINLP) which can be solved to identify the optimal scheduling, process modifications, and selection as well as design of the EMUs. On the other hand, F&EI is used to quantify the safety metrics of the process. In this work, F&EI is the measurement of inherently safer design of the process with respect to the various scheduling alternatives that provide environmental impact minimization. The calculations and related procedures of F&EI where introduced earlier. Fig. 5.3 illustrates the procedure of simultaneous inherently safer design and process scheduling.

5.6 Case study: scheduling and safety for a NO_X management system of a refinery

Scheduling is an important activity in refineries. Most of the research contributions in refinery scheduling have focused on responding to market demands to maximize profit. For instance, in the US, the demand for gasoline usually increases during summer while the demand for diesel typically increases in winter. Various process units (e.g., the fluid catalytic cracker FCC) are operated differently along with pooling and blending to obtain the desired products. It is worth noting as the refinery is operated differently; its environmental emissions will also change. Here, we expand the scope of scheduling to include the need for compliance with environmental regulations including NOx emissions. We also allow for the addition of NOx removal units as needed.

Figure 5.3. Flowchart of process scheduling, environmental control and inherently safer design

There are several technologies that can reduce NOx emissions. Selective catalytic reduction units (SCR) units may be installed in oil refineries in order to assure that NOx is within the acceptable environmental range. NOx emissions fluctuate depending on the mode of operation, product demands or crude properties. Therefore, the design and operation of the SCR is tied to scheduling decisions and vice versa. In this case study, there is an anticipated profile for market demands. The objective is to determine the optimal refinery scheduling along with any process modifications and the number and design and the EMUs (SCR in this case).

Process safety is another of the important parameter in process design. The control of NOx is considered in this study with the process modifications along with different operations of FCC-SCR due to process or environmental regulations changes. The hazards in the control of NOx process is quantified by applying F&EI as the safety metrics. Based on the process conditions, chemical types, reaction types, and inventory involved, a range of F&EI values as a function of flammable material inventory involved in NOx control (Ammonia and Ethanol) is provided. This provides additional information for the decision maker about the hazards involved in the process under evaluation. The next step could include the selection of process with lower hazards or to accept higher hazards with addition cost for mitigation systems, all without sacrificing the business and environmental objectives at the same time. This adds one more layers is to the control of NOx where safety metrics (F&EI) values are considered here with the process modifications along with different operations of FCC-SCR due to process or

environmental regulations changes to have inherently safer design as well. The modeling aspects of FCC-SCR were covered earlier in Chapter III. Here, the main emphasis is upon showing the competition between FCC production schedules, SCR performance and NOx removal efficiency and all of that is linked with the safety of the process. Two SCR systems are considered using two different mass separating agents: ammonia and ethanol.[62, 63]

A Pareto chart is constructed to show the tradeoffs for each scenario. Fig. 5.4 illustrates the effect of variable scheduled production on the safety metrics for the ammonia SCR system. The figure shows as production increases, the need for NOx removal increase and, consequently, more ammonia is used in the SCR which leads to increased hazard. Although more net profit is achieve due to higher scheduled productions, the hazards of the process (quantified by F&EI) also increase as shown in Fig. 5.4. This is due to the fact that the ammonia (which is flammable) poses hazard in terms of energy that can be released at a certain condition and could lead to an incident. This energy is increased as the usage of ammonia increases which leads to increased ammonia inventory.
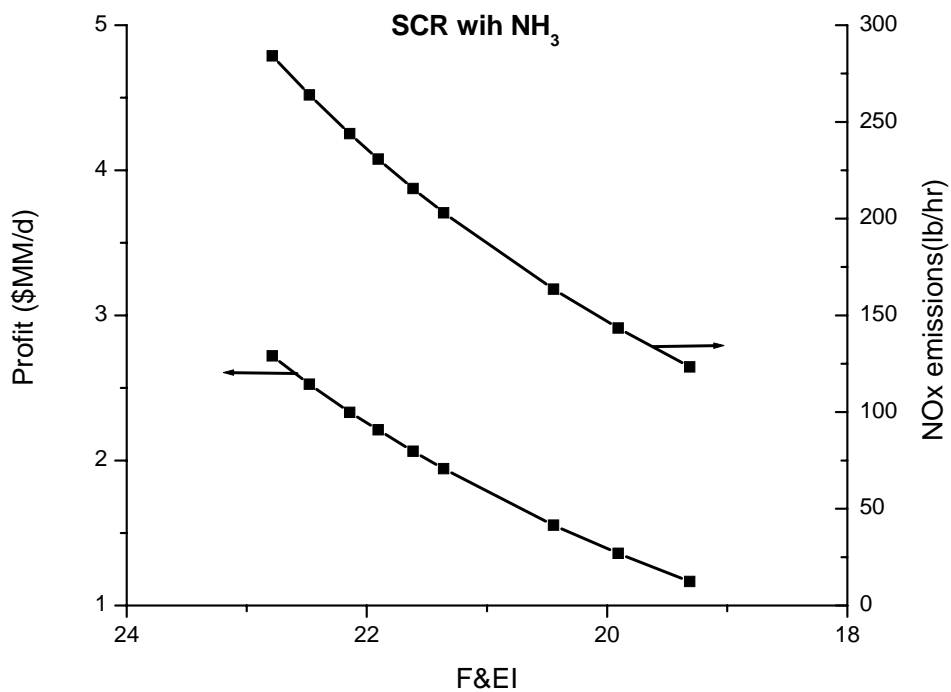
Figure 5.4. Pareto curve for Ammonia-SCR system

Similar trends are observed for ethanol-SCR technology as shown in Fig. 5.5. But, the hazards in this case are much higher than ammonia-SCR technology as a result of the higher energy content of ethanol and its associated flammability hazards.
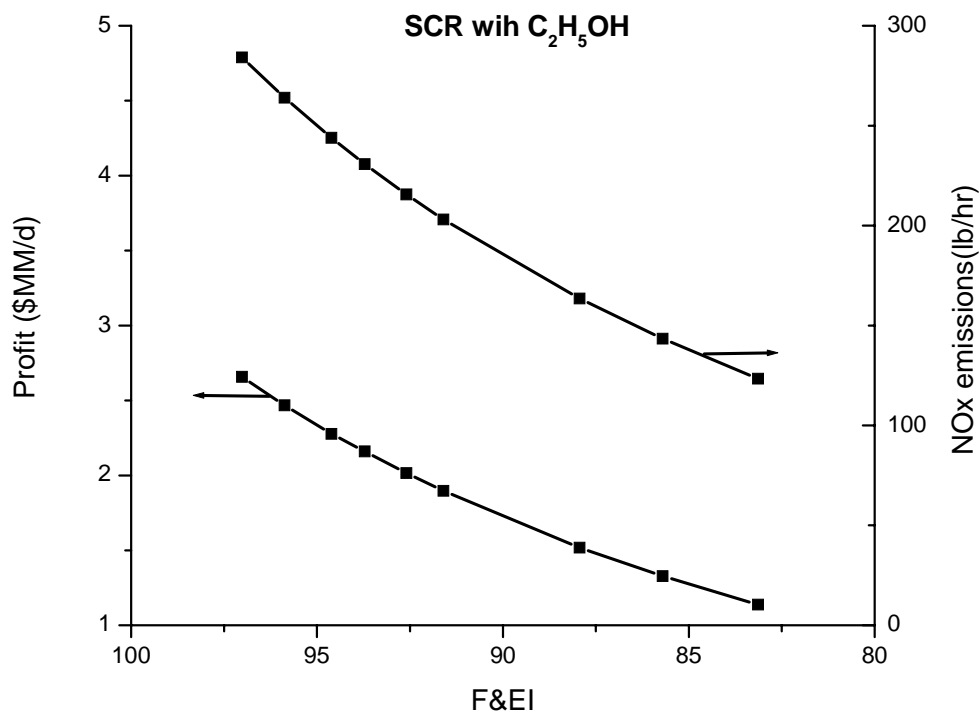
Figure 5.5. Pareto curve for Ethanol-SCR system

Instead of recommending a single operating point that works for all companies, the Pareto curves should be presented to the decision makers of the company as tradeoff curves. As such, a selection is made by considering the economic, environmental, and safety objectives of the company.

5.7 Conclusions

A new approach is introduced to consider both the inherently safer design and expected process scheduling. An optimization formulation is developed to generate design alternatives for addressing scheduling needs while accounting for technical, economic, and environmental aspects of the process. Dow F&EI index is used as a safety metric to assess design alternatives. The tradeoff between the inherently safer design and scheduling of production objectives is accomplished by a mathematical formulation of the process design. A case study on NOx removal in a refinery was considered. Two systems are considered for NOx removal: (a) Ammonia-SCR system and (b) Ethanol SCR system. Pareto curves are shown for both technologies and comparisons between the inherently safer designs for them were graphically shown. It can be shown that the integration of process scheduling and F&EI can be performed. The results obtained provided clearer picture regarding the process under evaluation. Decision makers and/or engineers could benefit from this information, especially when this methodology is performed at early stages of design or during process retrofitting.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

A novel approach and procedure to design and scheduling with economic and environmental objectives has been introduced in this dissertation. This approach has been presented through a systematic framework and the associated mathematical formulations for simultaneous process design and scheduling while addressing economic and environmental objectives. It establishes two types of proper tradeoffs (a) between design and scheduling and (b) between economic and environmental objectives. The environmental issues pertaining to the parameterized process retrofitting, scheduling, and operation strategies are simultaneously considered. An optimization formulation was developed for the case of project schedule while allowing design retrofitting changes that include new environmental units and modification of design and operating conditions in the process (without new process units). Also, a process model with the appropriate level of relevant details was included in the formulation. The projected schedule was discretized to allow for a multiperiod formulation with algebraic equations. The resulting framework identifies opportunities for synergism between the economic and environmental objectives. It also determines points of diminishing return beyond which tradeoffs between economic and environmental objectives are established. This

novel simultaneous approach overcomes the limitations of the conventional sequential approach where valuable synergisms and tradeoffs of economic and environmental objectives are often missed. The devised procedure is illustrated with a case study on an oil refinery with scheduling of different products and the design of an environmental system that addresses NO_x emission.

The work has also introduced a simultaneous approach to process design, scheduling, operation and heat integration. This approach simultaneously finds the HEN optimum design and optimum schedules of the process operation and production. It introduces a new MILP methodology for optimizing variable flow and temperature HEN. This new methodology is based upon discretizing the feasible ranges of supply and target temperatures, and dividing the process streams into substreams. It also provides a single configuration of HEN based on MILP formulation for synthesis of optimum HEN for various multiperiods. Moreover, it incorporates a flexible HEN synthesis into the design while considering expected schedules which are accounted for in the base-case design.

Finally, safety metrics are included in the assessment of various designs and scheduling alternatives to enhance the inherent safety of design while attaining the economic objectives and scheduling of operation and production. A mathematical formulation was developed to generate pareto curves that present the tradeoff between inherently safer design and the scheduling of the process simultaneously. Dow fire and explosion index (F&EI) was used as a measurement of the inherent safety of process design. An oil

refinery case study was discussed to study the effect of various expected schedules on process safety. The results were reported as tradeoff curves between safety and economic objectives. These curves are very useful for decision making and for learning insights about the interaction of the safety and the economic objectives of the process.

6.2 Recommendations for future work

The research conducted in this dissertation can be extended to address even broader areas. These include:

- Incorporating change in the process units (addition/removal) in considering the environmental impact reduction.

- Enhancement of uncertainty in the flexible HEN due to probabilistic aspects of expected schedules.

- Convexification of the MINLP models to guarantee global solutions.

- Including business objectives like contract deals within the scheduling and design frame of the process.

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APPENDIX A

MILP LINGO SOLVER AND OUTPUT FOR VARIABLE FLOW

AND TEMPERATURE HEN

```
! A program written by Eid Al-Mutairi as a generic
! solver for HEN
! Below is example of FCC-HEN system from CANMET work;
min=QHmin+QCmin;
! sets and their data;
data:
nu=14;
nz=30;
ntemp=31;
nv=5;
nhu=1;
ncu=1;
enddata
sets:
set_u/1..nu/:FhCp,su,eu;
set_z/1..nz/:HHtotal,HCtotal,r;
set_temp/1..ntemp/:Th,tc,Thh,tcc;
set_v/1..nv/:fcCp,sv,ev;
set_k/1..7/:tpinch,Mpinch;
LH(set_u,set_z):HH,I;
LC(set_v,set_z):HC,J;
set_hut/1..nhu/;
set_cut/1..ncu/;
IHUT(set_hut,set_z):IUT;
```

```
JCUT(set_cut,set_z):JUT;
Endsets
!Mathematical program;
@for(set_u(u):
@for(set_z(z)|z #GE# su(u) #and# z #LT# eu(u): I(u,z)=1));
@for(set_u(u):
@for(set_z(z)|z #LT# su(u) #or# z #GE# eu(u): I(u,z)=0));

@for(set_v(v):
@for(set_z(z)|z #GE# sv(v) #and# z #LT# ev(v): J(v,z)=1));
@for(set_v(v):
@for(set_z(z)|z #LT# sv(v) #or# z #GE# ev(v): J(v,z)=0));

@for(LH(u,z):HH(u,z)=FhCp(u)*I(u,z)*(Th(z)-Th(z+1)));
@for(LC(v,z):HC(v,z)=fcCp(v)*J(v,z)*(tcc(z)-tcc(z+1)));

@for(set_z(z):HHtotal(z)=@sum(set_u(u):HH(u,z)));
@for(set_z(z):HCtotal(z)=@sum(set_v(v):HC(v,z)));

@for(LH(u,z):@bin(I(u,z)));
@for(LC(v,z):@bin(J(v,z)));
! Data for HEN;
tcc(2)=@sum(set_k(k):Mpinch(k)*tpinch(k));
@for(set_temp(temp)|temp#NE#2:tcc(temp)=tc(temp));
@sum(set_k(k):Mpinch(k))=1;
Mpinch(4)=1;
!Thh(2)=@sum(set_k(k):Mpinch(k)*(tpinch(k)+dT));
!@for(set_temp(temp)|temp#NE#2:Thh(temp)=Th(temp)+dt);
```

DATA:

FhCp= 0.18484 0.1819355 0.3445 0.0082 0.0057 0.0195238 0.0256 0.0662295 0.0571 0.05657 0.125 0.13 0.3563 0.2283;

fcCp= 0.12457 0.0757047 0.2365 0.082 0.0824;

Th= 427 390 343 304 281 263 254 238 232 212 202 193 184 182 180 179 163 157 155 137 121 111 106 97 81 77 73 60 57 49 37;

tc= 397 360 313 274 251 233 224 208 202 182 172 163 154 152 150 149 133 127 125 107 91 81 76 67 51 47 43 30 27 19 7;

su= 3 3 5 3 6 11 24 7 12 16 17 18 22 28;

eu= 5 5 9 21 30 24 30 12 16 26 18 30 28 31;

sv= 3 4 2 23 19;

ev= 10 19 4 25 23;

tpinch= 375 370 365 360 355 350 345;

dt=30;

I=

0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 1 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

0 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 0

0 0 0 0 0 0 0 0 0 1 1 1 1 1 1 1 1 1 1 1 1 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 1 1 1 1 1 0

0 0 0 0 0 0 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0 0 0 1 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0 0 0 0 0 0 1 1 1 1 1 1 1 1 1 1 0 0 0 0 0

0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 1 1 1 1 1 1 1 1 1 1 1 0

0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 1 1 1 1 1 0 0 0

0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 1 1;

J=

0 0 1 1 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0

0 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 1 1 1 0 0 0 0 0 0 0 0 0;

enddata

r(1)-QHmin=HHtotal(1)-HCtotal(1);

@for(set_z(z)|z #GT# 1 #and# z #LT# nz:r(z)-r(z-1)=HHtotal(z)-HCtotal(z));

-r(29)+QCmin=HHtotal(30)-HCtotal(30);

!Costraints;

@for(set_z(z):r(z)>=0);

The output of the above program is:

Global optimal solution found.

  Objective value: 64.27778

  Total solver iterations: 5

Variable	Value	Reduced Cost
QHMIN	7.568000	0.000000
QCMIN	56.70978	0.000000
NU	14.00000	0.000000
NZ	30.00000	0.000000
NTEMP	31.00000	0.000000
NV	5.000000	0.000000

NHU	1.000000	0.000000
NCU	1.000000	0.000000
DT	30.00000	0.000000
FHCP(1)	0.1848400	0.000000
FHCP(2)	0.1819355	0.000000
FHCP(3)	0.3445000	0.000000
FHCP(4)	0.8200000E-02	0.000000
FHCP(5)	0.5700000E-02	0.000000
FHCP(6)	0.1952380E-01	0.000000
FHCP(7)	0.2560000E-01	0.000000
FHCP(8)	0.6622950E-01	0.000000
FHCP(9)	0.5710000E-01	0.000000
FHCP(10)	0.5657000E-01	0.000000
FHCP(11)	0.1250000	0.000000
FHCP(12)	0.1300000	0.000000
FHCP(13)	0.3563000	0.000000
FHCP(14)	0.2283000	0.000000
SU(1)	3.000000	0.000000
SU(2)	3.000000	0.000000
SU(3)	5.000000	0.000000
SU(4)	3.000000	0.000000
SU(5)	6.000000	0.000000
SU(6)	11.00000	0.000000
SU(7)	24.00000	0.000000
SU(8)	7.000000	0.000000
SU(9)	12.00000	0.000000
SU(10)	16.00000	0.000000
SU(11)	17.00000	0.000000
SU(12)	18.00000	0.000000

SU(13)	22.00000	0.000000
SU(14)	28.00000	0.000000
EU(1)	5.000000	0.000000
EU(2)	5.000000	0.000000
EU(3)	9.000000	0.000000
EU(4)	21.00000	0.000000
EU(5)	30.00000	0.000000
EU(6)	24.00000	0.000000
EU(7)	30.00000	0.000000
EU(8)	12.00000	0.000000
EU(9)	16.00000	0.000000
EU(10)	26.00000	0.000000
EU(11)	18.00000	0.000000
EU(12)	30.00000	0.000000
EU(13)	28.00000	0.000000
EU(14)	31.00000	0.000000
HHTOTAL(1)	0.000000	0.000000
HHTOTAL(2)	0.000000	0.000000
HHTOTAL(3)	14.62404	0.000000
HHTOTAL(4)	8.624436	0.000000
HHTOTAL(5)	6.348600	0.000000
HHTOTAL(6)	3.225600	0.000000
HHTOTAL(7)	6.794072	0.000000
HHTOTAL(8)	2.547777	0.000000
HHTOTAL(9)	1.602590	0.000000
HHTOTAL(10)	0.8012950	0.000000
HHTOTAL(11)	0.8968797	0.000000
HHTOTAL(12)	0.8147142	0.000000
HHTOTAL(13)	0.1810476	0.000000

HHTOTAL(14)	0.1810476	0.000000
HHTOTAL(15)	0.9052380E-01	0.000000
HHTOTAL(16)	1.439901	0.000000
HHTOTAL(17)	1.289963	0.000000
HHTOTAL(18)	0.4399876	0.000000
HHTOTAL(19)	3.959888	0.000000
HHTOTAL(20)	3.519901	0.000000
HHTOTAL(21)	2.117938	0.000000
HHTOTAL(22)	2.840469	0.000000
HHTOTAL(23)	5.112844	0.000000
HHTOTAL(24)	9.186720	0.000000
HHTOTAL(25)	2.296680	0.000000
HHTOTAL(26)	2.070400	0.000000
HHTOTAL(27)	6.728800	0.000000
HHTOTAL(28)	1.168800	0.000000
HHTOTAL(29)	3.116800	0.000000
HHTOTAL(30)	2.739600	0.000000
HCTOTAL(1)	0.000000	0.000000
HCTOTAL(2)	7.568000	0.000000
HCTOTAL(3)	9.223500	0.000000
HCTOTAL(4)	4.606318	0.000000
HCTOTAL(5)	3.604945	0.000000
HCTOTAL(6)	1.802472	0.000000
HCTOTAL(7)	3.204395	0.000000
HCTOTAL(8)	1.201648	0.000000
HCTOTAL(9)	4.005494	0.000000
HCTOTAL(10)	0.7570470	0.000000
HCTOTAL(11)	0.6813423	0.000000
HCTOTAL(12)	0.6813423	0.000000

HCTOTAL(13)   0.1514094   0.000000

HCTOTAL(14)   0.1514094   0.000000

HCTOTAL(15)   0.7570470E-01   0.000000

HCTOTAL(16)   1.211275   0.000000

HCTOTAL(17)   0.4542282   0.000000

HCTOTAL(18)   0.1514094   0.000000

HCTOTAL(19)   1.483200   0.000000

HCTOTAL(20)   1.318400   0.000000

HCTOTAL(21)   0.8240000   0.000000

HCTOTAL(22)   0.4120000   0.000000

HCTOTAL(23)   0.7380000   0.000000

HCTOTAL(24)   1.312000   0.000000

HCTOTAL(25)   0.000000   0.000000

HCTOTAL(26)   0.000000   0.000000

HCTOTAL(27)   0.000000   0.000000

HCTOTAL(28)   0.000000   0.000000

HCTOTAL(29)   0.000000   0.000000

HCTOTAL(30)   0.000000   0.000000

R(1)   7.568000   0.000000

R(2)   0.000000   2.000000

R(3)   5.400545   0.000000

R(4)   9.418663   0.000000

R(5)   12.16232   0.000000

R(6)   13.58545   0.000000

R(7)   17.17512   0.000000

R(8)   18.52125   0.000000

R(9)   16.11835   0.000000

R(10)   16.16260   0.000000

R(11)   16.37813   0.000000

R(12)	16.51150	0.000000
R(13)	16.54114	0.000000
R(14)	16.57078	0.000000
R(15)	16.58560	0.000000
R(16)	16.81423	0.000000
R(17)	17.64996	0.000000
R(18)	17.93854	0.000000
R(19)	20.41523	0.000000
R(20)	22.61673	0.000000
R(21)	23.91067	0.000000
R(22)	26.33914	0.000000
R(23)	30.71398	0.000000
R(24)	38.58870	0.000000
R(25)	40.88538	0.000000
R(26)	42.95578	0.000000
R(27)	49.68458	0.000000
R(28)	50.85338	0.000000
R(29)	53.97018	0.000000
R(30)	0.000000	0.000000
TH(1)	427.0000	0.000000
TH(2)	390.0000	0.000000
TH(3)	343.0000	0.000000
TH(4)	304.0000	0.000000
TH(5)	281.0000	0.000000
TH(6)	263.0000	0.000000
TH(7)	254.0000	0.000000
TH(8)	238.0000	0.000000
TH(9)	232.0000	0.000000
TH(10)	212.0000	0.000000

TH(11)	202.0000	0.000000
TH(12)	193.0000	0.000000
TH(13)	184.0000	0.000000
TH(14)	182.0000	0.000000
TH(15)	180.0000	0.000000
TH(16)	179.0000	0.000000
TH(17)	163.0000	0.000000
TH(18)	157.0000	0.000000
TH(19)	155.0000	0.000000
TH(20)	137.0000	0.000000
TH(21)	121.0000	0.000000
TH(22)	111.0000	0.000000
TH(23)	106.0000	0.000000
TH(24)	97.00000	0.000000
TH(25)	81.00000	0.000000
TH(26)	77.00000	0.000000
TH(27)	73.00000	0.000000
TH(28)	60.00000	0.000000
TH(29)	57.00000	0.000000
TH(30)	49.00000	0.000000
TH(31)	37.00000	0.000000
TC(1)	397.0000	0.000000
TC(2)	360.0000	0.000000
TC(3)	313.0000	0.000000
TC(4)	274.0000	0.000000
TC(5)	251.0000	0.000000
TC(6)	233.0000	0.000000
TC(7)	224.0000	0.000000
TC(8)	208.0000	0.000000

TC(9)	202.0000	0.000000
TC(10)	182.0000	0.000000
TC(11)	172.0000	0.000000
TC(12)	163.0000	0.000000
TC(13)	154.0000	0.000000
TC(14)	152.0000	0.000000
TC(15)	150.0000	0.000000
TC(16)	149.0000	0.000000
TC(17)	133.0000	0.000000
TC(18)	127.0000	0.000000
TC(19)	125.0000	0.000000
TC(20)	107.0000	0.000000
TC(21)	91.00000	0.000000
TC(22)	81.00000	0.000000
TC(23)	76.00000	0.000000
TC(24)	67.00000	0.000000
TC(25)	51.00000	0.000000
TC(26)	47.00000	0.000000
TC(27)	43.00000	0.000000
TC(28)	30.00000	0.000000
TC(29)	27.00000	0.000000
TC(30)	19.00000	0.000000
TC(31)	7.000000	0.000000
THH(1)	0.000000	0.000000
THH(2)	0.000000	0.000000
THH(3)	0.000000	0.000000
THH(4)	0.000000	0.000000
THH(5)	0.000000	0.000000
THH(6)	0.000000	0.000000

THH(7)	0.000000	0.000000
THH(8)	0.000000	0.000000
THH(9)	0.000000	0.000000
THH(10)	0.000000	0.000000
THH(11)	0.000000	0.000000
THH(12)	0.000000	0.000000
THH(13)	0.000000	0.000000
THH(14)	0.000000	0.000000
THH(15)	0.000000	0.000000
THH(16)	0.000000	0.000000
THH(17)	0.000000	0.000000
THH(18)	0.000000	0.000000
THH(19)	0.000000	0.000000
THH(20)	0.000000	0.000000
THH(21)	0.000000	0.000000
THH(22)	0.000000	0.000000
THH(23)	0.000000	0.000000
THH(24)	0.000000	0.000000
THH(25)	0.000000	0.000000
THH(26)	0.000000	0.000000
THH(27)	0.000000	0.000000
THH(28)	0.000000	0.000000
THH(29)	0.000000	0.000000
THH(30)	0.000000	0.000000
THH(31)	0.000000	0.000000
TCC(1)	397.0000	0.000000
TCC(2)	345.0000	0.000000
TCC(3)	313.0000	0.000000
TCC(4)	274.0000	0.000000

TCC(5)	251.0000	0.000000
TCC(6)	233.0000	0.000000
TCC(7)	224.0000	0.000000
TCC(8)	208.0000	0.000000
TCC(9)	202.0000	0.000000
TCC(10)	182.0000	0.000000
TCC(11)	172.0000	0.000000
TCC(12)	163.0000	0.000000
TCC(13)	154.0000	0.000000
TCC(14)	152.0000	0.000000
TCC(15)	150.0000	0.000000
TCC(16)	149.0000	0.000000
TCC(17)	133.0000	0.000000
TCC(18)	127.0000	0.000000
TCC(19)	125.0000	0.000000
TCC(20)	107.0000	0.000000
TCC(21)	91.00000	0.000000
TCC(22)	81.00000	0.000000
TCC(23)	76.00000	0.000000
TCC(24)	67.00000	0.000000
TCC(25)	51.00000	0.000000
TCC(26)	47.00000	0.000000
TCC(27)	43.00000	0.000000
TCC(28)	30.00000	0.000000
TCC(29)	27.00000	0.000000
TCC(30)	19.00000	0.000000
TCC(31)	7.000000	0.000000
FCCP(1)	0.1245700	0.000000
FCCP(2)	0.7570470E-01	0.000000

FCCP(3)	0.2365000	0.000000
FCCP(4)	0.8200000E-01	0.000000
FCCP(5)	0.8240000E-01	0.000000
SV(1)	4.000000	0.000000
SV(2)	4.000000	0.000000
SV(3)	2.000000	0.000000
SV(4)	23.00000	0.000000
SV(5)	19.00000	0.000000
EV(1)	10.00000	0.000000
EV(2)	19.00000	0.000000
EV(3)	4.000000	0.000000
EV(4)	25.00000	0.000000
EV(5)	23.00000	0.000000
TPINCH(1)	375.0000	0.000000
TPINCH(2)	370.0000	0.000000
TPINCH(3)	365.0000	0.000000
TPINCH(4)	360.0000	0.000000
TPINCH(5)	355.0000	0.000000
TPINCH(6)	350.0000	0.000000
TPINCH(7)	345.0000	0.000000
MPINCH(1)	0.000000	7.095000
MPINCH(2)	0.000000	5.912500
MPINCH(3)	0.000000	4.730000
MPINCH(4)	0.000000	3.547500
MPINCH(5)	0.000000	2.365000
MPINCH(6)	0.000000	1.182500
MPINCH(7)	1.000000	0.000000
HH(1, 1)	0.000000	0.000000
HH(1, 2)	0.000000	0.000000

HH(1, 3)	7.208760	0.000000
HH(1, 4)	4.251320	0.000000
HH(1, 5)	0.000000	0.000000
HH(1, 6)	0.000000	0.000000
HH(1, 7)	0.000000	0.000000
HH(1, 8)	0.000000	0.000000
HH(1, 9)	0.000000	0.000000
HH(1, 10)	0.000000	0.000000
HH(1, 11)	0.000000	0.000000
HH(1, 12)	0.000000	0.000000
HH(1, 13)	0.000000	0.000000
HH(1, 14)	0.000000	0.000000
HH(1, 15)	0.000000	0.000000
HH(1, 16)	0.000000	0.000000
HH(1, 17)	0.000000	0.000000
HH(1, 18)	0.000000	0.000000
HH(1, 19)	0.000000	0.000000
HH(1, 20)	0.000000	0.000000
HH(1, 21)	0.000000	0.000000
HH(1, 22)	0.000000	0.000000
HH(1, 23)	0.000000	0.000000
HH(1, 24)	0.000000	0.000000
HH(1, 25)	0.000000	0.000000
HH(1, 26)	0.000000	0.000000
HH(1, 27)	0.000000	0.000000
HH(1, 28)	0.000000	0.000000
HH(1, 29)	0.000000	0.000000
HH(1, 30)	0.000000	0.000000
HH(2, 1)	0.000000	0.000000

HH(2, 2)	0.000000	0.000000
HH(2, 3)	7.095485	0.000000
HH(2, 4)	4.184516	0.000000
HH(2, 5)	0.000000	0.000000
HH(2, 6)	0.000000	0.000000
HH(2, 7)	0.000000	0.000000
HH(2, 8)	0.000000	0.000000
HH(2, 9)	0.000000	0.000000
HH(2, 10)	0.000000	0.000000
HH(2, 11)	0.000000	0.000000
HH(2, 12)	0.000000	0.000000
HH(2, 13)	0.000000	0.000000
HH(2, 14)	0.000000	0.000000
HH(2, 15)	0.000000	0.000000
HH(2, 16)	0.000000	0.000000
HH(2, 17)	0.000000	0.000000
HH(2, 18)	0.000000	0.000000
HH(2, 19)	0.000000	0.000000
HH(2, 20)	0.000000	0.000000
HH(2, 21)	0.000000	0.000000
HH(2, 22)	0.000000	0.000000
HH(2, 23)	0.000000	0.000000
HH(2, 24)	0.000000	0.000000
HH(2, 25)	0.000000	0.000000
HH(2, 26)	0.000000	0.000000
HH(2, 27)	0.000000	0.000000
HH(2, 28)	0.000000	0.000000
HH(2, 29)	0.000000	0.000000
HH(2, 30)	0.000000	0.000000

HH(3, 1)	0.000000	0.000000
HH(3, 2)	0.000000	0.000000
HH(3, 3)	0.000000	0.000000
HH(3, 4)	0.000000	0.000000
HH(3, 5)	6.201000	0.000000
HH(3, 6)	3.100500	0.000000
HH(3, 7)	5.512000	0.000000
HH(3, 8)	2.067000	0.000000
HH(3, 9)	0.000000	0.000000
HH(3, 10)	0.000000	0.000000
HH(3, 11)	0.000000	0.000000
HH(3, 12)	0.000000	0.000000
HH(3, 13)	0.000000	0.000000
HH(3, 14)	0.000000	0.000000
HH(3, 15)	0.000000	0.000000
HH(3, 16)	0.000000	0.000000
HH(3, 17)	0.000000	0.000000
HH(3, 18)	0.000000	0.000000
HH(3, 19)	0.000000	0.000000
HH(3, 20)	0.000000	0.000000
HH(3, 21)	0.000000	0.000000
HH(3, 22)	0.000000	0.000000
HH(3, 23)	0.000000	0.000000
HH(3, 24)	0.000000	0.000000
HH(3, 25)	0.000000	0.000000
HH(3, 26)	0.000000	0.000000
HH(3, 27)	0.000000	0.000000
HH(3, 28)	0.000000	0.000000
HH(3, 29)	0.000000	0.000000

HH(3, 30)	0.000000	0.000000
HH(4, 1)	0.000000	0.000000
HH(4, 2)	0.000000	0.000000
HH(4, 3)	0.3198000	0.000000
HH(4, 4)	0.1886000	0.000000
HH(4, 5)	0.1476000	0.000000
HH(4, 6)	0.7380000E-01	0.000000
HH(4, 7)	0.1312000	0.000000
HH(4, 8)	0.4920000E-01	0.000000
HH(4, 9)	0.1640000	0.000000
HH(4, 10)	0.8200000E-01	0.000000
HH(4, 11)	0.7380000E-01	0.000000
HH(4, 12)	0.7380000E-01	0.000000
HH(4, 13)	0.1640000E-01	0.000000
HH(4, 14)	0.1640000E-01	0.000000
HH(4, 15)	0.8200000E-02	0.000000
HH(4, 16)	0.1312000	0.000000
HH(4, 17)	0.4920000E-01	0.000000
HH(4, 18)	0.1640000E-01	0.000000
HH(4, 19)	0.1476000	0.000000
HH(4, 20)	0.1312000	0.000000
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HH(4, 22)	0.000000	0.000000
HH(4, 23)	0.000000	0.000000
HH(4, 24)	0.000000	0.000000
HH(4, 25)	0.000000	0.000000
HH(4, 26)	0.000000	0.000000
HH(4, 27)	0.000000	0.000000
HH(4, 28)	0.000000	0.000000

HH(4, 29)   0.000000   0.000000

HH(4, 30)   0.000000   0.000000

HH(5, 1)   0.000000   0.000000

HH(5, 2)   0.000000   0.000000

HH(5, 3)   0.000000   0.000000

HH(5, 4)   0.000000   0.000000

HH(5, 5)   0.000000   0.000000

HH(5, 6)   0.5130000E-01   0.000000

HH(5, 7)   0.9120000E-01   0.000000

HH(5, 8)   0.3420000E-01   0.000000

HH(5, 9)   0.1140000   0.000000

HH(5, 10)   0.5700000E-01   0.000000

HH(5, 11)   0.5130000E-01   0.000000

HH(5, 12)   0.5130000E-01   0.000000

HH(5, 13)   0.1140000E-01   0.000000

HH(5, 14)   0.1140000E-01   0.000000

HH(5, 15)   0.5700000E-02   0.000000

HH(5, 16)   0.9120000E-01   0.000000

HH(5, 17)   0.3420000E-01   0.000000

HH(5, 18)   0.1140000E-01   0.000000

HH(5, 19)   0.1026000   0.000000

HH(5, 20)   0.9120000E-01   0.000000

HH(5, 21)   0.5700000E-01   0.000000

HH(5, 22)   0.2850000E-01   0.000000

HH(5, 23)   0.5130000E-01   0.000000

HH(5, 24)   0.9120000E-01   0.000000

HH(5, 25)   0.2280000E-01   0.000000

HH(5, 26)   0.2280000E-01   0.000000

HH(5, 27)   0.7410000E-01   0.000000

HH(5, 28)   0.1710000E-01   0.000000

HH(5, 29)   0.4560000E-01   0.000000

HH(5, 30)   0.000000   0.000000

HH(6, 1)   0.000000   0.000000

HH(6, 2)   0.000000   0.000000

HH(6, 3)   0.000000   0.000000

HH(6, 4)   0.000000   0.000000

HH(6, 5)   0.000000   0.000000

HH(6, 6)   0.000000   0.000000

HH(6, 7)   0.000000   0.000000

HH(6, 8)   0.000000   0.000000

HH(6, 9)   0.000000   0.000000

HH(6, 10)   0.000000   0.000000

HH(6, 11)   0.1757142   0.000000

HH(6, 12)   0.1757142   0.000000

HH(6, 13)   0.3904760E-01   0.000000

HH(6, 14)   0.3904760E-01   0.000000

HH(6, 15)   0.1952380E-01   0.000000

HH(6, 16)   0.3123808   0.000000

HH(6, 17)   0.1171428   0.000000

HH(6, 18)   0.3904760E-01   0.000000

HH(6, 19)   0.3514284   0.000000

HH(6, 20)   0.3123808   0.000000

HH(6, 21)   0.1952380   0.000000

HH(6, 22)   0.9761900E-01   0.000000

HH(6, 23)   0.1757142   0.000000

HH(6, 24)   0.000000   0.000000

HH(6, 25)   0.000000   0.000000

HH(6, 26)   0.000000   0.000000

HH(6, 27)	0.000000	0.000000
HH(6, 28)	0.000000	0.000000
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HH(7, 5)	0.000000	0.000000
HH(7, 6)	0.000000	0.000000
HH(7, 7)	0.000000	0.000000
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HH(7, 9)	0.000000	0.000000
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HH(7, 19)	0.000000	0.000000
HH(7, 20)	0.000000	0.000000
HH(7, 21)	0.000000	0.000000
HH(7, 22)	0.000000	0.000000
HH(7, 23)	0.000000	0.000000
HH(7, 24)	0.4096000	0.000000
HH(7, 25)	0.1024000	0.000000

HH(7, 26)	0.1024000	0.000000
HH(7, 27)	0.3328000	0.000000
HH(7, 28)	0.7680000E-01	0.000000
HH(7, 29)	0.2048000	0.000000
HH(7, 30)	0.000000	0.000000
HH(8, 1)	0.000000	0.000000
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HH(8, 3)	0.000000	0.000000
HH(8, 4)	0.000000	0.000000
HH(8, 5)	0.000000	0.000000
HH(8, 6)	0.000000	0.000000
HH(8, 7)	1.059672	0.000000
HH(8, 8)	0.3973770	0.000000
HH(8, 9)	1.324590	0.000000
HH(8, 10)	0.6622950	0.000000
HH(8, 11)	0.5960655	0.000000
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HH(8, 14)	0.000000	0.000000
HH(8, 15)	0.000000	0.000000
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HH(8, 18)	0.000000	0.000000
HH(8, 19)	0.000000	0.000000
HH(8, 20)	0.000000	0.000000
HH(8, 21)	0.000000	0.000000
HH(8, 22)	0.000000	0.000000
HH(8, 23)	0.000000	0.000000
HH(8, 24)	0.000000	0.000000

HH(8, 25)	0.000000	0.000000
HH(8, 26)	0.000000	0.000000
HH(8, 27)	0.000000	0.000000
HH(8, 28)	0.000000	0.000000
HH(8, 29)	0.000000	0.000000
HH(8, 30)	0.000000	0.000000
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HH(9, 8)	0.000000	0.000000
HH(9, 9)	0.000000	0.000000
HH(9, 10)	0.000000	0.000000
HH(9, 11)	0.000000	0.000000
HH(9, 12)	0.5139000	0.000000
HH(9, 13)	0.1142000	0.000000
HH(9, 14)	0.1142000	0.000000
HH(9, 15)	0.5710000E-01	0.000000
HH(9, 16)	0.000000	0.000000
HH(9, 17)	0.000000	0.000000
HH(9, 18)	0.000000	0.000000
HH(9, 19)	0.000000	0.000000
HH(9, 20)	0.000000	0.000000
HH(9, 21)	0.000000	0.000000
HH(9, 22)	0.000000	0.000000
HH(9, 23)	0.000000	0.000000

HH(9, 24)	0.000000	0.000000
HH(9, 25)	0.000000	0.000000
HH(9, 26)	0.000000	0.000000
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HH(9, 28)	0.000000	0.000000
HH(9, 29)	0.000000	0.000000
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HH(10, 12)	0.000000	0.000000
HH(10, 13)	0.000000	0.000000
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HH(10, 15)	0.000000	0.000000
HH(10, 16)	0.9051200	0.000000
HH(10, 17)	0.3394200	0.000000
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HH(10, 25)	0.2262800	0.000000
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HH(11, 9)	0.000000	0.000000
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HH(11, 18)	0.000000	0.000000
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HH(11, 20)	0.000000	0.000000
HH(11, 21)	0.000000	0.000000

HH(11, 22)	0.000000	0.000000
HH(11, 23)	0.000000	0.000000
HH(11, 24)	0.000000	0.000000
HH(11, 25)	0.000000	0.000000
HH(11, 26)	0.000000	0.000000
HH(11, 27)	0.000000	0.000000
HH(11, 28)	0.000000	0.000000
HH(11, 29)	0.000000	0.000000
HH(11, 30)	0.000000	0.000000
HH(12, 1)	0.000000	0.000000
HH(12, 2)	0.000000	0.000000
HH(12, 3)	0.000000	0.000000
HH(12, 4)	0.000000	0.000000
HH(12, 5)	0.000000	0.000000
HH(12, 6)	0.000000	0.000000
HH(12, 7)	0.000000	0.000000
HH(12, 8)	0.000000	0.000000
HH(12, 9)	0.000000	0.000000
HH(12, 10)	0.000000	0.000000
HH(12, 11)	0.000000	0.000000
HH(12, 12)	0.000000	0.000000
HH(12, 13)	0.000000	0.000000
HH(12, 14)	0.000000	0.000000
HH(12, 15)	0.000000	0.000000
HH(12, 16)	0.000000	0.000000
HH(12, 17)	0.000000	0.000000
HH(12, 18)	0.2600000	0.000000
HH(12, 19)	2.340000	0.000000
HH(12, 20)	2.080000	0.000000

HH(12, 21)	1.300000	0.000000
HH(12, 22)	0.6500000	0.000000
HH(12, 23)	1.170000	0.000000
HH(12, 24)	2.080000	0.000000
HH(12, 25)	0.5200000	0.000000
HH(12, 26)	0.5200000	0.000000
HH(12, 27)	1.690000	0.000000
HH(12, 28)	0.3900000	0.000000
HH(12, 29)	1.040000	0.000000
HH(12, 30)	0.000000	0.000000
HH(13, 1)	0.000000	0.000000
HH(13, 2)	0.000000	0.000000
HH(13, 3)	0.000000	0.000000
HH(13, 4)	0.000000	0.000000
HH(13, 5)	0.000000	0.000000
HH(13, 6)	0.000000	0.000000
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HH(13, 8)	0.000000	0.000000
HH(13, 9)	0.000000	0.000000
HH(13, 10)	0.000000	0.000000
HH(13, 11)	0.000000	0.000000
HH(13, 12)	0.000000	0.000000
HH(13, 13)	0.000000	0.000000
HH(13, 14)	0.000000	0.000000
HH(13, 15)	0.000000	0.000000
HH(13, 16)	0.000000	0.000000
HH(13, 17)	0.000000	0.000000
HH(13, 18)	0.000000	0.000000
HH(13, 19)	0.000000	0.000000

HH(13, 20)	0.000000	0.000000
HH(13, 21)	0.000000	0.000000
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HH(13, 23)	3.206700	0.000000
HH(13, 24)	5.700800	0.000000
HH(13, 25)	1.425200	0.000000
HH(13, 26)	1.425200	0.000000
HH(13, 27)	4.631900	0.000000
HH(13, 28)	0.000000	0.000000
HH(13, 29)	0.000000	0.000000
HH(13, 30)	0.000000	0.000000
HH(14, 1)	0.000000	0.000000
HH(14, 2)	0.000000	0.000000
HH(14, 3)	0.000000	0.000000
HH(14, 4)	0.000000	0.000000
HH(14, 5)	0.000000	0.000000
HH(14, 6)	0.000000	0.000000
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HH(14, 9)	0.000000	0.000000
HH(14, 10)	0.000000	0.000000
HH(14, 11)	0.000000	0.000000
HH(14, 12)	0.000000	0.000000
HH(14, 13)	0.000000	0.000000
HH(14, 14)	0.000000	0.000000
HH(14, 15)	0.000000	0.000000
HH(14, 16)	0.000000	0.000000
HH(14, 17)	0.000000	0.000000
HH(14, 18)	0.000000	0.000000

HH(14, 19)	0.000000	0.000000
HH(14, 20)	0.000000	0.000000
HH(14, 21)	0.000000	0.000000
HH(14, 22)	0.000000	0.000000
HH(14, 23)	0.000000	0.000000
HH(14, 24)	0.000000	0.000000
HH(14, 25)	0.000000	0.000000
HH(14, 26)	0.000000	0.000000
HH(14, 27)	0.000000	0.000000
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HH(14, 29)	1.826400	0.000000
HH(14, 30)	2.739600	0.000000
I(1, 1)	0.000000	0.000000
I(1, 2)	0.000000	0.000000
I(1, 3)	1.000000	0.000000
I(1, 4)	1.000000	0.000000
I(1, 5)	0.000000	0.000000
I(1, 6)	0.000000	0.000000
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I(1, 9)	0.000000	0.000000
I(1, 10)	0.000000	0.000000
I(1, 11)	0.000000	0.000000
I(1, 12)	0.000000	0.000000
I(1, 13)	0.000000	0.000000
I(1, 14)	0.000000	0.000000
I(1, 15)	0.000000	0.000000
I(1, 16)	0.000000	0.000000
I(1, 17)	0.000000	0.000000

I(1, 18)	0.000000	0.000000
I(1, 19)	0.000000	0.000000
I(1, 20)	0.000000	0.000000
I(1, 21)	0.000000	0.000000
I(1, 22)	0.000000	0.000000
I(1, 23)	0.000000	0.000000
I(1, 24)	0.000000	0.000000
I(1, 25)	0.000000	0.000000
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I(1, 27)	0.000000	0.000000
I(1, 28)	0.000000	0.000000
I(1, 29)	0.000000	0.000000
I(1, 30)	0.000000	0.000000
I(2, 1)	0.000000	0.000000
I(2, 2)	0.000000	0.000000
I(2, 3)	1.000000	0.000000
I(2, 4)	1.000000	0.000000
I(2, 5)	0.000000	0.000000
I(2, 6)	0.000000	0.000000
I(2, 7)	0.000000	0.000000
I(2, 8)	0.000000	0.000000
I(2, 9)	0.000000	0.000000
I(2, 10)	0.000000	0.000000
I(2, 11)	0.000000	0.000000
I(2, 12)	0.000000	0.000000
I(2, 13)	0.000000	0.000000
I(2, 14)	0.000000	0.000000
I(2, 15)	0.000000	0.000000
I(2, 16)	0.000000	0.000000

I(2, 17)	0.000000	0.000000
I(2, 18)	0.000000	0.000000
I(2, 19)	0.000000	0.000000
I(2, 20)	0.000000	0.000000
I(2, 21)	0.000000	0.000000
I(2, 22)	0.000000	0.000000
I(2, 23)	0.000000	0.000000
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I(2, 25)	0.000000	0.000000
I(2, 26)	0.000000	0.000000
I(2, 27)	0.000000	0.000000
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I(2, 30)	0.000000	0.000000
I(3, 1)	0.000000	0.000000
I(3, 2)	0.000000	0.000000
I(3, 3)	0.000000	0.000000
I(3, 4)	0.000000	0.000000
I(3, 5)	1.000000	0.000000
I(3, 6)	1.000000	0.000000
I(3, 7)	1.000000	0.000000
I(3, 8)	1.000000	0.000000
I(3, 9)	0.000000	0.000000
I(3, 10)	0.000000	0.000000
I(3, 11)	0.000000	0.000000
I(3, 12)	0.000000	0.000000
I(3, 13)	0.000000	0.000000
I(3, 14)	0.000000	0.000000
I(3, 15)	0.000000	0.000000

I(3, 16)	0.000000	0.000000
I(3, 17)	0.000000	0.000000
I(3, 18)	0.000000	0.000000
I(3, 19)	0.000000	0.000000
I(3, 20)	0.000000	0.000000
I(3, 21)	0.000000	0.000000
I(3, 22)	0.000000	0.000000
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I(3, 24)	0.000000	0.000000
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I(3, 26)	0.000000	0.000000
I(3, 27)	0.000000	0.000000
I(3, 28)	0.000000	0.000000
I(3, 29)	0.000000	0.000000
I(3, 30)	0.000000	0.000000
I(4, 1)	0.000000	0.000000
I(4, 2)	0.000000	0.000000
I(4, 3)	1.000000	0.000000
I(4, 4)	1.000000	0.000000
I(4, 5)	1.000000	0.000000
I(4, 6)	1.000000	0.000000
I(4, 7)	1.000000	0.000000
I(4, 8)	1.000000	0.000000
I(4, 9)	1.000000	0.000000
I(4, 10)	1.000000	0.000000
I(4, 11)	1.000000	0.000000
I(4, 12)	1.000000	0.000000
I(4, 13)	1.000000	0.000000
I(4, 14)	1.000000	0.000000

I(4, 15)	1.000000	0.000000
I(4, 16)	1.000000	0.000000
I(4, 17)	1.000000	0.000000
I(4, 18)	1.000000	0.000000
I(4, 19)	1.000000	0.000000
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HC(1, 5)	2.242260	0.000000
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HC(1, 8)	0.7474200	0.000000
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HC(1, 10)	0.000000	0.000000
HC(1, 11)	0.000000	0.000000
HC(1, 12)	0.000000	0.000000
HC(1, 13)	0.000000	0.000000
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HC(1, 19)	0.000000	0.000000
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HC(1, 23)	0.000000	0.000000
HC(1, 24)	0.000000	0.000000
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HC(1, 26)	0.000000	0.000000
HC(1, 27)	0.000000	0.000000
HC(1, 28)	0.000000	0.000000
HC(1, 29)	0.000000	0.000000
HC(1, 30)	0.000000	0.000000
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HC(2, 24)	0.000000	0.000000
HC(2, 25)	0.000000	0.000000
HC(2, 26)	0.000000	0.000000
HC(2, 27)	0.000000	0.000000
HC(2, 28)	0.000000	0.000000
HC(2, 29)	0.000000	0.000000
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HC(3, 30)	0.000000	0.000000

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J(1, 27)	0.000000	0.000000

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J(2, 16)	1.000000	0.000000
J(2, 17)	1.000000	0.000000
J(2, 18)	1.000000	0.000000
J(2, 19)	0.000000	0.000000
J(2, 20)	0.000000	0.000000
J(2, 21)	0.000000	0.000000
J(2, 22)	0.000000	0.000000
J(2, 23)	0.000000	0.000000
J(2, 24)	0.000000	0.000000
J(2, 25)	0.000000	0.000000
J(2, 26)	0.000000	0.000000

J(2, 27)	0.000000	0.000000
J(2, 28)	0.000000	0.000000
J(2, 29)	0.000000	0.000000
J(2, 30)	0.000000	0.000000
J(3, 1)	0.000000	0.000000
J(3, 2)	1.000000	0.000000
J(3, 3)	1.000000	0.000000
J(3, 4)	0.000000	0.000000
J(3, 5)	0.000000	0.000000
J(3, 6)	0.000000	0.000000
J(3, 7)	0.000000	0.000000
J(3, 8)	0.000000	0.000000
J(3, 9)	0.000000	0.000000
J(3, 10)	0.000000	0.000000
J(3, 11)	0.000000	0.000000
J(3, 12)	0.000000	0.000000
J(3, 13)	0.000000	0.000000
J(3, 14)	0.000000	0.000000
J(3, 15)	0.000000	0.000000
J(3, 16)	0.000000	0.000000
J(3, 17)	0.000000	0.000000
J(3, 18)	0.000000	0.000000
J(3, 19)	0.000000	0.000000
J(3, 20)	0.000000	0.000000
J(3, 21)	0.000000	0.000000
J(3, 22)	0.000000	0.000000
J(3, 23)	0.000000	0.000000
J(3, 24)	0.000000	0.000000
J(3, 25)	0.000000	0.000000

J(3, 26)	0.000000	0.000000
J(3, 27)	0.000000	0.000000
J(3, 28)	0.000000	0.000000
J(3, 29)	0.000000	0.000000
J(3, 30)	0.000000	0.000000
J(4, 1)	0.000000	0.000000
J(4, 2)	0.000000	0.000000
J(4, 3)	0.000000	0.000000
J(4, 4)	0.000000	0.000000
J(4, 5)	0.000000	0.000000
J(4, 6)	0.000000	0.000000
J(4, 7)	0.000000	0.000000
J(4, 8)	0.000000	0.000000
J(4, 9)	0.000000	0.000000
J(4, 10)	0.000000	0.000000
J(4, 11)	0.000000	0.000000
J(4, 12)	0.000000	0.000000
J(4, 13)	0.000000	0.000000
J(4, 14)	0.000000	0.000000
J(4, 15)	0.000000	0.000000
J(4, 16)	0.000000	0.000000
J(4, 17)	0.000000	0.000000
J(4, 18)	0.000000	0.000000
J(4, 19)	0.000000	0.000000
J(4, 20)	0.000000	0.000000
J(4, 21)	0.000000	0.000000
J(4, 22)	0.000000	0.000000
J(4, 23)	1.000000	0.000000
J(4, 24)	1.000000	0.000000

J(4, 25)	0.000000	0.000000
J(4, 26)	0.000000	0.000000
J(4, 27)	0.000000	0.000000
J(4, 28)	0.000000	0.000000
J(4, 29)	0.000000	0.000000
J(4, 30)	0.000000	0.000000
J(5, 1)	0.000000	0.000000
J(5, 2)	0.000000	0.000000
J(5, 3)	0.000000	0.000000
J(5, 4)	0.000000	0.000000
J(5, 5)	0.000000	0.000000
J(5, 6)	0.000000	0.000000
J(5, 7)	0.000000	0.000000
J(5, 8)	0.000000	0.000000
J(5, 9)	0.000000	0.000000
J(5, 10)	0.000000	0.000000
J(5, 11)	0.000000	0.000000
J(5, 12)	0.000000	0.000000
J(5, 13)	0.000000	0.000000
J(5, 14)	0.000000	0.000000
J(5, 15)	0.000000	0.000000
J(5, 16)	0.000000	0.000000
J(5, 17)	0.000000	0.000000
J(5, 18)	0.000000	0.000000
J(5, 19)	1.000000	0.000000
J(5, 20)	1.000000	0.000000
J(5, 21)	1.000000	0.000000
J(5, 22)	1.000000	0.000000
J(5, 23)	0.000000	0.000000

J(5, 24)	0.000000	0.000000
J(5, 25)	0.000000	0.000000
J(5, 26)	0.000000	0.000000
J(5, 27)	0.000000	0.000000
J(5, 28)	0.000000	0.000000
J(5, 29)	0.000000	0.000000
J(5, 30)	0.000000	0.000000
IUT(1, 1)	0.000000	0.000000
IUT(1, 2)	0.000000	0.000000
IUT(1, 3)	0.000000	0.000000
IUT(1, 4)	0.000000	0.000000
IUT(1, 5)	0.000000	0.000000
IUT(1, 6)	0.000000	0.000000
IUT(1, 7)	0.000000	0.000000
IUT(1, 8)	0.000000	0.000000
IUT(1, 9)	0.000000	0.000000
IUT(1, 10)	0.000000	0.000000
IUT(1, 11)	0.000000	0.000000
IUT(1, 12)	0.000000	0.000000
IUT(1, 13)	0.000000	0.000000
IUT(1, 14)	0.000000	0.000000
IUT(1, 15)	0.000000	0.000000
IUT(1, 16)	0.000000	0.000000
IUT(1, 17)	0.000000	0.000000
IUT(1, 18)	0.000000	0.000000
IUT(1, 19)	0.000000	0.000000
IUT(1, 20)	0.000000	0.000000
IUT(1, 21)	0.000000	0.000000
IUT(1, 22)	0.000000	0.000000

IUT(1, 23)	0.000000	0.000000
IUT(1, 24)	0.000000	0.000000
IUT(1, 25)	0.000000	0.000000
IUT(1, 26)	0.000000	0.000000
IUT(1, 27)	0.000000	0.000000
IUT(1, 28)	0.000000	0.000000
IUT(1, 29)	0.000000	0.000000
IUT(1, 30)	0.000000	0.000000
JUT(1, 1)	0.000000	0.000000
JUT(1, 2)	0.000000	0.000000
JUT(1, 3)	0.000000	0.000000
JUT(1, 4)	0.000000	0.000000
JUT(1, 5)	0.000000	0.000000
JUT(1, 6)	0.000000	0.000000
JUT(1, 7)	0.000000	0.000000
JUT(1, 8)	0.000000	0.000000
JUT(1, 9)	0.000000	0.000000
JUT(1, 10)	0.000000	0.000000
JUT(1, 11)	0.000000	0.000000
JUT(1, 12)	0.000000	0.000000
JUT(1, 13)	0.000000	0.000000
JUT(1, 14)	0.000000	0.000000
JUT(1, 15)	0.000000	0.000000
JUT(1, 16)	0.000000	0.000000
JUT(1, 17)	0.000000	0.000000
JUT(1, 18)	0.000000	0.000000
JUT(1, 19)	0.000000	0.000000
JUT(1, 20)	0.000000	0.000000
JUT(1, 21)	0.000000	0.000000

JUT(1, 22)	0.000000	0.000000
JUT(1, 23)	0.000000	0.000000
JUT(1, 24)	0.000000	0.000000
JUT(1, 25)	0.000000	0.000000
JUT(1, 26)	0.000000	0.000000
JUT(1, 27)	0.000000	0.000000
JUT(1, 28)	0.000000	0.000000
JUT(1, 29)	0.000000	0.000000
JUT(1, 30)	0.000000	0.000000

APPENDIX B

FCC EMPIRICAL AND MECHANISTIC MODELS: SAMPLE CALCULATIONS

The model for gasoline yield (wt%) is:

$$Gasoline = a(\frac{H}{C+S} + \log f_c T) + b(M_{eff}) + c(N_B) + d(C/O) + e(T) + f(Conversion)$$

For Arabian Heavy Crude (AHC)

H=12.08

C=85.94

S=3.27

$f_c T$ =0.765

M_{eff} =0.0022

N_B =0.01663

with following conditions of

C/O=6.255

T=490 ºC

X= 62%

and with following coefficients:

a=9.0428

b=-2.0002

c=0.2008

d=0.4906

e=-0.0171

f=0.5983

which gives the gasoline yield =38.35 wt%.

Coke yield calculations from modified Amoco model:

$$Coke = (C/O)^a (WHSV)^b \exp(E/RT)$$

The coefficients' values are:

a= 0.325

b= -0.198

Activation energy = E =6303 Btu/lb.mol

WHSV= 180 hr^{-1}

Gives a coke yield = 6.1%

For other liquid products:

$$LCO = 59.73 - 0.55(Conversion)$$
$$HCO = 100 - LCO - Conversion$$

with X= 62% gives LCO yield= 25.6 wt % and HCO yield= 12.4 wt%

which implies total yield of gases = 17.6 wt%

For mechanistic modeling part, the following figure shows different profiles inside the

reactor using detailed modeling for FCC reactor-regenerator system.
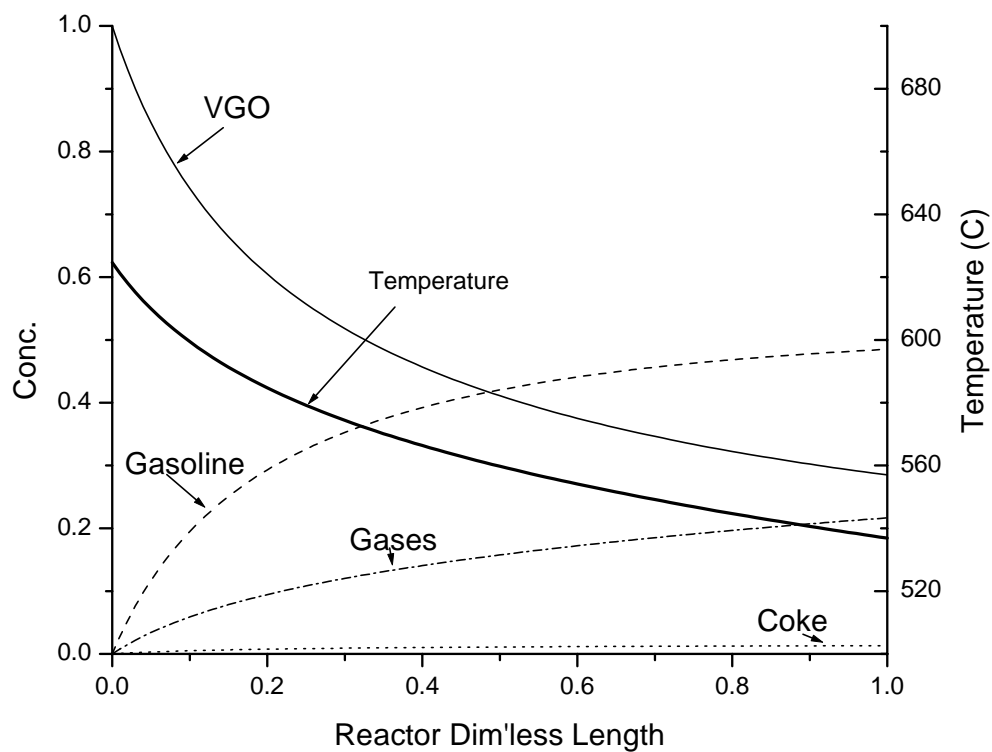
Figure B.1. Product yields and temperature profile inside FCC reactor

APPENDIX C

FCC-SCR CASE STUDIES OUTPUT FOR VARIOUS NOx LEVELS

Below are the outputs for three cases of NOx emissions. The first is the base case, the second is with no NOx environmental restrictions and the second is when there is a threshold limit on NOx emissions release.

C.1 Base case

```
Global optimal solution found.
  Objective value:                        24116.81
  Extended solver steps:                          0
  Total solver iterations:                      197


                    Variable           Value        Reduced Cost
                      GNEBBL         24116.81           0.000000
                          H1    0.5047309E+09           0.000000
                          MC         25441.36           0.000000
                          MH         2820.546           0.000000
                          MS         220.9599           0.000000
                          H2    0.1132798E+09           0.000000
                          MA         427470.8           0.000000
                         HAF         355.0000           0.000000
                         HAI         90.00000           0.000000
                          H3    0.4130016E+08           0.000000
                       MCOKE         28482.87           0.000000
                          H4         4420000.           0.000000
                         MST         13000.00           0.000000
                        HSTF         1519.000           0.000000
                        HSTI         1179.000           0.000000
                          H5         4830694.           0.000000
                        TREG         1309.000           0.000000
                       TROUT         885.0000           0.000000
                          H6         2266732.           0.000000
                          MG         453346.3           0.000000
                         HTG         370.0000           0.000000
                       HTREG         365.0000           0.000000
                          H7    0.2018924E+08           0.000000
                        LOSS         4.000000           0.000000
                          H8    0.3184443E+09           0.000000
                     CATCIRC         2635256.           0.000000
                         CTO         4.000000           0.000000
                        FEED         658814.0           0.000000
```

DELCOKE	0.7596703	0.000000
YCOKE	3.038681	0.000000
TROUTC	473.8889	0.000000
TROUTR	1344.670	0.000000
GNE	39.89407	0.000000
HCS	1.504000	0.000000
FCT	0.7650000	0.000000
MEFF	0.2200000E-02	0.000000
NB	0.1663000E-01	0.000000
X	65.00000	0.000000
GNEP	262827.7	0.000000
GNEPV	42204.42	0.000000
WHSV	3000.000	0.000000
R	1.987000	0.000000
QT	0.3000000	0.000000
NOX	270.9106	0.000000
NF	0.1200000	0.000000
NOXA	54.18212	0.000000
MNOX	122.8163	0.000000
MNOXA	24.56327	0.000000
MNH3	90.65015	0.000000
NOXCOST	103.0619	0.000000
GNEPROFIT	121126.7	0.000000
GNEPROFITBPD	69215.24	0.000000
MOLEAIR	14470.91	0.000000
FLOWAIR	94137.94	0.000000
FLUEGAS	13766.97	0.000000
MOLEO	206.5046	0.000000
MOLEC	2120.113	0.000000
MOLES	6.883485	0.000000
MOLEOOUT	2333.501	0.000000
MOLEOIN	3031.656	0.000000
MOLEOCOMB	698.1549	0.000000
MOLEH2O	1396.310	0.000000

C.2 No NOx restriction

```
Global optimal solution found.
  Objective value:                    27454.80
  Extended solver steps:                     0
  Total solver iterations:                 253
```

Variable	Value	Reduced Cost
GNEBBL	27454.80	0.000000
H1	0.5736340E+09	0.000000
MC	28914.48	0.000000
MH	3205.591	0.000000
MS	251.1241	0.000000
H2	0.1287441E+09	0.000000
MA	485826.8	0.000000

HAF	355.0000	0.000000
HAI	90.00000	0.000000
H3	0.4693823E+08	0.000000
MCOKE	32371.19	0.000000
H4	4420000.	0.000000
MST	13000.00	0.000000
HSTF	1519.000	0.000000
HSTI	1179.000	0.000000
H5	5490154.	0.000000
TREG	1309.000	0.000000
TROUT	885.0000	0.000000
H6	2576173.	0.000000
MG	515234.7	0.000000
HTG	370.0000	0.000000
HTREG	365.0000	0.000000
H7	0.2294536E+08	0.000000
LOSS	4.000000	0.000000
H8	0.3625200E+09	0.000000
CATCIRC	3000000.	0.000000
CTO	4.000000	0.000000
FEED	750000.0	0.000000
DELCOKE	1.255892	0.000000
YCOKE	5.023568	0.000000
TROUTC	473.8889	0.000000
TROUTR	1344.670	0.000000
GNE	39.89407	0.000000
HCS	1.504000	0.000000
FCT	0.7650000	0.000000
MEFF	0.2200000E-02	0.000000
NB	0.1663000E-01	0.000000
X	65.00000	0.000000
GNEP	299205.5	0.000000
GNEPV	48045.90	0.000000
WHSV	236.8421	0.000000
R	1.987000	0.000000
QT	3.800000	0.000000
NOX	447.8712	0.000000
NF	0.1200000	0.000000
NOXA	89.57424	0.000000
MNOX	230.7588	0.000000
MNOXA	46.15176	0.000000
MNH3	170.3220	0.000000
NOXCOST	193.6423	0.000000
GNEPROFIT	137891.7	0.000000
GNEPROFITBPD	78795.28	0.000000
MOLEAIR	16446.40	0.000000
FLOWAIR	106989.1	0.000000
FLUEGAS	15646.36	0.000000
MOLEO	234.6954	0.000000
MOLEC	2409.540	0.000000
MOLES	7.823181	0.000000
MOLEOOUT	2652.058	0.000000
MOLEOIN	3445.521	0.000000
MOLEOCOMB	793.4632	0.000000

MOLEH2O	1586.926	0.000000

C.3 NOx max<60ppm

```
Global optimal solution found.
  Objective value:                      25676.75
  Extended solver steps:                       3
  Total solver iterations:                   259


                    Variable           Value      Reduced Cost
                      GNEBBL        25676.75          0.000000
                          H1   0.1319770E+10          0.000000
                          MC        66524.05          0.000000
                          MH        7375.162          0.000000
                          MS        577.7657          0.000000
                          H2   0.2962038E+09          0.000000
                          MA         1117750.          0.000000
                         HAF        355.0000          0.000000
                         HAI        90.00000          0.000000
                          H3   0.1079916E+09          0.000000
                       MCOKE        74476.98          0.000000
                          H4        4420000.          0.000000
                         MST        13000.00          0.000000
                        HSTF        1519.000          0.000000
                        HSTI        1179.000          0.000000
                          H5   0.1263130E+08          0.000000
                        TREG        1309.000          0.000000
                       TROUT        885.0000          0.000000
                          H6        5927049.          0.000000
                          MG         1185410.          0.000000
                         HTG        370.0000          0.000000
                       HTREG        365.0000          0.000000
                          H7   0.5279080E+08          0.000000
                        LOSS        4.000000          0.000000
                          H8   0.8398055E+09          0.000000
                     CATCIRC        6949731.          0.000000
                         CTO        9.266308          0.000000
                        FEED        750000.0          0.000000
                     DELCOKE        0.8412410          0.000000
                       YCOKE        7.795198          0.000000
                      TROUTC        473.8889          0.000000
                      TROUTR        1344.670          0.000000
                         GNE        37.31042          0.000000
                         HCS        1.504000          0.000000
                         FCT        0.7650000          0.000000
                        MEFF   0.2200000E-02          0.000000
                          NB   0.1663000E-01          0.000000
                           X        65.00000          0.000000
```

GNEP	279828.2	0.000000
GNEPV	44934.32	0.000000
WHSV	102.2380	0.000000
R	1.987000	0.000000
QT	3.800000	0.000000
NOX	300.0000	0.000000
NF	0.1200000	0.000000
NOXA	60.00000	0.000000
MNOX	355.6229	0.000000
MNOXA	71.12458	0.000000
MNH3	262.4836	0.000000
NOXCOST	298.4226	0.000000
GNEPROFIT	128961.5	0.000000
GNEPROFITBPD	73692.28	0.000000
MOLEAIR	37838.54	0.000000
FLOWAIR	246151.8	0.000000
FLUEGAS	35997.87	0.000000
MOLEO	539.9680	0.000000
MOLEC	5543.671	0.000000
MOLES	17.99893	0.000000
MOLEOOUT	6101.638	0.000000
MOLEOIN	7927.173	0.000000
MOLEOCOMB	1825.535	0.000000
MOLEH2O	3651.070	0.000000

APPENDIX D

NOx EMISSIONS IN FCC PROCESS

Nitrogen oxide (NOx) emissions from the regenerator of FCC unit make up to 50% of the total NOx emissions in a modern integrated refinery. The NOx emissions in an FCC regenerator originate from the nitrogen containing species deposited on the catalyst during the cracking cycle. Depending on FCC operating conditions, about 5% of the gas oil feed forms coke. It has been reported that about 40% of the nitrogen contained in the FCC feed is deposited with the coke on the cracking catalyst.

NOx levels in the FCC regenerators' flue gas are typically in the range of 100-500 ppm. NO is the primary component of NOx from the FCC regenerator. Fig. D.1 and Fig. D.2 shows the NOx emissions as functions of N2 wt % in the feed and as a function of excess O_2 in regenerator operation.
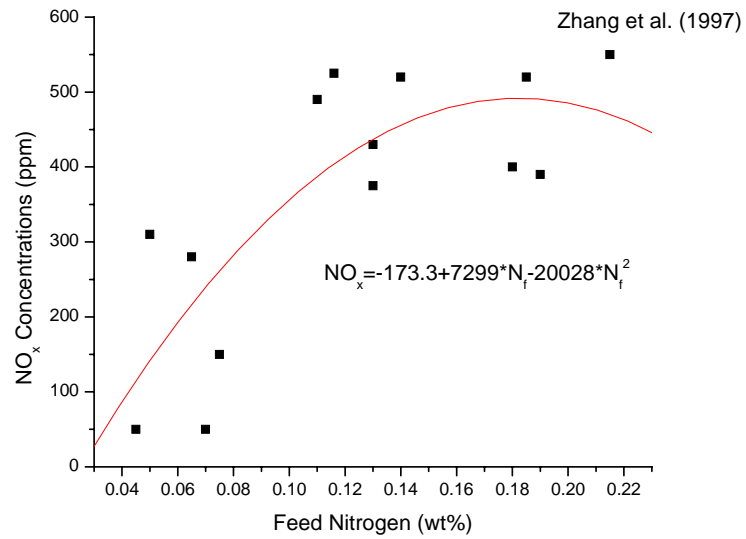
Figure D.1. NOx emissions changes with N_2 of feed
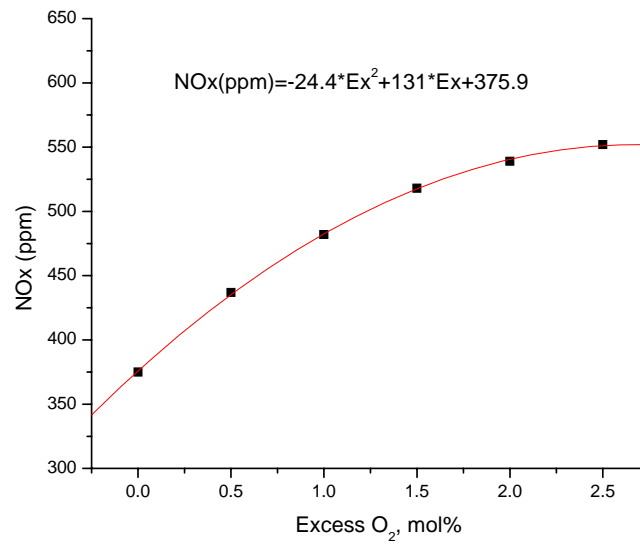

Figure D.2. NOx emissions levels w.r.t. Excess O_2

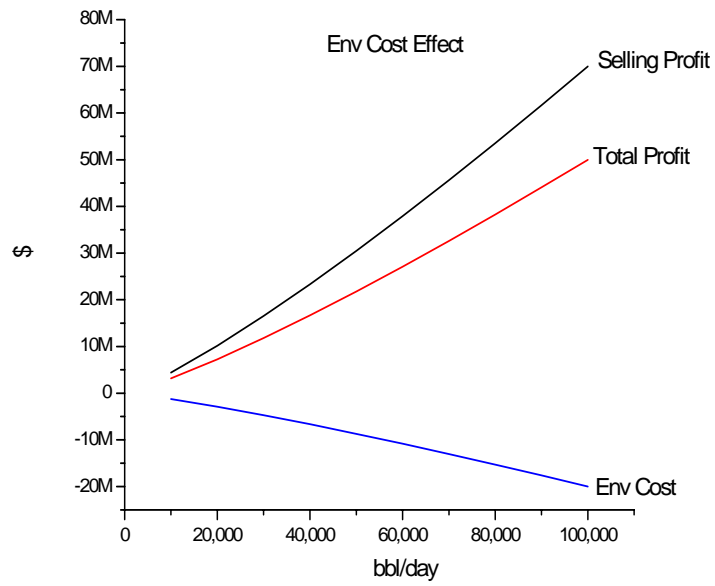An analysis of effect of NOx removal on TAC is shown in Fig. D.3.

Figure D.3. NOx removal cost deducting sales profits

APPENDIX E

DOW'S FIRE AND EXPLOSION INDEX VERSUS CHEMICAL

INVENTORY

Following tables and figure illustrate F&EI versus different levels of ammonia and

ethanol when used in Selective Catalytic Reduction (SCR) process.

Table E.1. F&EI vs. Ammonia Amount

NH3 in reactor (1000 lb)	btu/lb	10^9 Btu	Penalty	General	Specific	F3	MF	Dow FEI
10000.	8000.	0.08	0.09	1.50	2.66	4.00	4.00	15.99
20000.	8000.	0.16	0.31	1.50	2.88	4.32	4.00	17.28
30000.	8000.	0.24	0.52	1.50	3.09	4.63	4.00	18.54
40000.	8000.	0.32	0.70	1.50	3.27	4.90	4.00	19.62
50000.	8000.	0.40	0.85	1.50	3.42	5.13	4.00	20.52
60912.	8000.	0.49	0.99	1.50	3.56	5.34	4.00	21.36
64668.	8000.	0.52	1.03	1.50	3.60	5.40	4.00	21.61
69227.	8000.	0.55	1.08	1.50	3.65	5.48	4.00	21.91
1164802.	8000	9.32	2.36	1.50	4.93	7.40	4.00	29.60
1359159.	8000.	10.87	2.40	1.50	4.97	7.45	4.00	29.81
1553517.	8000.	12.43	2.43	1.50	5.00	7.50	4.00	29.99
2330947.	8000	18.65	2.52	1.50	5.09	7.64	4.00	30.56
2525305.	8000	20.20	2.54	1.50	5.11	7.67	4.00	30.67
2719662.	8000.	21.76	2.56	1.50	5.13	7.70	4.00	30.78
3000000.	8000.	24.00	2.59	1.50	5.16	7.73	4.00	30.93
3050000.	8000.	24.40	2.59	1.50	5.16	7.74	4.00	30.96
3100000.	8000.	24.80	2.59	1.50	5.16	7.75	4.00	30.98
3150000.	8000.	25.20	2.60	1.50	5.17	7.75	4.00	31.01

Table E.2. F&EI vs. Ammonia Amount

| Ethanol in reactor (1000 lb)	btu/lb	10^9 Btu	Penalty	General	Specific	F3	MF	Dow FEI
10000.	11500	0.12	0.19	1.50	2.76	4.13	16.00	66.14
20000.	11500.	0.23	0.50	1.50	3.07	4.60	16.00	73.56
30000	11500.	0.35	0.75	1.50	3.32	4.98	16.00	79.66
40000.	11500.	0.46	0.95	1.50	3.52	5.28	16.00	84.46
50000.	11500	0.58	1.11	1.50	3.68	5.52	16.00	88.26
60912.	11500.	0.70	1.25	1.50	3.82	5.73	16.00	91.60
64668.	11500.	0.74	1.29	1.50	3.86	5.79	16.00	92.59
69227.	11500.	0.80	1.33	1.50	3.90	5.86	16.00	93.71
1164802.	11500.	13.40	2.45	1.50	5.02	7.52	16.00	120.37
1359159.	11500.	15.63	2.48	1.50	5.05	7.58	16.00	121.23
1553517.	11500.	17.87	2.51	1.50	5.08	7.62	16.00	121.98
2330947.	11500.	26.81	2.61	1.50	5.18	7.78	16.00	124.41
2525305.	11500.	29.04	2.64	1.50	5.21	7.81	16.00	124.92
2719662.	11500.	31.28	2.66	1.50	5.23	7.84	16.00	125.41
3000000.	11500.	34.50	2.68	1.50	5.25	7.88	16.00	126.06
3050000.	11500.	35.08	2.69	1.50	5.26	7.89	16.00	126.17
3100000.	11500.	35.65	2.69	1.50	5.26	7.89	16.00	126.28
3150000.	11500.	36.23	2.70	1.50	5.27	7.90	16.00	126.39
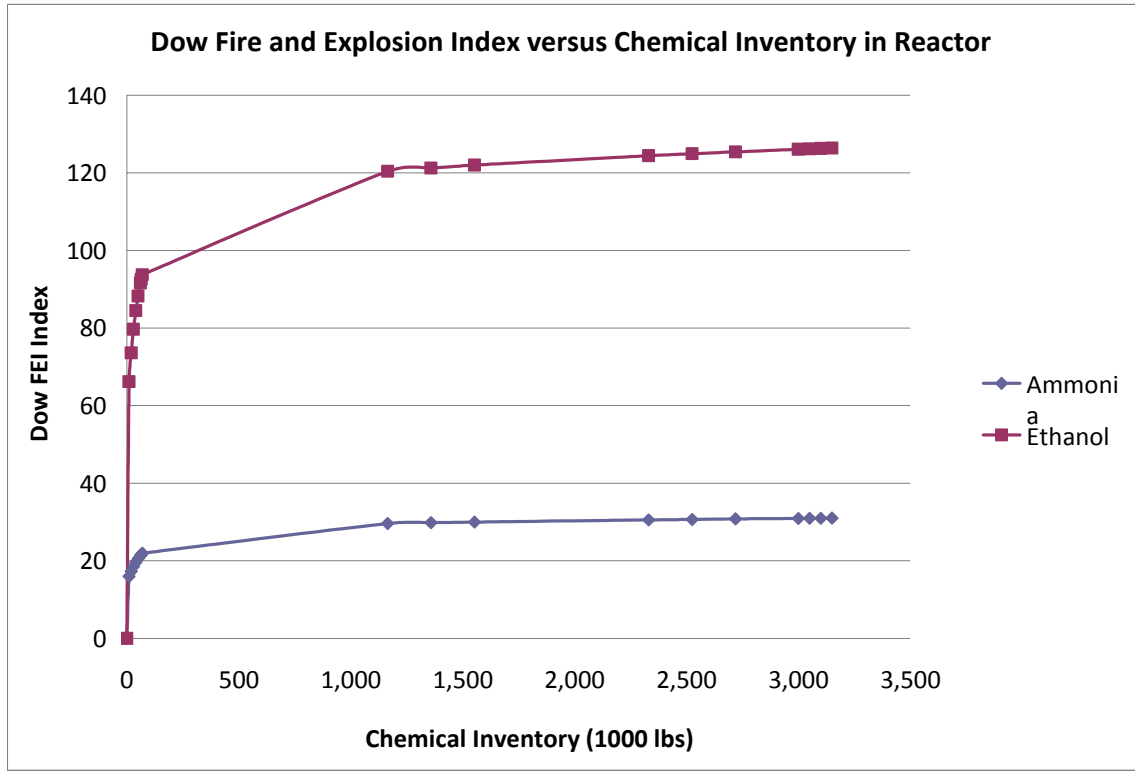
Figure E.1. F&EI vs. NH$_3$ and C$_2$H$_5$OH

APPENDIX F

ILLUSTRATION OF SEQUENTIAL AND SIMULTANEOUS

CONSIDERATION OF PROCESS OBJECTIVES

Figs. F.1 and F.2 shows the limitations of sequential approach in regard to economic and environmental objectives. Fig. F.1. shows the market demands not met because of environmental stringent operation mode of the plant. On the other hand, Fig. F.2 shows the violation of environmental regulations due to prioritizing the production to meet the market demand upon the environmental objectives.
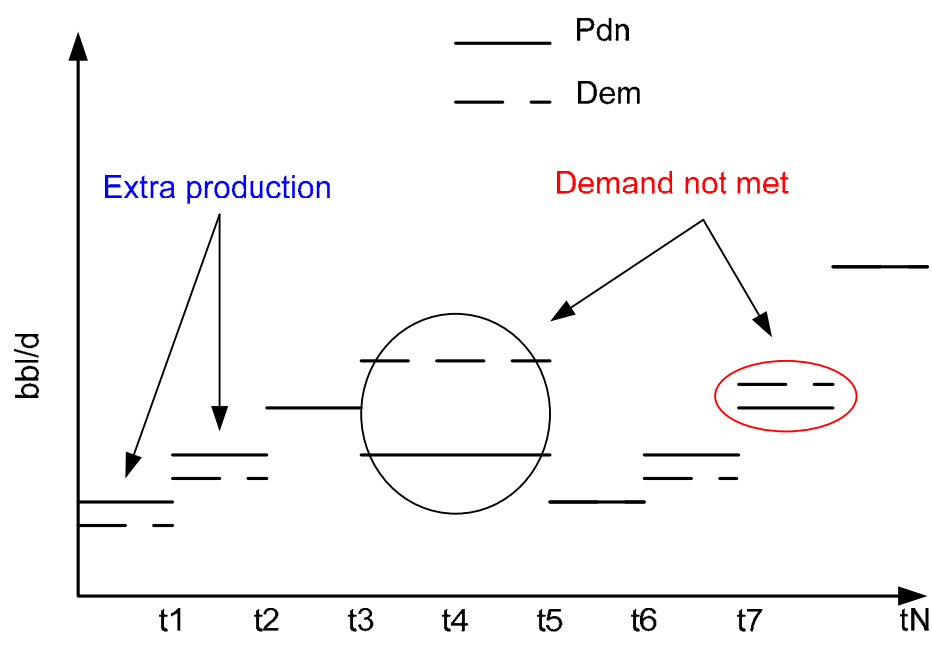
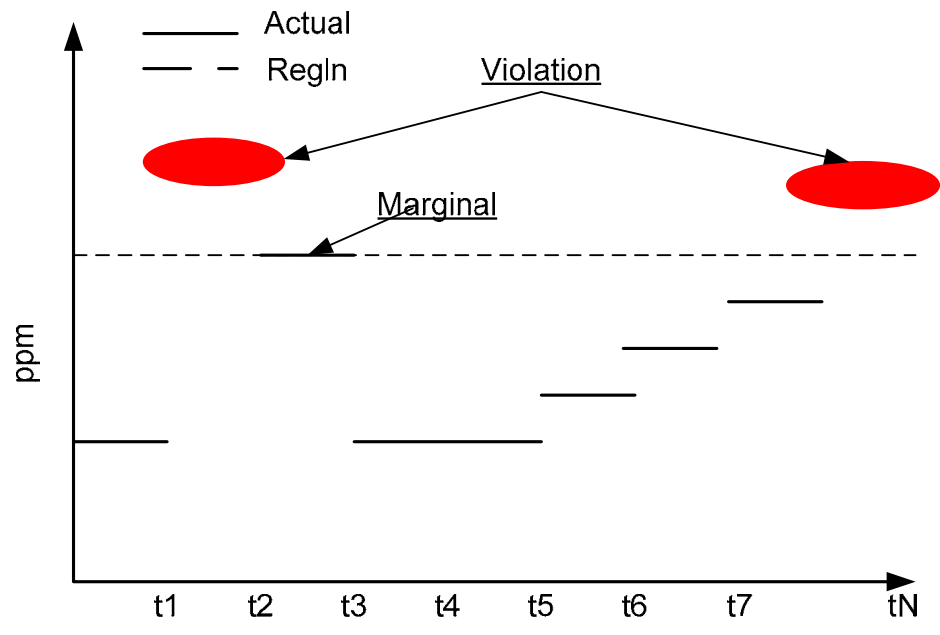**Figure F.1. Environmental objective domination regime representation**

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Figure F.2. Economic objective domination regime representation

VITA

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