Development of a Sustainable Eco-industrial park via Process System Design and Optimization

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Abstract

Discharge of industrial wastes represents one of the paramount threats to the environment. The adoption of integration and monetization schemes presents a sustainable approach to handling industrial wastes through the utilization of an eco-industrial park (EIP). One particular case of an EIP involving hydrocarbons is known as the carbon-hydrogen-oxygen symbiosis network (CHOSYN). Distinctive characteristics of the CHOSYN include converting the wastes into value-added chemicals and the ability to perform multiscale targeting that benchmarks the performance from the atomic scale to the large-scale implementation.

In this research, it is desired to design a sustainable CHOSYN. Several models were formulated to address various research gaps and design areas within the CHOSYN. For instance, the current approaches focused on incorporating mass and economic objectives to guide the synthesis of the CHOSYN. Major criteria such as safety and sustainability were not included as driving objectives for the CHOSYN design. Therefore a rigorous model was developed to guide the design of a CHOSYN based on multi-criteria such as economic, safety and sustainability. The previous criteria are optimized simultaneously to reach a sustainable CHOSYN design. A recycling framework was also integrated into the CHOSYN design to elevate the economic and sustainability performance of the proposed CHOSYN

Next, research on water integration was not covered in the CHOSYN design. Additionally, in most cases, mass and water networks are designed separately. Water can exist in mass networks as a raw material or waste, while it can also exist in water networks as a utility for cooling or heating purposes. Thus, a universal model was developed to design mass and water integration networks simultaneously in the CHOSYN. The model is also embedded with economic and sustainability criteria for multi-criteria optimization.

Finally, the existing approaches assumed steady-state operations in the design of CHOSYNs. Various plants can have multiple operation modes. For instance, biorefineries may have more than one operation period depending on the raw material availability. Thereupon, a model was formulated to address multiperiod operations in the CHOSYN design. A storage and dispatch system has been integrated to provide valuable degrees of freedom for the CHOSYN design and operation

It is anticipated that the formulated mathematical models are applicable for the design of any future CHOSYN project. The developed models can also be used as a preliminary design tool to assist engineers during the initial design phase.

Publications during enrolment

The following journal articles were published during my candidature. Journal article 1 is included in Chapter 3, while journal article 2 is included in Chapter 4.

Journal Article

1. Farouk, A. A., El-Halwagi, M. M., Foo, D. C., & Chew, I. M. L. (2021). Development of a C–H–O Symbiosis Network during Conceptual Design via Economic, Sustainability, and Safety Metrics. ACS Sustainable Chemistry & Engineering, 9(10), 3735-3749. https://doi.org/10.1021/acssuschemeng.0c08553 (Published)
2. Farouk, A. A., Chew, I. M. L. (2021). Development of a Simultaneous Mass-Water C-H-O Symbiosis Network. Sustainable production and consumption. doi: https://doi.org/10.1016/j.spc.2021.06.004 (Published)

Thesis including published works declaration

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes two original papers published in peer-reviewed journals. The core theme of the thesis is sustainable eco-industrial parks. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the student, working within the department of chemical engineering under the supervision of Dr. Irene Chew.

(The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.)

In the case of chapter 3 and 4, my contribution to the work involved the following:

Thesis Chapter	Publication Title	Status	Nature and % of student contribution	Co-author name(s) Nature and % of Co-author's contribution*	Co-author(s), Monash student Y/N*
3	Development of a C−H−O Symbiosis Network during Conceptual Design via Economic, Sustainability, and Safety Metrics	Published	85%	Irene Chew (7%) Mahmoud El-Halwagi (4%) Dominic Foo (4%)	No
4	Development of a Simultaneous Mass-Water Carbon-Hydrogen-Oxygen Symbiosis Network	Published	90%	Irene Chew (10%)	No

I have not renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

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I hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author I have consulted with the responsible author to agree on the respective contributions of the authors.

Main Supervisor name: Irene Chew

Main Supervisor signature: **Date:**

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Table of contents

Copyright notice	i
Abstract	ii
Publications during enrollment	iv
Thesis including published works declaration	v
Acknolgements	vi
Table of contents	vii
List of figures	ix
List of tables	ix
Chapter 1 Introduction	1
1.1 Overview	1
1.1.1 Sustainable Development	1
1.1.2 Integrated Biorefinery	1
1.2 Research Objectives	3
1.3 Research gaps and contributions	3
1.4 Research Strategy	5
Chapter 2 Literature Review	6
2.1 Process System Engineering	6
2.2 Eco-industrial Park	6
2.3 Water network - Eco-industrial Park	7
2.4 Mass network - Eco-industrial Park	9
2.5 Carbon-hydrogen-oxygen symbiosis network	9
Chapter 3 Multi-criteria CHOSYN	12
3.1 Development of a C–H–O Symbiosis Network during Conceptual Design via Economic, Sustainability, and Safety Metrics	12
Chapter 4 Mass-water CHOSYN	28
4.1 Development of a Simultaneous Mass-Water C-H-O Symbiosis Network	28
Chapter 5 Incorporation of a Storage and Dispatch System in Multiperiod C-H-O Symbiosis Network	51
5.1 Introduction	51

5.2 Problem statement	**53**
5.3 Mathematical formulation	**54**
5.3.1 Atomic targeting	**55**
5.3.2 Candidate reactions	**57**
5.3.3 Storage and dispatch system	**57**
5.3.4 Economics	**58**
5.3.5 Objective function	**59**
5.4 Case study	**59**
5.4.1 Participating plants	**59**
5.4.2 Candidate interceptors	**62**
5.5 Results and discussion	**63**
5.5.1 First scenario	**63**
5.5.2 Second scenario	**66**
5.5.3 Third scenario	**69**
5.5.4 Sensitivity analysis	**72**
5.6 Conclusion	**73**
Chapter 6 Conclusion and future work	**74**
References	**76**
Appendices	**83**

List of Figures

Figure 1.1: Research overview	5
Figure 5.1: Schematic representation of the CHOSYN with storage and dispatch system	54
Figure 5.2: Multiperiod CHOSYN with storage and dispatch system optimization algorithm	55
Figure 5.3: An optimum CHOSYN for the first operational period in scenario one	65
Figure 5.4: An optimum CHOSYN for the second operational period in scenario one	66
Figure 5.5: An optimum CHOSYN for the first operational period in scenario two	68
Figure 5.6: An optimum CHOSYN for the second operational period in scenario two	69
Figure 5.7: An optimum CHOSYN for the first operational period in scenario three	71
Figure 5.8: An optimum CHOSYN for the second operational period in scenario three	72
Figure 5.9: Sensitivity analysis of the increase in raw material costs on ROI	73

List of Tables

Table 5.1: Molar composition and total flowrates of the participating plants by-products for the first operation period	61
Table 5.2: Molar composition and total flowrates of the participating plants by-products for the second operation period	61
Table 5.3: Available external sources and their corresponding prices	61
Table 5.4: Participating plants demands flowrates (kmole/hr) during the first and second operation period.	62
Table 5.5: Candidate interceptors description	62
Table 5.6: Equipment costs and operating costs of different reactions used in the EIP.	63
Table 5.7: Flow rates (kmole/hr) of external, stored and discharged species in the CHOSYN for the first scenario	64
Table 5.8: Economic analysis of the first scenario CHOSYN	64
Table 5.9: Flow rates (kmole/hr) of external, stored and discharged species in the CHOSYN for the second scenario	67
Table 5.10: Economic analysis of second scenario CHOSYN	67
Table 5.11: Flow rates (kmole/hr) of external, stored and discharged species in the CHOSYN for the third scenario	70
Table 5.12: Economic analysis of third scenario CHOSYN	70

Chapter 1 Introduction

1.1 Overview

1.1.1 Sustainable development

Sustainable development is a concept that emerged in 1987, which can be defined as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" [1]. Sustainability possesses three reinforcing pillars, which are often used as sustainability indicators for industries. The first pillar is environmental sustainability, which prevents nature from being used as an inexhaustible resource and ensures its protection and rational usage. The second pillar is social sustainability, which points to the development of people, communities, and cultures in order to achieve reasonably, and fairly distributed quality of life, healthcare, and education across the globe. The third and final pillar is economic sustainability, which focuses on equal economic growth, thereby generating wealth for all individuals without harming the environment.

Within the chemical industry, numerous literature reviews attempted to quantify the three pillars of sustainability [2-4]. For instance, Azapgic et al. [5] introduced a framework that entails environmental (environmental impacts and efficiency), economical (financial and human capital indicators) and social (ethics and welfare indicators) aspects in the plant design. Later, a categorization framework with sustainability assessment tools based on indicators/indices, product-related assessment, and integrated assessment tools was reported [6]. Additionally, critical review and analysis for environmental indicators were performed [7-9].

1.1.2 Integrated biorefinery

Despite the necessity for being sustainable, there exists a huge gap between the global energy demand and its supply, in addition to a sharp increase in greenhouse gas emissions [10]. The global energy demand is forecasted to progressively escalate by 1.3% each year till 2040 [10]. The international energy agency [10] predicted a sharp decrease in 2040 in oil demand by up to 50%. Renewable energy, on the other hand, is expected to provide up to 2260 Mtoe in 2040 [10]. These significant changes in energy consumption are primarily due to the non-renewable fossil fuel contributing massively to carbon emissions [11]. As a result, global energy researchers are veering towards

sustainability and renewable sources of energy [12]. To alleviate these detrimental effects, significant initiatives have been launched in order to generate fuels from renewable resources (e.g., biofuels) and upgrade current designs to achieve environmental sustainability. An emerging solution to increase economic performance while acquiring sustainability is the formation of integrated biorefineries based on eco-industrial park (EIP) concept.

The concept of biorefinery arose in the late 1990s due to the scarcity of fossil fuels and the increasing tendency of biomass usage as a renewable feedstock for the production of biofuels [13]. Green biorefinery is defined as "A complex (to fully integrated) systems of sustainable, environmentally and resource-friendly technologies for the comprehensive (holistic) material and energetic utilization as well as the exploitation of biological raw materials in the form of green and residue biomass from a targeted, sustainable regional land utilization" [14]. The term biorefinery was also defined by the American National Renewable Energy Laboratory (NREL) as "A facility that integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass" [15]. The early development of biorefineries was confined to individual feedstocks of biomass. Later, integrated biorefineries that can handle multiple biomass feedstocks were developed. The goal of such a system is to supply a sustainable biofuel in addition to the production of biochemicals (e.g., methanol, syngas, glycerol, ether, etc.) with minimum wastes [16]. To date, immense well-established bioconversion technologies have been proposed for the conversion of biomass into a wide range of value-added products [17]. As a result, the need for systematic screening tools to filter the available numerous reaction pathways into optimum pathways has increased [17]. Numerous mathematical optimization techniques have been developed for the design of integrated biorefineries, as well as insight-based approaches [17]. For instance, Ng et al. developed several methods to synthesize and screen the potential alternatives for an integrated biorefinery [18-21].

Despite the various studies on biorefineries design, it is not yet as competitive as petrochemical refineries. This is generally due to the costs stemming from the design and technologies used to convert the biomasses to value-added products. One of the main prevailing technologies in biorefineries is the production of biodiesel. Although the biodiesel production route is very attractive than the petro-diesel, it is faced with several economic hurdles. One way to overcome these hurdles is glycerol valorization,

a by-product of the biodiesel production process. For that particular reason, the general EIP design model proposed in this research can be utilized in order to improve the competitiveness of biorefineries in terms of profit, sustainability, and safety. Additionally, glycerol valorization has been integrated as part of the case study solved.

1.2 Research objectives

The proposed research aims to achieve the following objectives:

- To synthesize a carbon-hydrogen-oxygen symbiosis network (CHOSYN) via multi-objective mathematical optimization modeling with minimal resource consumption.
- To synthesize a simultaneous mass and water network in the CHOSYN.
- To synthesize a multiperiod CHOSYN via the incorporation of a storage and dispatch system.

1.3 Research gaps and contribution

- A special case of EIPs is known as carbon-hydrogen-oxygen symbiosis network (CHOSYN). The CHOSYN is based on the same concept as the EIP, but it focuses on hydrocarbon processing plants and chemical species that have carbon, hydrogen and oxygen atoms in their atomic constituents. Currently, the focal point of most of the approaches in the design of CHOSYNs is economics. Safety and sustainability criteria were not embraced in the CHOSYNs design as driving objectives in the early process development phase. Therefore in this research, a universal mathematical model has been developed to synthesize a CHOSYN via multi-criteria optimization. The model reconciles multiple criteria, including economic, safety and sustainability criteria. The solutions output of the model can not only show the number of collaborating plants and the extent of the collaboration but also the chemistry needed to transform the by-products and wastes into value-added products and the allocation of the products to participating plant sinks.
- Various researches addressed mass and energy integration within the CHOSYN design. However, water integration was not studied before in the CHOSYN design. In general, water and mass networks are predominantly

designed separately. Water may be regarded as either raw material, by-product or waste in mass networks, while it can be used for heating and cooling purposes in the water network. Consequently, a rigorous model was developed to synthesize mass and water networks within the CHOSYN simultaneously. The model performs multi-objective optimization based on economic and environmental aspects to pinpoint the preferable integrated mass-water CHOSYN design.

- Almost all the research in the area of the design of CHOSYN assumed steady-state operations. This is may not be the actual case for some of the plants. For instance, biorefineries depend on the seasonal availability of biomass feedstock. Therefore, in the present research, a model has been formulated to design a CHOSYN with multiple operation periods. The model embeds the time variability in the CHOSYN design. Subsequently, a storage and dispatch system has been included in the multiperiod CHOSYN to increase the design degrees of freedom and elevate the economic and sustainability performance of the CHOSYN.

1.4 Research strategy

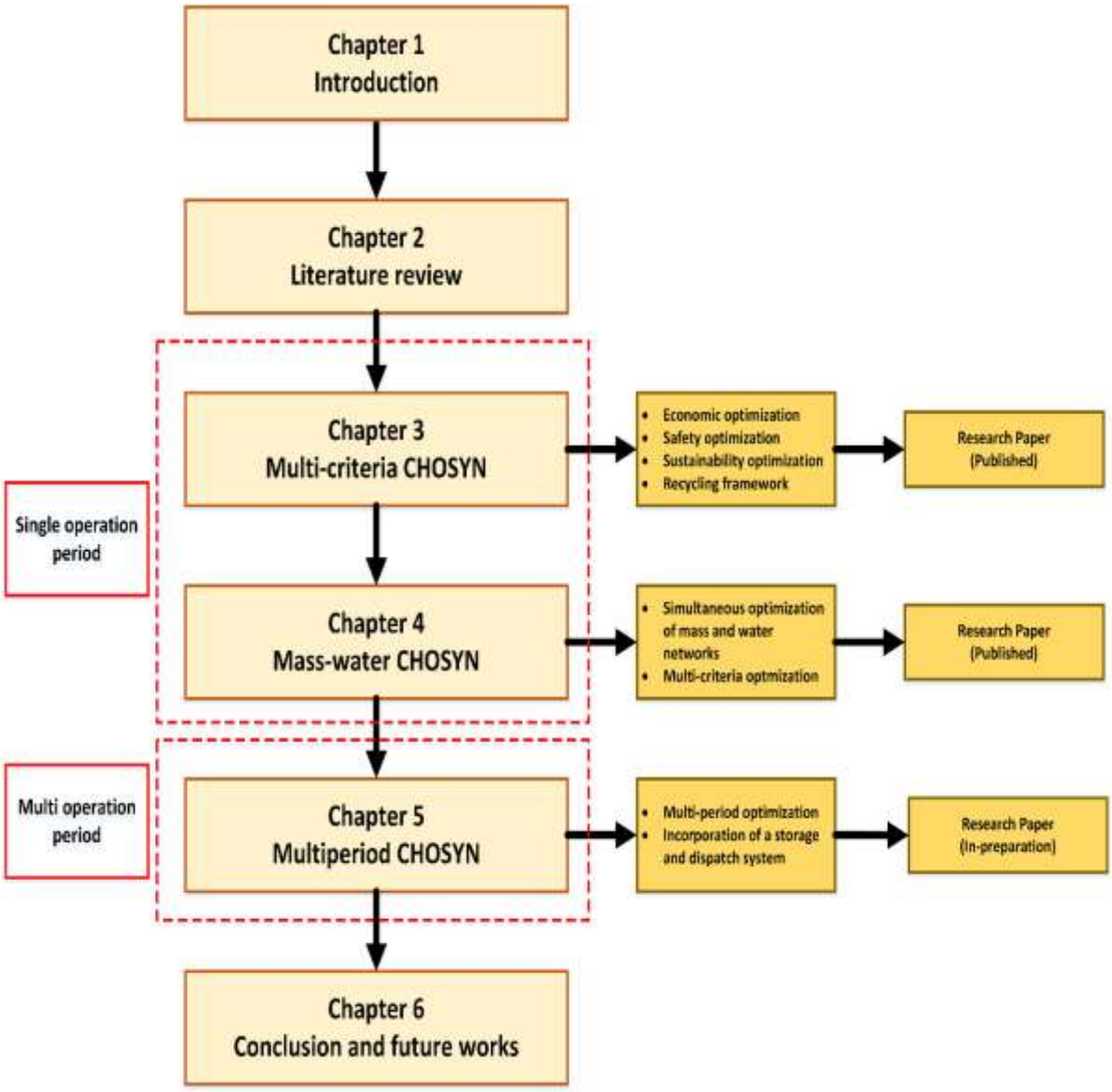

Figure 1.1: Research overview

Chapter 2 Literature review

2.1 Process system engineering

Sustainability implementation became more and more of a necessity in modern process design due to resources diminishing, environmental agitation, and global warming. Process system engineering (PSE) incorporates the field of process integration (PI), which is a systematic tool that can be used to tackle sustainability issues in EIP. PI is defined as a "holistic approach to process design, retrofitting, and operation, which emphasizes the unity of the process" [22]. The focal point of PI is the optimization techniques applied for resource conservation and wastes reduction to facilitate the design of sustainable systems such as an EIP.

There have been several studies that employed PSE to synthesis an EIP through mathematical optimization techniques. For instance, Ng et al. [23] developed a generic approach for the synthesis and optimization of the integrated palm oil processing complex. Numerous other researches further employed a fuzzy optimization method to synthesize sustainable biorefineries [24-30]. Bao et al. [31] introduced a shortcut method for the synthesis and optimization of integrated biorefineries. In the same year, Pham et al. [32] addressed the optimization of biorefineries using a forward-backward approach. Andiappan et al. [33] adopted a multi-objective optimization approach to synthesize a biorefinery considering energy requirements, economic performance, and environmental impact simultaneously. It is evident from the above literature that several PSE tools were employed to develop sustainable biorefineries and EIPs, given their beneficial ability. As such, the main objective of this research is the employment of process integration and optimization techniques in order to synthesize a sustainable EIP.

2.2 Eco-industrial park

Sustainable development can be attained through the implementation of an EIP. An EIP can be defined as a cluster of manufacturing companies located together in the same vicinity. The companies seek to share their resources, by-products, and wastes, thereby enhancing the overall environmental, economic, and social performance [34]. One crucial concept of EIPs is that working collectively is better than working as a standalone facility [34]. The fundamental principle behind the operation of an EIP is

the exchange of mass (raw materials, by-products) and energy (electricity, heat), a principle known as industrial symbiosis. Multiple felicitous EIPs have been initiated in numerous locations, in particular, the Kalundborg and NISP EIPs in Denmark and UK, respectively [35-37]. Previously, governmental authorities were not involved in the EIPs initiation and EIPs design was rather initiated spontaneously. Nonetheless, the Kalundborg EIP successfulness has promoted the development of EIPs worldwide, notably in Korea [38-39], Europe [40] and China [41]. The most prominent difference is the encouragement of governmental authorities towards the systematic planning and design of EIPs to meet sustainable and environmental goals.

Since the beginning of this century, process integration and optimization techniques have been widely used in designing water, hydrocarbons and hydrogen networks within EIPs. The magnitude of the EIP utility depends on the configuration and connections among the participating plants [42]. Therefore it is crucial to make proper process integration to achieve maximum advantages. Consequently, a massive amount of data related to participating plant operations and available technologies are essential, which makes the EIP configuration more complex [42]. To help decision makers in planning and designing these complex configurations, process integration techniques were employed [42]. Two particular cases were the focal point of EIPs research, i.e., water networks and mass networks.

2.3 Water integration - Eco-industrial park

Although 70% of the planet is covered with water, only 2.5% of the available water sources are freshwater. From this 2.5%, only 0.4% is available and accessible to people like rivers and lakes. There is no proper replacement for water as compared to oil, gas and other resources that have several energy forms and substitutes [43]. Due to the unprecedented augmentation of human activities, the depletion of earth freshwater hyoed [44]. The continual increase of these activities can lead to human survival be jeopardized [44]. Consequently, the need for sustainable development and sustainable solutions implementation increased due to the growing environmental concerns [44]. EIPs have been one of the major initiatives to reach sustainable development in water integration.

A plethora of research was centered on water integration within the EIPs. Water integration can be optimized through two main approaches, i.e., pinch technology and

mathematical modeling [44-45]. According to Yo et al. [45], pinch technologies have every easy-to-understand solution, but it is unable to design water networks involving more than one containment and performing multi-objective optimization, which is the usual case for EIPs. Within the context of mathematical modeling approaches, a mixed-integer linear model for direct and indirect wanter integration within the EIP was developed by Chew et al. [46]. The same authors later introduced a game theory approach for the analysis of interactions among different participating plants, given that each firm prioritizes its individual benefits and goals [47]. Lovelady et al. [48] further investigated the design of EIPs water networks by introducing a mathematical model capable of determining the optimum recycling and separating strategies while reducing overall costs concomitantly. Since the synthesis of water networks necessitate the availability of the process data of each participating plant, a fuzzy mixed-integer linear model was proposed to design water networks while anticipating that the process data may be incomplete [49]. Another work was reported by Binshne et al. [50], who proposed a multiperiod water planning framework since previous research assumed a single operation mode. Jui et al. [51] introduced a mathematical model for mixer continuous and batch inter-plant networks. Cheng et al. [52] introduced a novel scheme incorporating centralized and decentralized water mains, which are interconnected with the individual plants.

The preceding research focal point was the design of water networks within the EIP. Therefore, the environmental impact of industrial water discharged into watersheds was analyzed [53]. The work introduced an optimization model considering the influence of wastewater on the environment [54] and the number of pipelines in the water network [55]. From the above literature, we can deduce that the main objectives in the water integration models focused on two main objectives, i.e., economic and environmental objectives. The economic indicators have been the most studied and developed as compared to the environmental objectives [44,55]. For instance, several works considered the costs of purchasing, treating, and transporting water between plants [56-58]. Other studies considered minimizing the consumption of water by the EIP, which was then converted into financial savings and economic objectives [46, 48, 57, 59, 60]. On the other hand, the studies focusing on the environmental indicators considered the volume of freshwater consumed [45, 46], wastewater discharged [61] and the quality of water [44], were initiated.

2.4 Mass network - Eco-industrial park

Another substantial application of the EIP was hydrocarbon networks where by-products and wastes are transformed to valued-added chemical species, leading to augmented economic, environmental and sustainable benefits [62]. Consequently, various frameworks and approaches were introduced for the design of hydrocarbon EIPs. For instance, a non-linear mathematical model was developed for the synthesis of a fuel gas network [63]. Furthermore, two mathematical models were formulated for the design of a syngas network [64] and a low carbon integration network [65] as a means of contributing toward greenhouse gas mitigation. Additionally, a plethora of work has been reported for the synthesis of interplant hydrogen networks. The majority of these works were based on the previous work on in-plant hydrogen integration [66-67]. The interplant hydrogen network design methods are divided into either pinch-based or mathematical modeling approaches. The focal point of pinch-based methods is to establish minimum targets for fresh resource and waste flowrates for an interplant hydrogen reuse/recycle network [68] and hydrogen utility consumption [69] or to set targets for purifier capacity for a regeneration network [70]. Contrarily, the mathematical modeling approaches were inaugurated for handling complex systems such as intermediate headers [71-72], pressure ratio and adsorbent selectivity [73], purification techniques selectivity [74], multiperiod operations with regeneration schemes [75], and design of multiperiod interplant hydrogen networks while taking into consideration the fluctuation of operating conditions in each participating plant [76]. Over and above that, multiple types of research were reported on combined pinch-based and mathematical programming techniques [77].

2.5 Carbon-hydrogen-oxygen symbiosis network

The aforesaid EIPs research has predominantly focused on designing mass and energy networks within an EIP on species and plant levels. Noureldin [78] introduced a multiscale approach for the synthesis of carbon-hydrogen–oxygen symbiosis networks (CHOSYN) on an atomic level. The CHOSYN is a particular case of the EIPs centering around hydrocarbon chemical species. The CHOSYN can be defined as “a cluster of manufacturing plants with centralized shared facilities to enable the exchange, conversion, separation, treatment, splitting, mixing and allocation of streams containing C-H-O compounds” [78]. The CHOSYN is synthesized through the employment of the

atomic targeting technique [78]. The atomic targeting technique is a multiscale approach that allows the tracking of individual carbon, hydrogen, and oxygen atoms through a mass integration framework. A special feature of atomic targeting is enabling us to utilize the atomic-level information to identify performance benchmarks at multiple levels ranging from atomic, molecular and equipment levels up to process and macroscopic levels [78]. Multiple studies focused on addressing several design areas within the CHOSYN. El-Halwagi [79] developed an algebraic atomic targeting framework for synthesizing the CHOSYN. Based on the atomic targeting approach, Topolski et al. [80] introduced the anchor–tenant approach for synthesizing a CHOSYN based on both new (tenant) and existing (anchor) plants. Later, the anchor–tenant approach was enhanced to further optimize mass and energy within the CHOSYN simultaneously [81]. An optimization model was developed by Al-Fadhli et al. [82] to design a CHOSYN with multiperiod operations. Later, Al-Fadhli et al. developed an optimization model to synthesize a CHOSYN over a time horizon and with capacity planning [83-84]. Juárez-García et al. [85] introduced two optimization disjunctive programming approaches for the synthesis of the CHOSYN. The first approach is based on two stages, initially calculating the CHO atomic targets followed by economic disjunctive optimization modeling. The second approach entails determining the atomic targets and network configuration simultaneously using a disjunctive optimization model. Mukherjee [86] addressed the uncertainty associated with the exchanged streams during the synthesis of the CHOSYN. In more recent work, Panu et al. [87] tackled the problem of industrial CO_2 footprint reduction within the CHOSYN using a mathematical modeling approach. The majority of the approaches developed for the design of CHOSYNs had an economic focal point. There has been rising interest in consolidating other objectives in the process design, particularly safety and sustainability. Additionally, it is worth noting that the aforementioned CHOSYN contributions have focused on the conservation of hydrocarbons and energy, but there has not been significant work done to tackle the problem of water integration within the CHOSYN. Subsequently, the literature reviewed above has delved into the multiperiod operations problem in the CHOSYN where only the time variable was incorporated in the modeling equations. Consequently, in this research work, a multi-criterion approach is utilized to design a CHOSYN while accounting for economic, sustainability and safety objectives. Thereafter, a mathematical model has been developed to synthesize water and mass integration networks simultaneously within a CHOSYN. Afterward, a

mathematical optimization model was developed to integrate a storage and dispatch system in the CHOSYN design to address multiperiod operations within the CHOSYN.

Chapter 3 Multi-criteria Carbon-hydrogen-oxygen symbiosis network

3.1 Development of a C–H–O Symbiosis Network during Conceptual Design via Economic, Sustainability, and Safety Metrics

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Amr A. Farouk, Mahmoud M. El-Halwagi, Dominic C.Y. Foo, and Irene Mei Leng Chew

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The ability to set performance benchmarks ahead of detailed design using the multiscale atomic targeting technique allowed us to synthesize the CHOSYN. Various research has focused on multiple design areas within the CHOSYN. The journal article in this chapter investigated the design of CHOSYN based on multi-criteria optimization. The work overcame the limitations of the earlier works in which safety and sustainability criteria were not considered during the synthesis of a CHOSYN in addition to the introduction of recycling strategies. The model developed in this work was simulated in LINGO v.13 to acquire the requisite atomic benchmarks, hence evaluating the economic and safety/sustainability metrics in one single step. Furthermore, a recycling framework has been integrated into the model to maximize the efficiency of the resulting CHOSYN. The results in the journal article in this chapter demonstrate the capability of the developed model. The newly developed approach was applied to a case study based on glycerol valorization. The case study elucidated how this model could be utilized to cover sustainability and safety aspects for a CHOSYN from the atomic to multiple plant level during conceptual design. Two cases were first assessed based on economic performance and compared with each other to show the advantages of the newly introduced recycling framework. Afterward, two scenarios based on case two were investigated to show the merits of the multicriterion objective approach, which is based on economic, sustainability, and safety criteria. The first scenario had an objective function of maximum annual net profit, while the second scenario had an objective function of minimum purchased external sources. The optimized scenario with maximum annual net profit as an objective function had the highest ROI of 23%/year and the SASWROIM of 30%/year compared to ROI of 10%/year and the SASWROIM of 12%/year in the second scenario. Thereupon, a sensitivity analysis with respect to feedstock market price was carried out on scenario one.

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Research Article

Development of a C−H−O Symbiosis Network during Conceptual Design via Economic, Sustainability, and Safety Metrics

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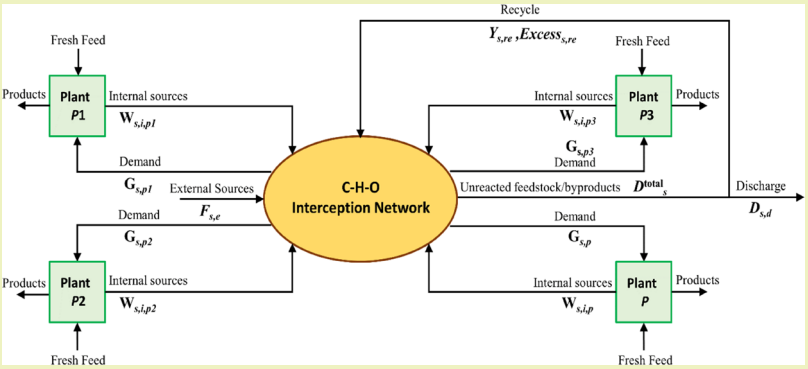

ABSTRACT: Discharge of industrial wastes constitutes one of the primary threats to the environment. A sustainable approach to handling industrial wastes is the adoption of integration and monetization schemes through the concept of an *eco-industrial park* (EIP). An EIP involving hydrocarbons is a particular case known as a *carbon−hydrogen−oxygen symbiosis network* (CHOSYN). Special features of the CHOSYN involve the conversion of wastes into value-added chemicals and the ability to perform multiscale targeting that benchmarks the performance from the atomic scale to large-scale implementation. Economic and mass conservation objectives have been used to guide the design of CHOSYNs. In this work, sustainability and safety are included as part of multicriterion objectives for the design of CHOSYNs. A rigorous and universal model for the optimization of a CHOSYN is developed with economic, sustainability, and safety objectives. An economic framework is used for reconciling the multiple criteria using the *safety and sustainability weighted return on investment metric*. The solution of the optimization formulation determines which plants participate and the extent of participation, the chemical pathways to convert wastes into value-added chemicals, and the allocation of the products to the users. The solution also reconciles the various design objectives. Subsequently, the proposed model is applied to a case study focusing on glycerol valorization.

KEYWORDS: *eco-industrial park, multicriterion optimization, atomic targeting, industrial symbiosis, process integration*

INTRODUCTION

Industrial wastes pose a substantial negative impact on the environment and also represent a major source of wasted energy. As such, there is an enormous gap between global energy demand and supply with an epic hike in greenhouse gas emissions.[1] The global energy demand is forecasted to escalate by 1.3% each year to 2040.[1] The International Energy Agency[1] predicted a sharp decrease in 2040 in oil demand up to 50%. On the other hand, renewable energy is expected to provide up to 2260 Mtoe in 2040. These significant changes in energy consumption are due to fossil fuels contributing massively to CO_2 emissions in addition to being nonrenewable.[2] As a result, global energy researchers are veering toward sustainability and renewable energy sources.[3] Concurrent to this, various initiatives of sustainable design have been proposed and practiced in the process industry. One way to realize sustainability is the employment of an *eco-industrial park* (EIP).

An EIP is formed by the integration of material and energy resources among multiple plants in close vicinity, thereby enhancing the overall environmental, economic, and social performance.[4] Currently, there are more than 250 EIPs worldwide, either operating or under development.[5] One of the most successful EIPs is arguably the Ulsan Mipo and Onsan industrial park in South Korea.[5] The latter has more than 1000

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companies with diverse background, including those in vehicle manufacturing, shipbuilding, and oil refining industries.[5] The investments in the Ulsan Mipo and Onsan industrial park reached $520 million, which yielded $554 million in savings.[5] The participating companies, on the other hand, gained $91.5 billion in revenues, alongside the recycling of 79,357 tons per year of water and the reduction of 665,712 tons per year of CO_2 emissions.[5]

Since the beginning of this century, *process integration* (PI) approaches were adopted in the EIP design, such as for water, hydrocarbon, and hydrogen networks. Spriggs et al.[6] proposed an EIP framework that adopts a mass integration approach using the graphical pinch approach proposed by El-Halwagi et al.[6] Within the context of water systems, Chew et al.[8] developed a mixed-integer linear program for direct and indirect water integration schemes within an EIP. A follow-up work was later reported using a game theory approach to analyze the interactions among the participating plants, as each firm typically tends to prioritize its own benefits.[9] The previous concept was further developed by Lovelady and El-Halwagi.[10] They investigated the design of water networks within an EIP using a mathematical model to determine optimum recycle and separation strategies while minimizing overall costs simultaneously.[10] The synthesis of water networks within an EIP requires process data of the participating plants, which can be incomplete for some plants. Therefore, a fuzzy mixed-integer linear programming model incorporating these design aspects was introduced.[11] Another work on EIP water systems involving continuous and batch production modes was also reported.[12] Bishnu et al.[13] proposed a multiperiod water planning approach owing to the fact that preceding research focused solely on a single period. Instead of focusing on the design of water networks in the EIP only, the environmental impact of industrial water discharged into watersheds was studied.[14] Consequently, a mathematical optimization model was formulated for water integration considering the environmental impact of discharged water from the network[14] and the number of pipelines in the network,[15] thus bringing forth further optimization and complexity.

Another important application of an EIP was reported on hydrocarbon networks, where intermediate products, by-products, and wastes were converted into value-added chemicals; this leads to increased economic and sustainable benefits.[16] As such, synthesis approaches were proposed for the design of EIPs handling hydrocarbons. For instance, a nonlinear model was formulated to synthesize a fuel gas network.[17] Two other models for synthesizing a syngas network from renewable sources[18] and a low carbon integration network[19] were introduced as a means of contributing toward the reduction of greenhouse gases.

Moreover, plenty of work has been reported for the design of interplant hydrogen networks. Most of these works were rooted based on the earlier work on in-plant hydrogen integration.[7,20,21] The design approaches for interplant hydrogen networks are divided into pinch-based and mathematical programming methods. Pinch-based approaches focused mainly on setting targets such as minimum hydrogen utility consumption[21] and minimum fresh resource and waste flow rates for an interplant hydrogen reuse/recycle network[22] or purifier capacity for a regeneration network.[23] On the other hand, mathematical programming approaches were proposed to handle complex systems such as intermediate headers,[24] pressure ratio and adsorbent selectivity,[25] selection of purification techniques,[26] a multiperiod with regeneration schemes,[27] and multiperiod interplant hydrogen integration taking into consideration the fluctuation of operating conditions in each participating plant.[28] Additionally, some research veering toward combined mathematical programming and pinch-based approaches has also been reported.[29]

The aforementioned EIP studies have mainly pertained to material and energy exchange within an EIP on species and plant levels. Noureldin and El-Halwagi[30] introduced a multiscale atomic targeting approach to address the problem of synthesizing *carbon−hydrogen−oxygen symbiosis networks* (CHOSYN) within the EIP on an atomic level. This approach is based on tracking individual carbon, hydrogen, and oxygen atoms through a mass integration framework. The main advantage of this method is that atomic-level information can be utilized to identify benchmarks for the purpose of determining the overall reactions necessary to achieve the preset targets of the participating plants. El-Halwagi[31] further introduced a shortcut approach to multiscale atomic targeting for synthesizing the CHOSYN. Using the atomic targeting methodology, Topolski et al.[32] synthesized the CHOSYN based on both new (tenant) and existing (anchor) plants based on the anchor−tenant approach. A follow-up work by Topolski et al.[33] enhanced the anchor−tenant approach to further account for both mass and energy within a CHOSYN. Al-Fadhli et al.[34] developed an optimization model based on atomic targeting to account for multiperiod operations in the CHOSYN. Al-Fadhli et al. introduced an optimization approach to design a CHOSYN over a time horizon and with capacity planning.[35,36] Juárez-García et al.[37] described two optimization approaches based on disjunctive programming for the design of the CHOSYN. The first approach entails two steps, initially determining the targets of the CHO atoms followed by disjunctive economic optimization. The second approach is based on a disjunctive optimization model where the targets and network configuration are determined simultaneously. Mukherjee and El-Halwagi[38] tackled the problem of the uncertainty associated with the exchanged streams during the design of the CHOSYN. In more recent work, Panu et al.[39] addressed the reduction in the industrial CO_2 footprint using an atomic targeting and optimization model.

It is worth noting that the aforementioned CHOSYN contributions have focused on the economic objectives as well as conservation of mass and energy. There has been growing interest in incorporating other objectives in engineering design, especially safety and sustainability. Within the context of sustainability, several metrics were proposed for assessing the sustainability aspects in terms of costs. For example, sustainability metrics were measured[40] and included in process design.[41,42] Additionally, a variety of studies aimed at including safety and sustainability during the design and optimization of different industries and processes such as syngas from shale gas,[43] ethylene technologies,[44] biorefineries,[45] solvent selection,[46] synthesis of an algae processing network,[47] energy systems,[48] and pollution trading.[49] El-Halwagi[50] introduced a new *sustainability weighted return on investment metric* (SWROIM). This metric is an extension of the traditional return on investment (ROI) that includes the sustainability factors of a process. Guillen-Cuevas et al.[51] amended the SWROIM to the *safety and sustainability weighted return on investment metric* (SASWROIM) to additionally encompass safety aspects during the initial design of a plant or a process. However, this metric is typically limited to a single process or a

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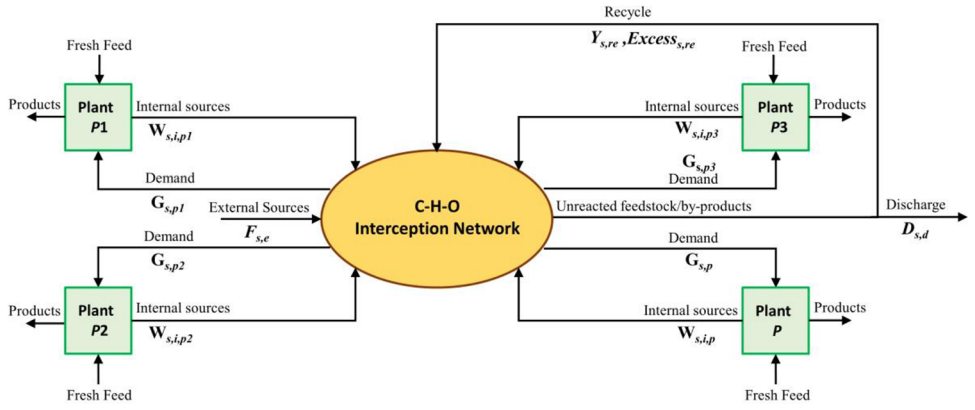

Figure 1. Systematic representation of the CHOSYN design problem.

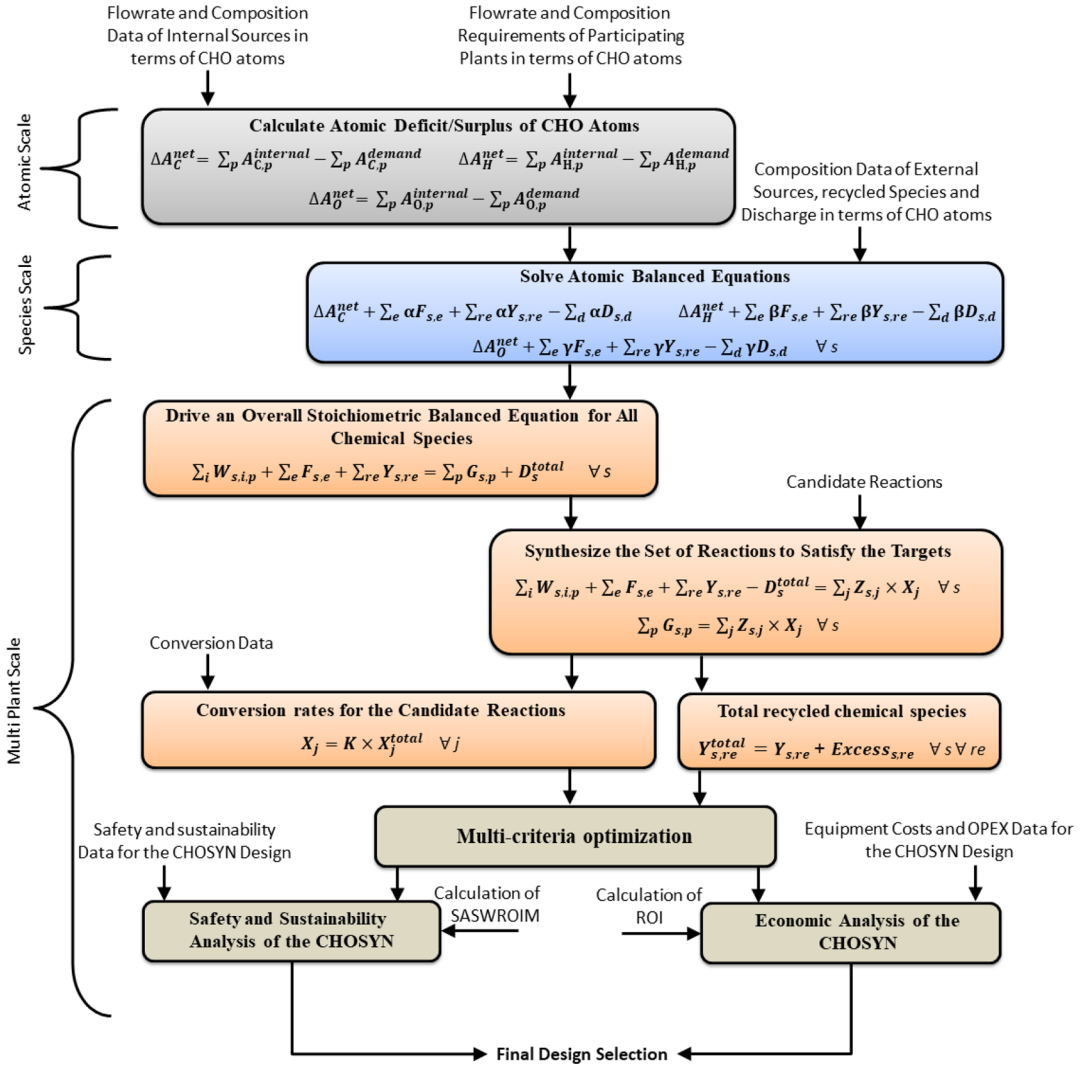

Figure 2. Multicriterion CHOSYN model algorithm.

plant. It is only used to calculate the safety and sustainability indicators after the respective process or plant has already been preliminarily designed. The existing approaches for the design of CHOSYNs do not include safety and sustainability as driving objectives. In this work, a multicriterion approach is used to address economic, sustainability, and safety objectives for the design of multiproduct CHOSYNs. A CHOSYN model has been developed to minimize resource consumption through the recycle of the CHOSYN unreacted feedstock and discharge. Subsequently, ROI and the SASWROIM are employed in the mathematical model to account for multicriterion objectives simultaneously, i.e., economic, safety, and sustainability criteria, in order to reach an optimal design. The *process safety index* (PSI) is used to measure the inherent safety of the process, which is then employed in the SASWROIM. The proposed final model is then applied to a glycerol case study given the critical

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ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

nature of this industry. The model offers several advantages, such as performing multiscale mass targeting on an atomic level with limited data, recycling any beneficial unreacted feedstock and discharge, accounting for safety during the preliminary CHOSYN design, and obtaining the final outcome based on both economic and sustainability criteria.

The paper is structured as follows. In the following section, the problem statement is first presented. This is followed by the model formulation illustrating the model algorithm. Subsequently, a case study is used to emphasize the merits of the model followed by results, discussion, and conclusion sections.

PROBLEM STATEMENT

First, a generalized problem overview was written, as shown in Figure 1. The problem to be addressed can be stated as follows:

Consider a cluster of manufacturing plants $\{p|p = 1,2,....,p^{\text{plant}}\}$ located in the same industrial zone. Figure 1 shows the CHOSYN, which functions as a centralized facility to convert internal resources to various useful products. Each plant produces internal sources $\{i|i = 1,2,....,i^{\text{internal sources}}\}$ that contains a set of chemical species $\{s|s = 1,2,....,s^{\text{species}}\}$. The molar flow rate of chemical species s in internal stream i from plant p is given by $W_{s,i,p}$. The CHOSYN can purchase external fresh resources $\{e|e = 1,2,....,e^{\text{external}}\}$ of chemical species s at a cost, with the stream flow rate indicated by $F_{s,e}$. The unreacted feedstock and byproducts will either be recycled to the interception network for further reuse or be discharged. The variable $Y_{s,re}$ denotes the flow rate of byproducts of chemical species s in the recycle stream $\{re|re = 1,2,....,re^{\text{recycle}}\}$, $\text{Excess}_{s,\,re}$ denotes the flow rate of excess raw materials of chemical species s, while $D_{s,d}$ denotes the flow rate of chemical species s in the discharge stream $\{d|d = 1,2,....,d^{\text{discharge}}\}$. Each plant can set its own demand flow rate indicated by $G_{s,p}$ to substitute a part of its fresh feed. $W_{s,i,p}$ and $G_{s,p}$ flow rates are known, while $F_{s,e}$, $D_{s,d}$, $\text{Excess}_{s,re}$ and $Y_{s,re}$ are unknown. $F_{s,e}$ and $D_{s,d}$ flow rates can be bound by maximum allowable limits, i.e., $F_{s,\,e}^{\max}$ and $D_{s,\,d}^{\max}$. Several chemical reactions $\{j|j = 1,2,....,j^{\text{reactions}}\}$ are available to convert the incoming chemical species to the participating plant demand. The EIP comprises major processing equipment, such as reactors, pumps, compressors, distillation columns, heaters, mixers, etc. that would process the sources (i.e., internal, recycled, and external) into useful products predetermined by each participating plant. Each plant can import products from a CHOSYN or export its internal sources. Waste disposal technologies exist in a CHOSYN to treat wastes for disposal. It is intended to synthesize an optimal CHOSYN with maximum profit or minimum resource consumption that achieves multiple criteria.

MATHEMATICAL FORMULATION

In this section, the mathematical model for CHOSYN is developed. The modeling algorithm for the proposed model is shown in Figure 2.

Atomic Targeting. Each plant in the EIP provides internal sources. The flow rates of the internal sources of all plants are indicated by $A_{\text{C},\,p}^{\text{internal}}$, $A_{\text{H},\,p}^{\text{internal}}$, and $A_{\text{O},\,p}^{\text{internal}}$. These flow rates are calculated in terms of carbon, hydrogen, and oxygen atoms (C, H, and O, respectively) through eqs 1−3, where α_s, β_s, and γ_s are the atomic coefficients for CHO atoms. The demand flow rates of CHO atoms of the plants are indicated by $A_{\text{C},\,p}^{\text{demand}}$, $A_{\text{H},\,p}^{\text{demand}}$, and $A_{\text{O},\,p}^{\text{demand}}$. These flow rates are calculated in the same manner through eqs 4−6. $W_{s,i,p}$ is the molar flow rate of chemical species s from internal stream i in plant p, while $G_{s,p}$ indicates the demand molar flow rate of chemical species s in plant p.

$$A_{\text{C},p}^{\text{internal}} = \sum_i \left(\sum_s \alpha_s W_{s,i,p} \right);\ \forall\ p \tag{1}$$

$$A_{\text{H},p}^{\text{internal}} = \sum_i \left(\sum_s \beta_s W_{s,i,p} \right);\ \forall\ p \tag{2}$$

$$A_{\text{O},p}^{\text{internal}} = \sum_i \left(\sum_s \gamma_s W_{s,i,p} \right);\ \forall\ p \tag{3}$$

$$A_{\text{C},p}^{\text{demand}} = \sum_s \alpha_s G_{s,p};\ \forall\ p \tag{4}$$

$$A_{\text{H},p}^{\text{demand}} = \sum_s \beta_s G_{s,p};\ \forall\ p \tag{5}$$

$$A_{\text{O},p}^{\text{demand}} = \sum_s \gamma_s G_{s,p};\ \forall\ p \tag{6}$$

The net supply of atoms represented by eqs 7−9 is calculated to determine the minimum flow rates of CHO atoms needed to meet the plant's demands. Positive signs indicate an excess of this atom, which represents a benchmark for the minimum target of discharge. In contrast, a negative sign implies a shortage of this atom, which indicates the minimum target of external sources.

$$\Delta A_{\text{C}}^{\text{net}} = \sum_p A_{\text{C},p}^{\text{internal}} - \sum_p A_{\text{C},p}^{\text{demand}} \tag{7}$$

$$\Delta A_{\text{H}}^{\text{net}} = \sum_p A_{\text{H},p}^{\text{internal}} - \sum_p A_{\text{H},p}^{\text{demand}} \tag{8}$$

$$\Delta A_{\text{O}}^{\text{net}} = \sum_p A_{\text{O},p}^{\text{internal}} - \sum_p A_{\text{O},p}^{\text{demand}} \tag{9}$$

Since there may be a deficit of specific atoms from eqs 7−9, an overall atomic balance equation for the CHOSYN is written. External fresh resources may be needed to overcome the lack of certain atoms or to meet the plant's demands. In some cases, discharge of wastes may occur when there is an excess of specific atoms. Beneficial byproducts can be recycled to the CHOSYN. Equations 10−12 represent the overall atomic balance for CHO atoms in an EIP. Note that four unknowns are observed in eqs 10−12. This would translate to several possible solutions for the EIP system. Through mathematical modeling, an overall objective function can be used to determine the minimum flow rates of external sources. The total discharge of the CHOSYN is composed of recyclable and discharged chemical species represented by eq 13. The maximum allowable flow rate of purchased and discharged chemical species is shown in eqs 14 and 15.

$$\Delta A_{\text{C}}^{\text{net}} + \sum_e \alpha F_{s,e} + \sum_{re} \alpha Y_{s,re} - \sum_d \alpha D_{s,d} = 0;\ \forall\ s \tag{10}$$

$$\Delta A_{\text{H}}^{\text{net}} + \sum_e \beta F_{s,e} + \sum_{re} \beta Y_{s,re} - \sum_d \beta D_{s,d} = 0;\ \forall\ s \tag{11}$$

$$\Delta A_{\text{O}}^{\text{net}} + \sum_e \gamma F_{s,e} + \sum_{re} \gamma Y_{s,re} - \sum_d \gamma D_{s,d} = 0;\ \forall\ s \tag{12}$$

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ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

$$D_s^{\text{total}} = \sum_d \alpha D_{s,d} + \sum_{re} Y_{s,re};\ \forall\ s \tag{13}$$

$$D_{s,d}^{\max} \geq D_{s,d} \tag{14}$$

$$F_{s,e}^{\max} \geq F_{s,e} \tag{15}$$

where $F_{s,e}$ is the flow rate of external chemical species, $Y_{s,re}$ is the flow rate of recycled chemical species s, $D_{s,d}$ is the discharge flow rate for chemical species s, D_s^{total} is the total discharge of the CHOSYN, $D_{s,d}^{\max}$ is the maximum allowable discharge subject to the country's environmental regulations, and $F_{s,e}^{\max}$ is the maximum available external feedstock that can be purchased subject to the feedstock availability.

Next, an overall balance equation is written to encompass all involved chemical species in the CHOSYN through eq 16. The purpose of the overall equation is to aid the determination of the flow rates of the candidate reactions needed to convert the chemical species according to plant demands. The flow rates of the candidate reactions are determined through eqs 17 and 18. The left-hand side of eq 17 describes the overall balance of species s in the CHOSYN. In eq 18, $\sum_p G_{s,p}$ is the overall balance of species s demanded by the participating plants. Since the conversion of chemical species is not 100%, eq 19 is employed to determine the total molar flow rate coefficient for reaction j. Recycled chemical species are divided to excess raw materials and byproducts. Recycled byproducts are determined using eqs 10−12, while recycled raw materials are represented by eq 20. In eq 20, the difference between the total and theoretical molar flow rate coefficients for consumed chemical species determines the excess raw materials needed to be recycled for each reaction. The total recycled flow rate of chemical species s is determined using eq 21.

$$\sum_i W_{s,i,p} + \sum_e F_{s,e} + \sum_{re} Y_{s,re} = \sum_p G_{s,p} + D_s^{\text{total}};\ \forall\ s \tag{16}$$

$$\sum_i W_{s,i,p} + \sum_e F_{s,e} + \sum_{re} Y_{s,re} - D_s^{\text{total}} = \sum_j Z_{s,j} \times X_j;\ \forall\ s \tag{17}$$

$$\sum_p G_{s,p} = \sum_j Z_{s,j} \times X_j;\ \forall\ s \tag{18}$$

$$X_j = K \times X_j^{\text{total}};\ \forall\ j \tag{19}$$

$$\text{Excess}_{s,re} = \sum_j Z_{s,j} \times X_j^{\text{total}} - \sum_j Z_{s,j} \times X_j;\ \forall\ s \tag{20}$$

$$Y_{s,re}^{\text{total}} = Y_{s,re} + \text{Excess}_{s,re};\ \forall\ s,\ \forall\ re \tag{21}$$

where $Z_{s,j}$ denotes the stoichiometric coefficient of species s in reaction j, X_j is the theoretical molar flow rate coefficient of reaction j, which is to be determined, K is the conversion of each reaction, X_j^{total} is the total molar flow rate coefficient for reaction j, $\text{Excess}_{s,re}$ is the excess recycled raw material, and $Y_{s,re}^{\text{total}}$ is the total flow rate of recycled chemical species s.

Economic Analysis. Each reaction represents an interceptor consisting of several types of equipment capable of converting the incoming chemical species to the required chemical species. Every interceptor has an overall equipment cost (EQUIP) and operating expenditure (OPEX), represented by eqs 22 and 23. Data for EQUIP and OPEX can be extracted either through actual plant data, literature review, or simulation programs. Equations 24 and 25 contain a binary variable (L_j) that has been integrated into the model to indicate which reactions occur in the EIP, in which σ is a small number, taken as one in this case. On the other hand, τ is a very large number, taken as 100,000 in this case.

$$\text{EQUIP} = \text{EQ}_{j,s} \times X_j^{\text{total}} \times L_j;\ \forall\ j,\ \forall\ s \tag{22}$$

$$\text{OPEX} = \text{OP}_{j,s} \times X_j^{\text{total}} \times M_{\text{wt},s};\ \forall\ j,\ \forall\ s \tag{23}$$

$$X_j \geq \sigma \times L_j \tag{24}$$

$$X_j \leq \tau \times L_j \tag{25}$$

where $\text{EQ}_{j,s}$ is the unit equipment cost (per kg of product chemical species s per year), X_j^{total} is the molar flow rate of species s in reaction j, L_j is the binary variable for reaction j, and $\text{OP}_{j,s}$ denotes the unit operating cost (per kg of product chemical species s) in reaction j.

Next, equipment cost is used to calculate fixed capital investment (FC) using the factorial method. The FC components are divided into physical plant cost and indirect plant cost and are assumed as a factor of the equipment costs.[52] Subsequently, the total capital expenditure (CAPEX) is determined through eq 26, where the working capital investment (WC) is assumed as 15% of the CAPEX.[52,53]

$$\text{CAPEX} = \text{FC} + \text{WC} \tag{26}$$

Next, the annualized fixed cost (AFC) in eq 27, which is the depreciation of the capital cost, is calculated. Using a 10-year linear scheme with negligible salvage, the value is assumed to be 10% of the overall capital cost. Subsequently, annualized net profit (ANP) is evaluated through eq 28.[53] Note that TR is the tax rate. Thereafter, the return on investment metric (ROI) in eq 29 is employed to determine project feasibility in terms of costs.

$$\text{AFC} = 0.1 \times \text{CAPEX} \tag{27}$$

$$\text{ANP} = \left[\left(\sum_p \sum_S \text{SALE}_s \times G_{s,p} - \sum_e \sum_S \text{COST}_s \times F_{s,e} - \text{OPEX} - \text{AFC}\right) \times (1 - \text{TR})\right] + \text{AFC} \tag{28}$$

$$\text{ROI} = \text{ANP}/\text{CAPEX} \tag{29}$$

where SALE_s is the sale price of the demanded chemical species s, and G_s is the demand molar flow rate of the chemical species s. On the other hand, COST_s is the cost of external chemical species s, and $F_{s,e}$ is the molar flow rate of the external chemical species s.

Safety and Sustainability Analysis. In this model, the PSI[54] is used to determine the inherent safety of the reactions utilized in the CHOSYN. Equations 30−34 are used to calculate the safety parameters, while eq 35 is used to evaluate the PSI.

$$\text{Flammability: } U_{\text{CE},j} = \frac{\text{LFL}_{\text{avg},j} - \text{LFL}_{\text{avg},j}}{\text{UFL}_{j\ total} - \text{LFL}_{j\ \text{total}}} \times L_j;\ \forall\ j \tag{30}$$

$$\text{Density: } U_{\text{CD},j} = \frac{\rho_{\text{avg},j}}{\rho_{j\ \text{total}}} \times L_j;\ \forall\ j \tag{31}$$

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ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

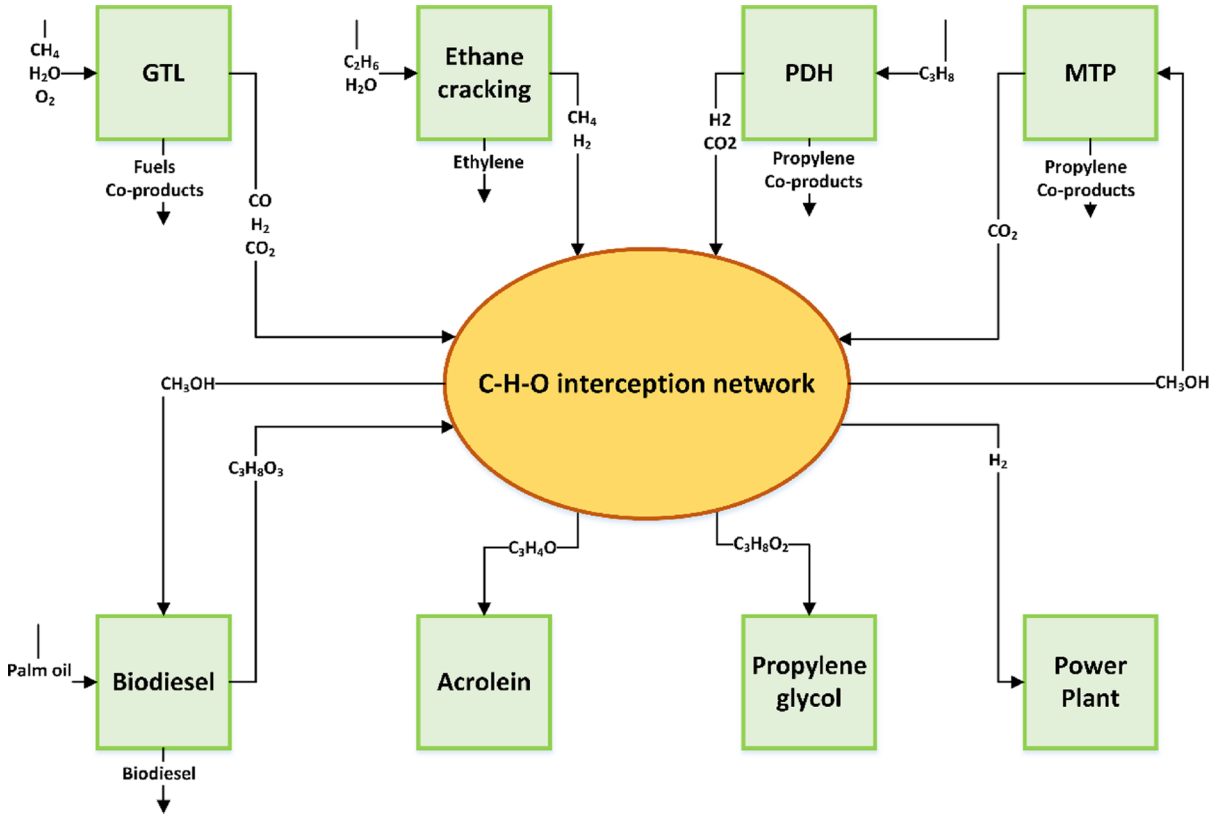

Figure 3. Raw materials, products, and byproducts of the participating plants.

Heating value:

$$U_{\mathrm{CH},j} = \frac{H_{\mathrm{avg},j}}{H_{j\ \mathrm{total}}} \times L_j;\ \forall\ j \tag{32}$$

Pressure:

$$U_{\mathrm{PP},j} = \frac{P_{\mathrm{avg},j}}{P_{j\ \mathrm{total}}} \times L_j;\ \forall\ j \tag{33}$$

$$\text{Temperature: } U_{\mathrm{PT},j} = \frac{T_{\mathrm{avg},j}}{T_{j\ \mathrm{total}}} \times L_j;\ \forall\ j \tag{34}$$

Process safety index:

$$U_{\mathrm{PSI},j} = A_o \times U_{\mathrm{CE},j} \times U_{\mathrm{CD},j} \times U_{\mathrm{CH},j} \times U_{\mathrm{PP},j} \times U_{\mathrm{PT},j};\ \forall\ j \tag{35}$$

where $U_{\mathrm{CE},j}$ is the flammability index for reaction j, $U_{\mathrm{CD},j}$ is the density index for reaction j, $U_{\mathrm{CH},j}$ is the heating value index for reaction j, $U_{\mathrm{PP},j}$ is the pressure index for reaction j, $U_{\mathrm{PT},j}$ is the temperature index for reaction j, $U_{\mathrm{PSI},j}$ is the process safety index for reaction j, $\mathrm{UFL}_{\mathrm{avg},j}$ is the average (avg) upper flammability limit for reaction j, $\mathrm{LFL}_{\mathrm{avg},j}$ is the average lower flammability limit for reaction j, $\rho_{\mathrm{avg},j}$ is the average density for reaction j, $\rho_{j\ \mathrm{total}}$ is the total density of all reactions, $H_{\mathrm{avg},j}$ is the average heating value for reaction j, $H_{j\ \mathrm{total}}$ is the total heating value of all reactions, $P_{\mathrm{avg},j}$ is the average pressure for reaction j, $P_{j\ \mathrm{total}}$ is the total pressure of all reactions, $T_{\mathrm{avg},j}$ is the average temperature for reaction j, $T_{j\ \mathrm{total}}$ is the total temperature of all reactions, A_o is a magnifying factor.

The *annual safety and sustainability profit* (ASSP) is calculated via eq 36. ASSP is used to compute the SASWROIM in eq 37.[51]

$$\mathrm{ASSP} = \mathrm{ANP} \times \left\{1 + \sum_{r=1} W_r \times \left[\frac{\mathrm{IN}_{\mathrm{Base},r} - \mathrm{IN}_{\mathrm{Project},r}}{\mathrm{IN}_{\mathrm{Base},r} - \mathrm{IN}_{\mathrm{Target},r}}\right]\right\} \tag{36}$$

$$\mathrm{SASWROIM} = \mathrm{ASSP}/\mathrm{CAPEX} \tag{37}$$

where W_r is a weighting factor in the form of a ratio representing the relative importance of the safety or sustainability indicator $\{r|r = 1,2,....,r^{\mathrm{indicators}}\}$ as compared to the ANP. These weights are determined based on the company's own values and what they are attempting to achieve. In eq 36, the denominator represents the indented improvement in the r indicator (IN), while the numerator signifies the actual positive step up or negative step down of the r indicator of the p plant. Note that CAPEX and ANP have been calculated in eqs 26 and 28, respectively.

Objective Function. The objective of the model may be set to maximize ANP, as shown in eq 38. Alternatively, one may also minimize the flow rate of external sources, following eq 39.

$$\text{Maximum (ANP)} \tag{38}$$

$$\text{Minimum } (F_{s,e});\ \forall\ s,\ \forall\ e \tag{39}$$

Equations 1−37 are optimized simultaneously to determine the overall reaction flow rates needed to satisfy the plant's demands through internal, recycle, and external chemical species using a global objective from eqs 38 and 39. These are influenced by the EIP economics through capital and operating costs, safety constraints through the PSI, and sustainability considerations through wastewater and CO_2 emissions reduction. The modeling and optimization approach proposed in this work adopts a systematic methodology for the accounting of the EIP

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ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

complexity characteristics and addressing the associated optimization challenges. The proposed approach allows a sustainable and robust EIP design taking into consideration the multicriteria and recycling of unreacted feedstock and byproducts.

CASE STUDY

Existing Plants. The merits of the multicriterion CHOSYN model are illustrated through a case study involving several chemical process plants. These plants are located in close vicinity and decided to participate in creating an EIP. The participation of the plants can be in the form of supplying wastes and byproducts to the EIP or demanding certain materials. One of the preeminent plants involved is a biodiesel plant, which produces glycerol as a byproduct. Glycerol is considered a paramount byproduct in the case study because the cost of producing biodiesel is usually higher than that of fossil fuels. Therefore, it is beneficial to valorize glycerol to increase the value added to the biodiesel plant.

The case study includes an industrial complex,[31] which consists of gas to liquid (GTL), ethylene cracking, propane dehydrogenation (PDH), and methanol to propylene (MTP) plants. In addition, it is assumed that new processes such as biodiesel, acrolein, propylene glycol, and power generation plants are to be added as part of the industrial complex. Primary fresh feed, byproducts, wastes, products of the participating plants, and the suggested participation network are summarized in Figure 3. The reactions involved in these plants are summarized as follows.

I. GTL: the GTL plant converts methane to syngas followed by Fischer−Tropsch reaction[55,56]

$$CH_4 + H_2O \rightarrow CO + 3H_2O \quad (40)$$

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O \quad (41)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (42)$$

$$nCO + (2n + 1)H_2 \rightarrow H(CH_2)_nH + nH_2O \quad (43)$$

II. Ethane cracking: ethylene is produced through ethane cracking reactions,[57] as given in eq 44. Note that there are side reactions associated with this process,[57] given in eqs 45−47

$$C_2H_6 \rightarrow C_2H_4 + H_2 \quad (44)$$

$$C_2H_6 + C_2H_4 \rightarrow C_3H_6 + CH_4 \quad (45)$$

$$2C_2H_6 \rightarrow C_3H_8 + CH_4 \quad (46)$$

$$C_3H_8 \rightarrow C_3H_6 + H_2 \quad (47)$$

III. PDH: catalytic reaction with high temperature is employed to produce polymer-grade propylene from propane[58]

$$C_3H_8 \rightarrow C_3H_6 + H_2 \quad (48)$$

IV. MTP: water is removed first from methanol to produce dimethyl ether followed by another reaction to produce propylene according to the following overall reaction[59]

$$3CH_3OH \rightarrow C_3H_6 + 3H_2O \quad (49)$$

V. Biodiesel: palm oil ($CH_3(CH_2)_{14}COOH$) is converted through transesterification reaction to biodiesel ($C_{14}H_{28}$), where glycerol ($C_3H_8O_3$) is generated as a byproduct

$$CH_3(CH_2)_{14}COOH + CH_3OH \rightarrow C_{14}H_{28} + C_3H_8O_3 \quad (50)$$

Three other new plants, i.e., propylene glycol to polyester compounds, acrolein to acrylic acid, and power generation plants, are treated as black boxes, where only the plant demands are known.

Available feedstocks and their prices are shown in Table 1. Note that these are subjected to geographical location. The data for internal sources of each participating plant are summarized in Table 2.

Table 1. Available Feedstocks and Their Corresponding Prices

available feedstock	price ($/kg)
$C_3H_8O_3$	1.09
CH_4	7.25
H_2	3
CO	0.18

Intermediate Reactions. In addition to the above, the EIP requires specific reactions and processes to meet the plant's demands through the transformation of internal sources into value-added products. The EIP is governed by a set of reactions to meet the demands of the plants. Any sets of the reactions can be chosen according to the optimization objectives (X_j represents the molar flow rate of each reaction)

- Methanol synthesis from syngas

$$X_{j1} \times (2H_2 + CO - CH_3OH) = 0 \quad (51)$$

$$X_{j2} \times (3H_2 + CO_2 - CH_3OH - H_2O) = 0 \quad (52)$$

- Steam reforming of methane to carbon monoxide, carbon dioxide, and hydrogen

$$X_{j3} \times (CH_4 + H_2O - 3H_2 - CO) = 0 \quad (53)$$

$$X_{j4} \times (CH_4 + 2H_2O - 4H_2 - CO_2) = 0 \quad (54)$$

- Glycerol to syngas overall reaction

$$X_{j5} \times (C_3H_8O_3 + 3H_2O - 3CO_2 - 7H_2) = 0 \quad (55)$$

- Forward and reverse water-gas shift reaction

$$X_{j6} \times (H_2O + CO - H_2 - CO_2) = 0 \quad (56)$$

$$X_{j7} \times (H_2 + CO_2 - H_2O - CO) = 0 \quad (57)$$

- Glycerol to propylene glycol

$$X_{j8} \times (C_3H_8O_3 + H_2 - C_3H_8O_2 - H_2O) = 0 \quad (58)$$

- Glycerol to acrolein

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Table 2. Internal Source Flow Rates in kmol/h

	GTL	ethylene cracking	PDH	MTP	biodiesel	propylene glycol	acrolein	power generation plant	total
CO	930	0	0	0	0				930
CO_2	2910	0	180	900	0				3990
H_2	7830	135	2000	0	0				9965
CH_4	0	39	0	0	0				39
$C_3H_8O_3$	0	0	0	0	1000				1000

$$X_{j9} \times (C_3H_8O_3 - C_3H_4O - 2H_2O) = 0 \quad (59)$$

Economic Data. As explained in the earlier section (see eq 26), total capital expenditure (CAPEX) is divided into fixed (FC) and working capital investments (WC). The fixed capital investment has two components, i.e., physical plant cost (PPC) and indirect plant cost (IPC),[52] as summarized in Tables 3 and 4. Working capital investment is calculated as 15% of fixed capital investment. The EQUIP and OPEX per kg of product of all technologies used in the case study are summarized in Table 5. Note that the water-gas shift reaction equipment costs and OPEX are assumed as a very small number because they occur as side reactions.

Table 3. Parameters for PCC

items of physical plant cost (PPC)	fraction of the equipment cost
equipment	1
installation	0.4
piping	0.7
instrumentation	0.2
electrical	0.1
buildings	0.15
storage	0.15
utilities	0.5
site development	0.1
auxiliary buildings	0.15

Table 4. Parameters for IPC

items of indirect plant cost (IPC)	fraction of the physical plant cost (PPC)
design and engineering	0.3
contractor's fee	0.05
contingency	0.1

Table 5. EQUIP and OPEX for Different Reactions Used in the EIP

technology	EQUIP ($/kg product/year)	OPEX ($/kg product)
methanol synthesis from syngas[60]	0.31	0.61
methanol synthesis from CO_2 and H_2[60]	0.49	1.01
steam reforming of methane to H_2 and CO[61]	0.29	0.66
steam reforming of methane to H_2 and CO_2[61]	0.29	0.66
glycerol to syngas overall reaction[62]	0.66	2.6
water-gas shift reaction	0.1	0.1
glycerol to propylene glycol[63]	0.28	0.85
glycerol to acrolein[64]	0.21	0.42

OPEX is divided into direct and indirect costs. Table 6 summarizes the parameter used for the factorial method of OPEX.[52] The CHOSYN is assumed to have 300 working days, and the cost of electricity is assumed to be $0.078/kWh. For labor costs, this study assumes that a total of 120 persons are needed for each technology, with an average working salary of $350/person/month. Note that raw materials are not calculated for each technology; instead, it is calculated for the whole CHOSYN in a separate step, which is a part of eq 28.

Table 6. Parameters for OPEX

direct costs		
variable	fixed	indirect costs
	labor	sales (10%)
miscellaneous (10% of maintenance)	supervision (20% of labor)	research and development (5%)
utilities	plant overhead (50% of labor)	general overhead (5%)
	interest (2% of fixed capital investment)	
	insurance (1% of fixed capital investment)	
	rent (1% of fixed capital investment)	
	royalties (1% of fixed capital investment)	
	maintenance (10% of fixed capital investment)	
direct costs = variable costs + fixed costs		
operating costs = direct costs + indirect costs		

Demand of Participating Plants. The chemical species demanded in the case study are shown in Table 7. These demands are fulfilled using internal sources, external sources, and recycled byproducts to substitute the freshly purchased feedstocks indicated by the participating plants, and wastes are discharged in the process. The maximum allowable discharge is subject to the geographical location and environmental regulations of each country. The weighting factors in eq 36 for CO_2 emissions and H_2O reduction and PSI, i.e. W_{CO2}, W_{H2O} and W_{PSI} are assumed as 0.2, 0.3 and 0.2, while its indicators $IN_{base,CO2}$, $IN_{target,CO2}$, $IN_{base,H2O}$, $IN_{target,H2O}$, $IN_{base,PSI}$, $IN_{target,PSI}$ are assumed as 13000 kmole/hr, 0 kmole/hr, 5000 kmole/hr and 0 kmole/hr, 15 and 1, respectively. The overall objective is

Table 7. Demands of Participating Plants

plant	demand	flow rate (kmol/h)
MTP	methanol	6500
biodiesel	methanol	1000
propylene glycol	propylene glycol	1000
acrolein	acrolein	1000
power production	H_2	5000

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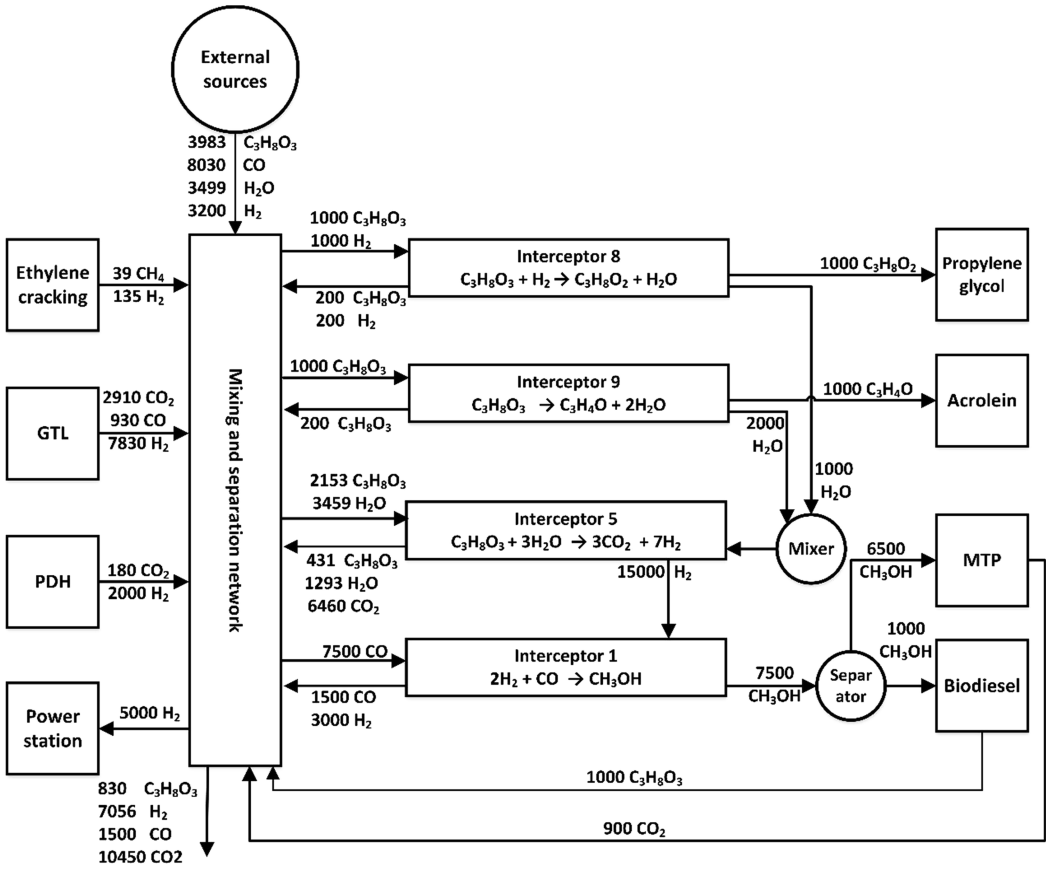

Figure 4. Optimum CHOSYN for case 1 (no recycling).

to set atomic targets, identify reaction pathways to achieve minimum resource consumption, and to determine the feasibility of the project at the conceptual design phase.

RESULTS AND DISCUSSION

Recycling Network Model. The CHOSYN is first evaluated for its economic performance. Two cases are conceived in this part. The first case is the conventional CHOSYN using atomic targeting,[31] while the second case is the modified CHOSYN with a recycling network. The objective function is set to maximize the ANP using eq 38, subject to the constraints in eqs 1−29 to show the merits of the recycling networks. Note that in case one, the $Y_{s,re}$ variable is set to zero, which indicates that no recycling occurs. The model is a linear program (LP) that has a global optimum if a solution exists and is solved using LINGO v13.0. Note that any unreacted feedstock or beneficial byproducts in the second case can be recycled to the CHOSYN. On the contrary, these unreacted feedstocks are discharged in the first case. The resulted CHOSYN configurations for both cases are shown in Figures 4 and 5.

Figure 6 shows that the external resources that need to be purchased in the first case are higher than those in the second case by 36%. Furthermore, results show that the total flow rate of the recycled chemical species is 5530 kmol/h in the second case, as compared to 0 kmol/h in the first case. Additionally, Figure 6 also shows that case two has a lower discharge flow rate. This is due to the fact that all unreacted species in the first case are discharged due to the absence of a recycling network, which in return increases the total flow rates of external and discharged chemical species as compared to case two. The flow rates of all species within the CHOSYN summarized in Tables 8 and 9 indicate that 830, 3200, 1500 kmol/h of $C_3H_8O_3$, H_2, and CO are recycled in case 2.

The economic performance is evaluated based on the ROI metric. The incurred costs, ANP and ROI for each scenario are shown in Figure 7. From Figure 7, case one has a higher overall raw material cost ($\$3243 \times 10^6$/year), as compared with case two ($\$2513 \times 10^6$/year) due to recycling of unreacted feedstock and beneficial byproducts, which leads to lower raw material costs. The economic results in Figure 7 yielded $\$865 \times 10^6$/year ANP, with ROI equal to 14%/year in the first case compared to $\$1394 \times 10^6$/year ANP and 23.0%/year ROI in the second case. Noted that the OPEX remained identical in both cases due to the fact that raw materials cost is being excluded in the eq (23), but included in eq (28). However, the second case had a recycling network where any beneficial byproducts or unreacted species can be sent back to the CHOSYN. Therefore, case two had lower raw materials costs, which in turn increased the ROI by 9%.

Multicriterion Objective Model. In this section, the second case CHOSYN is evaluated for its sustainability, safety, and economic performance simultaneously. The multicriterion optimization model was solved using an objective from eqs 38 and 39, subject to constraints in eqs 1−37. The criteria utilized in the model are economics, sustainability, and safety. The economic aspects are represented by the ANP, while CO2 emissions and wastewater reduction are utilized to quantify the sustainability features of the EIP. On the other hand, safety features in the case study are based on the PSI, which focuses on the individual interactions among different chemical species in mixtures. Two scenarios based on case two are investigated in this section. In each scenario, a different objective was used to

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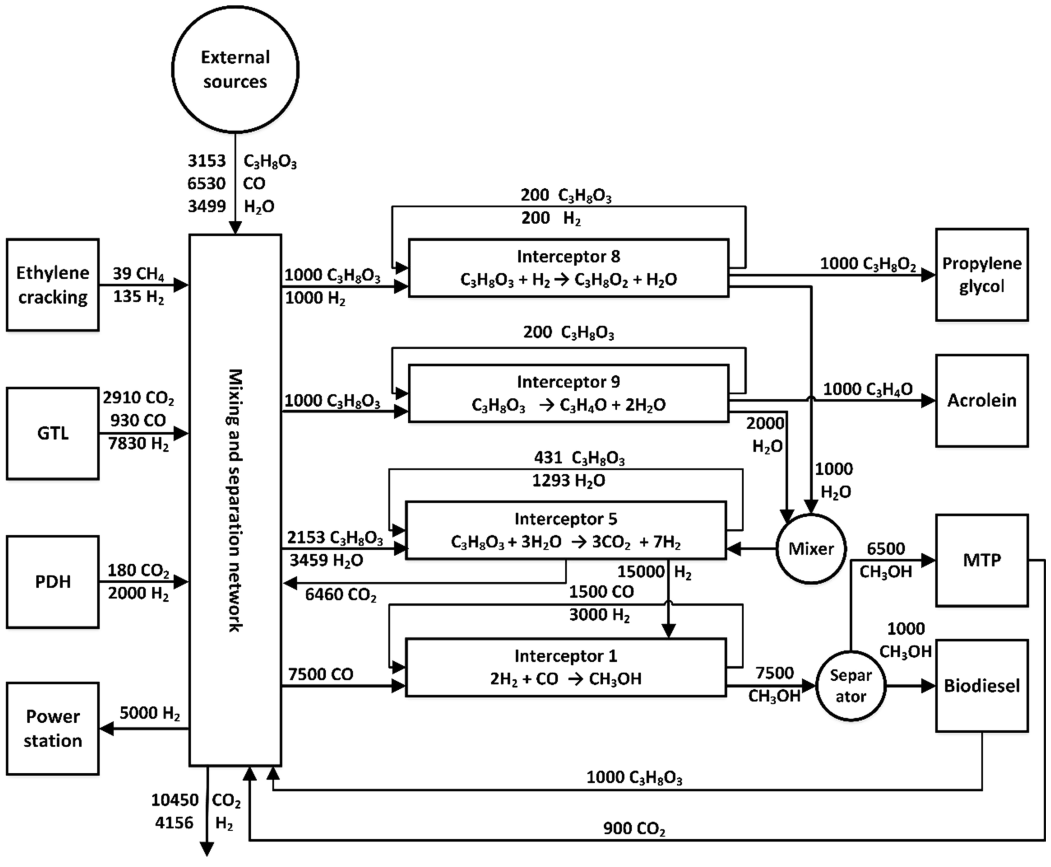

Figure 5. Optimum CHOSYN (case 2—with recycling).

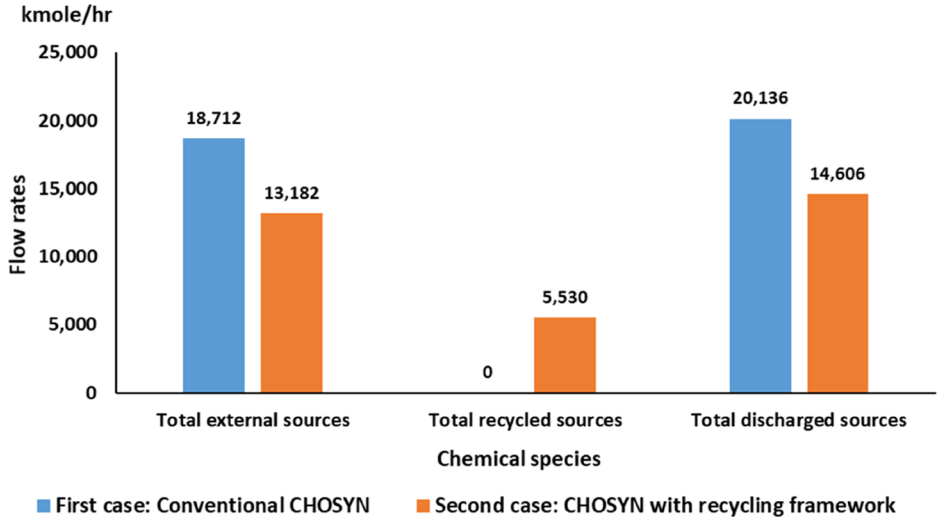

Figure 6. Total external, recycled, and discharged source flow rates (kmol/h).

Table 8. Flow Rate (kmol/h) of Involved Species in the CHOSYN (Case 1—No Recycling)

	glycerol	methane	hydrogen	carbon monoxide	water	carbon dioxide
internal sources (kmol/h)	1000	39	9965	930	0	3990
external sources (kmol/h)	3983	0	3200	8030	3499	0
recycle (kmol/h)	0	0	0	0	0	0
discharge (kmol/h)	830	0	7356	1500	0	10450

solve the model. The objective functions used for each scenario are demonstrated through eqs 38 and 39.The model is formulated as a mixed-integer nonlinear program (MINLP) that is solved by using LINGO v13.0 with a Global Solver invoked to reach an optimum solution. The nonlinearity

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ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

Table 9. Flow Rate (kmol/h) of Involved Species in the CHOSYN (Case 2—with Recycling)

	glycerol	methane	hydrogen	carbon monoxide	water	carbon dioxide
internal sources (kmol/h)	1000	39	9965	930	0	3990
external sources (kmol/h)	3153	0	0	6530	3499	0
recycle (kmol/h)	830	0	3200	1500	0	0
discharge (kmol/h)	0	0	4156	0	0	10450

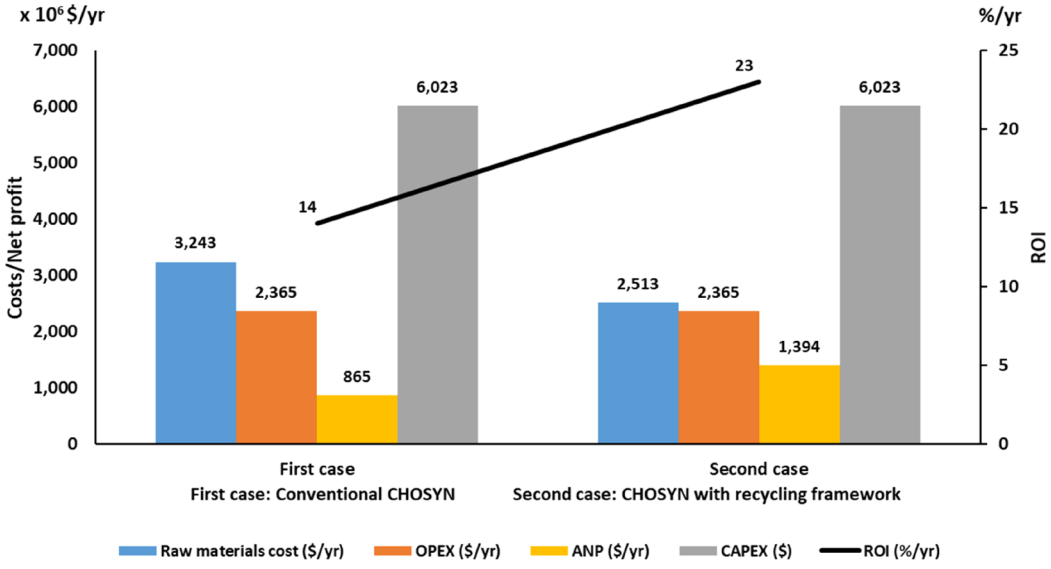

Figure 7. Economic performance for both cases.

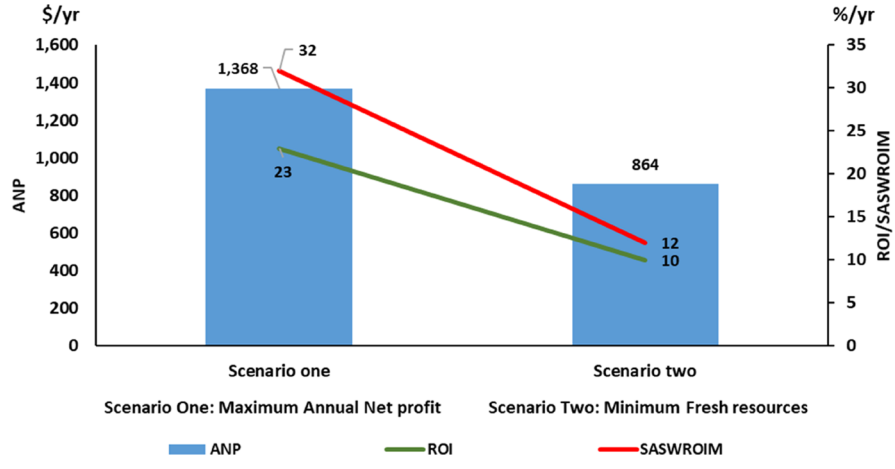

Figure 8. ANP, ROI, and SASWROIM metrics for both scenarios.

originates from the safety calculations in eqs 30−35 and SASWROIM calculations in eqs 36 and 37.

Scenario one was solved with maximum ANP in eq 38 as the objective function, while scenario two was solved with minimum fresh resources using eq 39 as the objective function. Based on Figure 8, scenario one achieved \$504 × 10^6/year higher ANP and an ROI of 23%, in contrast with scenario two with an ROI of 10%. This is because scenario two uses minimum external fresh resource flow rates as an objective function, which led to the use of reactions with higher CAPEX/OPEX in order to satisfy the plant's demands, which led to lower annual profit and ROI.

Aside from that, Figure 8 concludes that the SASWROIM of scenario one is higher by 20% compared to scenario two. This is due to the lower wastewater discharge in scenario one. Despite having lower ANP, the CO_2 discharge and PSI in scenario two are lower. Figure 9 shows that the CO_2 and H_2O discharges are equal to 10,450 and 0 kmol/h, respectively in scenario one compared to 2626 and 4000 kmol/h in scenario two. Figure 9 also shows that the total PSI in scenario two is lower than that in scenario one. This is because the reactions chosen in scenario two are safer because it utilizes less chemical resources. Overall, scenario one is more sustainable in terms of costs and some environmental aspects. Thus, sensitivity analysis will be made based on scenario one in order to provide more insights.

Sensitivity Analysis. Next, a sensitivity analysis is carried out with respect to the feedstock costs. It is desired to determine the effect of the feedstock cost parameter on the optimization model. Scenario one was selected as it has the highest ANP, ROI, and SASWROIM. The effect of altering the feedstock market prices of glycerol is examined. Figure 10 indicates the results of

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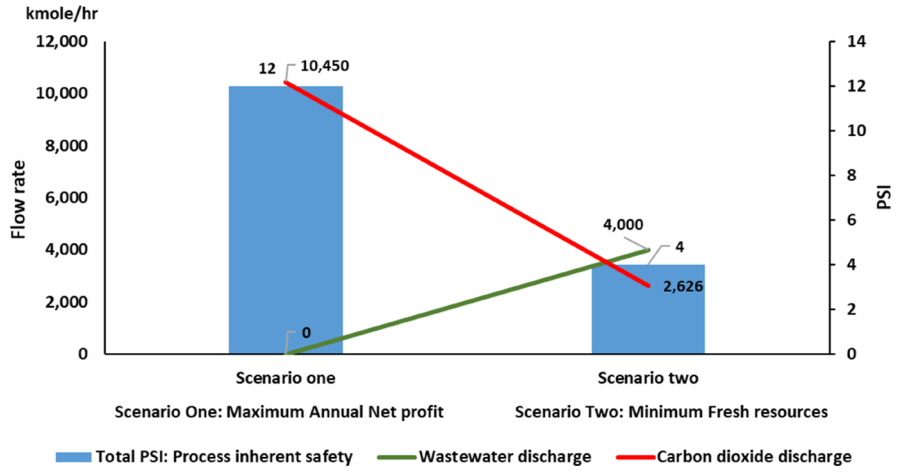

Figure 9. Total PSI and wastewater and carbon dioxide discharges for both scenarios.

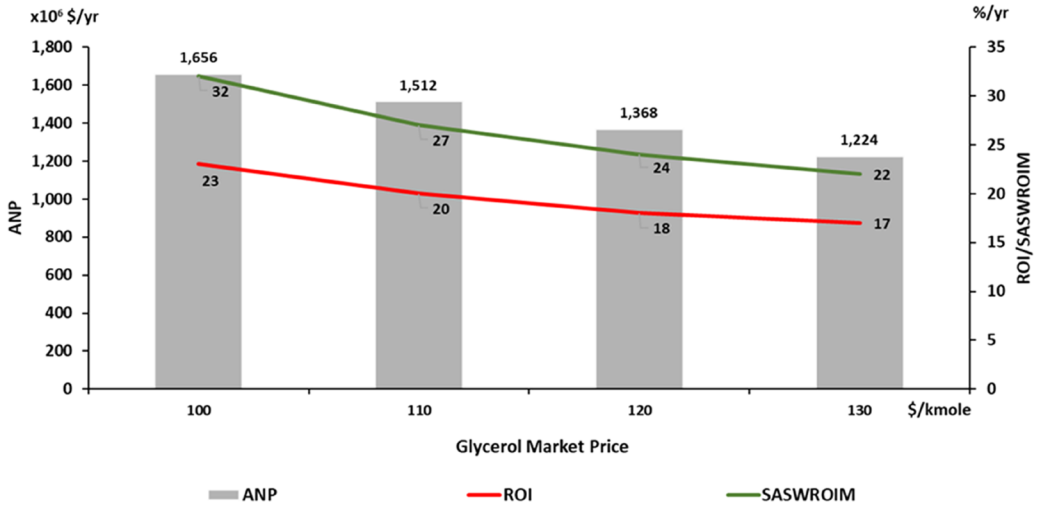

Figure 10. Sensitivity analysis of glycerol market price on ANP, ROI, and SASWROIM metrics.

changing the glycerol price. From Figure 10, it can be seen that as glycerol price increases, ANP, ROI, and SASWROIM decrease gradually. The ROI value levels off when the glycerol price reaches $120/t. This is due to the availability of other feedstocks such as methane, which substitutes glycerol at high glycerol prices.

CONCLUSION

This work has introduced a multiscale atomic optimization model embedded with safety and sustainability criteria in a CHOSYN. This model overcomes the limitations of the earlier model in which safety and sustainability criteria were not considered during the synthesis of a CHOSYN in addition to recycling any beneficial unreacted feedstock and byproducts. The approach devised in this work was simulated in LINGO to obtain the required atomic benchmarks, hence evaluating the economic and safety/sustainability metrics in one single step. The newly developed approach was applied to a case study based on glycerol valorization. The case study illustrated how this model could be used to cover sustainability and safety aspects for a CHOSYN from the atomic to multiple plant level during conceptual design. Two cases were evaluated based on economic performance and compared with each other to show the merits of the recycling framework. Afterward, two scenarios based on case two were conceived to show the advantages of the multicriterion objective function based on economic, sustainability, and safety aspects. The optimized scenario with maximum net profit as an objective function had the highest ROI of 23%/year and the SASWROIM of 30%/year. Subsequently, a sensitivity analysis with respect to feedstock market price was carried out on scenario one. As a preliminary tool, this model provides a clear representation of the sustainability, safety, and economic performance of the synthesized CHOSYN. It assists plant engineers in achieving sustainability targets by design. Future work should consider integrating other criteria as reliability and resilience to provide more insights as preliminary tools.

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Notes

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PARAMETERS

$A_{C,p}^{demand}$ total demand of carbon atoms in plant p (in molar flow rate)
$A_{H,p}^{demand}$ total demand of hydrogen atoms in plant p (in molar flow rate)
$A_{O,p}^{demand}$ total demand of oxygen atoms in plant p (in molar flow rate)
$A_{C,p}^{internal}$ total carbon atoms of plant p (molar flow rate)
$A_{H,p}^{internal}$ total hydrogen atoms of plant p (molar flow rate)
$A_{O,p}^{internal}$ total oxygen atoms of plant p (molar flow rate)
A_{C}^{net} net difference between internal supply and demand of carbon atoms in the CHOSY
A_{H}^{net} net difference between internal supply and demand of hydrogen atoms in the CHOSYN
A_{O}^{net} net difference between internal supply and demand of oxygen atoms in the CHOSYN
$COST_s$ cost of external chemical species s
$D_{s,d}^{max}$ maximum allowable flow rate of chemical species s in discharge stream d
$EQ_{j,s}$ equipment cost per annual mass of product chemical species s in reaction j
$F_{s,e}^{max}$ maximum allowable flow rate of chemical species s in external stream e
$G_{s,p}$ demand of chemical species s for plant p (molar flow rate)
K reaction conversion percentage
$OP_{j,s}$ operating cost per mass of product chemical species s in reaction j
$SALE_s$ sale price of the demanded chemical species s
TR tax rate
$W_{s,i,p}$ molar flow rate of chemical species s from internal stream i in plant p
$Z_{s,j}$ stoichiometric coefficient of species s in reaction j
α_s atomic coefficient of carbon atoms in chemical species s
β_s atomic coefficient of hydrogen atoms in chemical species s
γ_s atomic coefficient of oxygen atoms in chemical species s

Sets

d discharge stream
e external stream
i internal source stream
j chemical reaction number
p existing chemical plants
r number of sustainability and safety indicators
re recycled stream
s chemical species

Variables

AFC	annualized fixed cost
ANP	annual net profit
ASSP	annual safety and sustainability profit
CAPEX	capital cost expenditures
D_s^{Total}	total molar flowrate of chemical species s discharge from CHOSYN
$D_{s,d}$	molar flow rate of discharged species s in discharge stream d
$Excess_{s,re}$	molar flow rate of excess raw materials of chemical species
$F_{s,e}$	molar flow rate of the chemical species s in external stream e
L_j	binary variable denoting the existence of reaction j in an EIP
PSI	process safety index
OPEX	operating cost expenditures
ROI	return on investment metric
SASWROIM	safety and sustainability weighted return on investment metric
U_{CD}	density index
U_{CE}	flammability index
U_{CH}	heating value index
U_{PP}	pressure index
U_{PT}	temperature index
X_j	theoretical molar flow rate coefficient of reaction j
W_r	weighting factor
X_j^{total}	total molar flow rate coefficient of reaction j
$Y_{s,re}$	molar flow rate of the byproduct of chemical species s in recycled stream re

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Chapter 4 Mass-water CHOSYN

4.1 Development of a Simultaneous Mass-Water C-H-O Symbiosis Network

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Various research has focused on mass and energy integration within the CHOSYN. Furthermore, mass and water networks are designed separately. Water can exist in mass networks as raw material, by-product or waste. Water can also exist in water networks as a utility. The journal article in this chapter investigated the simultaneous design of water and mass networks in the CHOSYN. A systematic methodology for the design of a mass-water carbon hydrogen oxygen symbiosis network was introduced. The model was formulated to integrate both water and mass networks in the CHOSYN design, where the economic performance was maximized while accounting for the sustainability performance simultaneously. The meritoriousness of the MWCHOSYN model was highlighted through a case study involving several hydrocarbons plants. Three scenarios were conceived to accentuate the robustness of the model. Scenario one was utilized to synthesize separate mass and water networks in a two-step approach, using a single-objective function of minimum external species. Scenario two was solved with a multi-objective optimization approach, in which economic and environmental indicators were incorporated in the model to design a simultaneous mass-water CHOSYN in a single step. Scenario three was solved to design mass-water CHOSYN in a one-step model, using a single-objective function of minimum purchased chemical species. The results indicated that scenario two achieved better overall environmental and economic performance where the return on investment and sustainability weighted return on investment metrics reached 29 and 36%/yr.

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Development of a simultaneous mass-water carbon-hydrogen-oxygen symbiosis network

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ABSTRACT

The carbon-hydrogen-oxygen symbiosis network, which deals with hydrocarbon chemical species, is considered a special case of the eco-industrial park. The carbon-hydrogen-oxygen symbiosis network is based on the atomic targeting technique, which can be defined as a multi-scale approach to minimize resources and wastes. Nevertheless, previous works neglected the opportunity to perform water integration within the carbon-hydrogen-oxygen symbiosis network to minimize wastewater discharged to the environment. In this work, a rigorous model for the design of simultaneous mass and water carbon-hydrogen-oxygen symbiosis network is introduced. The objective of this model is the utilization of multi-objective optimization to maximize the economic and the environmental performance of the mass-water carbon-hydrogen-oxygen symbiosis network simultaneously to reach a sustainable design. The simultaneous mass-water carbon-hydrogen-oxygen symbiosis network is performed in a single-step model using the sustainability weighted return on investment metric. The solution from the model indicates which plants participate and the extent of participation, the chemical pathways to convert the incoming chemical species into value-added chemicals, , the allocation of the products to the usersand the mass and water network configuration. Three scenarios were investigated to show the merits of the developed model. Scenario one was solved using a single-objective function of minimum external species to design separate mass and water networks in a two-step model. Scenario two was solved using sustainability weighted return on investment metric, in which economic and environmental indicators were incorporated in the model to achieve multi-objective optimization to design a simultaneous mass-water CHOSYN in one single step. Scenario three was solved using a single-objective function of minimum purchased chemical species to synthesize a simultaneous mass-water CHOSYN in a single step. The results indicated that scenario two achieved better overall environmental and economic performance where the return on investment and sustainability weighted return on investment metrics reached 29 and 36%/yr. In conclusion, the multi-objective optimization of simultaneous mass-water CHOSYN provided eminent results and outstanding performance in terms of economic (annual net profit, total operating costs, return on investment metric) and environmental (carbon dioxide and wastewater discharge) aspects, leading to significant advantage compared to either separate mass and water network integration or single-objective optimization.

1. Introduction

Sustainability development is becoming a necessity in the contemporary design of industrial processes to address the global challenges of diminishing natural resources and the escalation of global warming. The incorporation of sustainability in process system design enables the process to efficiently use natural resources and reduce the negative impact on the surrounding environment. The eco-industrial park (EIP) is a favorable method of attaining sustainability without compromising the economic performance. An EIP can be defined as "a community of manufacturing and service businesses located together on common property. Members in EIP seek enhanced environmental, economic, and social performance through collaboration in managing environmental and resource issues" (Lowe, 2001). The EIP entails cooperation among

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Nomenclature

Parameters

$A_{C,p}^{demand}$	total demand of carbon atoms from plant p (kmole/hr).
$A_{H,p}^{demand}$	total demand of hydrogen atoms from plant p (kmole/hr).
$A_{O,p}^{demand}$	total demand molar flowrate of oxygen atoms from plant p (kmole/hr).
$A_{C,p}^{internel}$	total internal flowrate of carbon atoms from plant p (kmole/hr).
$A_{H,p}^{internel}$	total internal flowrate of hydrogen atoms from plant p (kmole/hr).
$A_{O,p}^{internel}$	total internal flowrate of oxygen atoms from plant p (kmole/hr).
A_{C}^{net}	net difference between internal supply and demand of carbon atoms in the mass- water CHOSYN.
A_{H}^{net}	net difference between internal supply and demand of hydrogen atoms in the mass- water CHOSYN.
A_{O}^{net}	net difference between internal supply and demand of oxygen atoms in the mass- water CHOSYN.
AH	annual operating hours.
$C_{f}^{overall}$	containment concentration of water from freshwater source (mg/l).
$C_{f,n}$	containment concentration of water from freshwater source f to mixer n (mg/l).
C_{l}^{max}	maximum allowable concentration of discharged water from treatment facility l (mg/l).
C_{m}^{in}	containment concentration of water from mass network m (mg/l).
C_{m}^{out}	concentration of water to mass network m (mg/l).
$C_{m,n}$	containment concentration of water from mass network m to mixer n (mg/l).
$C_{m,t}$	containment concentration of water from mass network m to regeneration facility t (mg/l).
$C_{m,l}$	containment concentration of water from mass network m to treatment facility l (mg/l).
C_{n}	containment concentration of water from mixer n (mg/l).
$C_{p,v}^{demand}$	containment concentration of water to water sink v in plant p (mg/l).
$C_{q}^{overall}$	containment concentration of water from water source q (mg/l).
$C_{q,n}$	containment concentration of water from water source q to mixer n (mg/l).
$C_{q,t}$	containment concentration of water from water source q to regeneration facility t (mg/l).
$C_{q,l}$	containment concentration of water from water source q to treatment facility l (mg/l).
$C_{t,n}^{out}$	containment concentration of water from regeneration facility t (mg/l).
$COST_{s}$	cost price of purchased chemical species s ($/kmole).
$D_{s,d}^{max}$	maximum allowable discharge of chemical species s (kmole/hr).
$EQ_{j,s}$	equipment cost per annual mass of product chemical species s in reaction j ($/kg/yr)
$F_{s,i,p}$	flowrate of chemical species s in internal stream i from plant p (kmole/hr).
$F_{s,e}^{max}$	maximum allowable flowrate of chemical species s in external stream e (kmole/hr).
FRC_{f}	purchased freshwater unit cost ($/ton).
$G_{s,p}$	chemical species s demand for plant p (kmole/hr).
OC	water network operating cost ($/ ton).
$OP_{j,s}$	operating cost per mass of product chemical species s in reaction j ($/kg).
PC	piping cost ($/m).
PD_{f}	distance from freshwater source f to water network (m).
PD_{m}	distance from mass network m to water network (m).
PD_{q}	distance from participating plant water source q to water network (m).
PD_{t}	distance from regeneration facility t to water network (m).
PD_{l}	distance from treatment facility l to water network (m).
$SALE_{s}$	sales price for sold products from mass network ($/kmole).
TRC_{t}	water regeneration unit cost t ($/ton).
W_{n}	water flowrate from mixer n.
$W_{p,v}^{demand}$	denotes the demand water for water sink v in plant p.
$W_{q}^{overall}$	denotes the overall water flowrate from water source q.
WWC_{l}	wastewater treatment unit cost ($/ton).
WE_{wi}	weighting factor representing the relative importance of water discharge indicator to annual net profit.
WE_{ci}	weighting factor representing the relative importance of carbon discharge indicator to annual net profit.
WI^{target}	target value for the water discharge indicator
$Z_{s,j}$	denotes the stoichiometric coefficient of chemical species s in reaction j.
α_{s}	number of carbon atoms in species s.
β_{s}	number of hydrogen atoms in species s.
γ_{s}	number of oxygen atoms in species s.

Sets

d	mass network discharge.
e	external source stream.
i	internal source stream.
j	chemical reaction number.
l	treatment facility.
m	mass network.
n	mixer.
p	existing chemical plants.
q	water source.
s	chemical species.
t	regeneration facility.
v	water sink.

Variables

ANP	annualized net profit ($/yr).
AFC	annualized fixed cost ($/yr).
CI	carbon discharge indicator
$CAPEX$	capital investment expenditures ($).
CV_{l}	containment concentration of water at the treatment facility l (mg/l).
CV_{t}^{in}	containment concentration of water to regeneration facility t (mg/l).
CI	carbon discharge indicator
$DI_{l}^{overall}$	total flowrate of water at treatment facility l.
$DI_{m,l}$	flowrate of water from mass network m to treatment facility l.

$DI_{q,l}$	flowrate of the water from water source q to treatment facility l.
$DR_{m,n}$	flowrate of water from mass network m to mixer n.
$DR_{q,n}$	flowrate of water from water source q to mixer n.
$F_{s,e}$	flowrate of chemical species s in e external stream (kmole/hr).
$F_{s,d}$	flowrate of chemical species s in d discharge stream (kmole/hr).
FR_f^{overall}	total flowrate of freshwater from freshwater source f.
$FR_{f,n}$	flowrate of freshwater from freshwater source f to mixer n.
MD	mass network water demand flowrate.
MW	mass network water source flowrate.
$OPEX$	operating costs expenditures.
TR_t^{overall}	total flowrate of the regenerated water from regeneration facility t
$TR_{t,n}$	flowrate of regenerated water from regeneration facility t to mixer n.
$UN_{q,t}$	flowrate of water from water source q to regeneration facility t.
$UN_{m,t}$	flowrate of the water from mass network m to regeneration facility t.
WI	water discharge indicator.
X_j	molar flowrate coefficient of reaction j.

several companies through the synergistic integration of resources and infrastructure. Nonetheless, the methodical utilization of resources is one of the key attributes of a sustainable and efficient chemical process to address the EIP design. The core concept of the EIP is known as industrial symbiosis, which involves the integration of mass (raw material, by-product, wastes), energy (heat, electricity) and utilities (water) between the different companies. Currently, there are more than 250 EIPs worldwide, either operating or under development (Farouk et al., 2021). There are a lot of successfully introduced EIPs worldwide, notably the Kalundborg EIP in Denmark, NISP EIP in UK and Ulsan Mipo and Onsan industrial park in South Korea (Chertow, 2007; Park et al., 2008).

The process system engineering (PSE) approaches provide a systematic methodology to addressing various issues of sustainability in an EIP. The PSE techniques incorporate the field of process integration (PI). PI can be defined as a "holistic approach to process design, retrofitting and operation which emphasizes the unity of the process" (El-Halwagi, 1997). PI primarily focuses on a given process in its entirety while encompassing the interactions between various resources and process units, leading to ameliorated mass and energy recovery. Analogously, in the EIP, the interactions between multiple companies and enterprises are considered a whole compared to a single enterprise. There is various research addressing the synthesis of EIPs while utilizing PSE techniques and PI approaches (NG et al., 2009; Chew et al., 2010). The PSE techniques provide a powerful tool for addressing sustainability issues in EIPs.

2. Literature review

There have been numerous works on the synthesis of EIPs. Two of the most common resources being studied in an EIP are water and hydrocarbon networks. Water integration within an eco-industrial park can generally be optimized using two main approaches, i.e., pinch technology and mathematical optimization. A plethora of research followed the pinch technology approaches for water network integration (Foo, 2009; Manan et al., 2004; Tan et al., 2007; Skouteris et al., 2018; Jia et al., 2015; Parand et al., 2016; Foo et al., 2014; Mohammadnejad et al., 2010; Ng et al., 2006). For instance, Foo (2009) provided a state-of-the-art overview of various insight-based approaches for single containment and fixed flowrate water systems. Manan et al. (2004) introduced a water cascade analysis technique to establish the minimum water and wastewater targets for continuous water-using processes. Tan et al. (2007) developed a systematic approach for retrofitting the water networks with regeneration using water pinch analysis. Skouteris et al. (2018) developed a rigorous analytical tool for water management and optimization based on water pinch analysis. Jia et al. (2015) utilized a water footprint pinch analysis technique based on the decomposition of total water footprint into external and internal footprint components. Parand et al. (2016) extended the automated composite table algorithm technique to study the interactions of key parameters in water networks of single containment. Foo et al. (2014) introduced a pinch-based approach to design chilled water networks. Ng et al. (2006) presented a novel and non-interactive numerical technique based on pinch analysis for flowrate targeting in water networks. However, pinch-based approaches have some drawbacks. For instance, it lacks the ability to deal with multi-objective optimization, which is generally the case of an EIP (Boix et al., 2015). Therefore, the mathematical optimization approach is more suitable for these types of large and complex problems (Boix et al., 2015). Chew et al. (2008) synthesized an EIP for direct and indirect water integration using mixed-integer linear programming. Lovelady and El-Halwagi, 2009 further investigated the water network design by introducing water recycle and separation strategies in a mathematical model. Considering the participating plants individual fuzzy cost goals, a bi-level fuzzy optimization model was developed by Avisoet al. (2010) to optimize the water exchange network in an EIP. A follow-up work was later reported using a robust optimization model to incorporate the future changes in the capacity or characteristic of industrial processes in the water network design (Aviso, 2014). The studies on water network integration within an EIP were further improved by introducing a multi-objective mixed-integer linear programming model to minimize freshwater, regenerated water flowrates as well as the number of network connections (Boix et al., 2012). Since most of the previous studies considered the minimization of freshwater consumed, Avisoet al. (2011) developed an optimization model to account for freshwater consumption and wastewater disposal simultaneously. Jiang et al. (2019) developed a superstructure-based approach for synthesizing EIP water systems while considering the single and inter-plant water integration and the sharing strategy of water utility sub-system of each participating plant. Instead of focusing on continuous modes, Bishnu et al. (2014) adopted a multi-period water planning approach to address batch systems, which is a common EIP setup due to different operating schedules. To bring forth further EIP complexity, the environmental impact of industrial wastewater discharged into watersheds (López-Díáz et al., 2015), water treatment systems and the number of pipelines in the network (Alnouri et al., 2016) were also investigated. Other works focused on addressing water network failures in the EIPs, especially failure propagation characteristics (Xu et al., 2019). On the other hand, the establishment of the EIPs requires a decision-making process through various participants and decision-makers. Thus, Chew et al. (2009) analyzed the interaction of the participating plants within the water network using a game theory approach. Leong et al. (2016) proposed a multi-objective optimization approach using the analytic hierarchy process.

In the context of hydrocarbon network synthesis, several works developed mathematical models to synthesize fuel gas (Hasan et al., 2011) and syngas networks (Roddy, 2013). Another vital application of hydrocarbon network was reported on interplant hydrogen networks. The works were divided into pinch-based and

mathematical programming approaches. Works using pinch-based methods pertained to setting targets such as minimum fresh resources (Chew et al., 2010) and minimum hydrogen utility consumption (Zhao et al., 2006). Other works focused on minimizing the purifier capacity for regeneration networks (Chew et al., 2010). Contrastingly, the mathematical programming techniques were more suitable for handling complex systems. Several design areas within the hydrogen network were addressed using mathematical modeling approaches, such as pressure ratio and adsorbent selectivity (Deng et al., 2017), intermediate headers (Kang et al., 2018), purification techniques selection (Shehata, 2016), multi-period operations considering the fluctuation of operating conditions in various participating enterprises (Han et al., 2020). Moreover, other works were reported on combined mathematical programming and pinch-based techniques (Lou et al., 2019).

The previous research designed EIPs mass and energy exchanges based on species and plant level. Noureldin and El-Halwagi (2015) introduced the concept of atomic targeting and species allocation to synthesize a centralized material exchange system, known as carbon-hydrogen-oxygen symbiosis network (CHOSYN). El-Halwagi (2017a) further improved the previous work by developing a shortcut multi-scale atomic targeting approach to design the CHOSYN. Recently, Toplski et al. (2018) introduced an anchor-tenant approach to design a CHOSYN by using not only existing plants but also grassroots plants. Later, the same authors extended the anchor-tenant approach to further incorporate both mass and energy in the design of the CHOSYN (Toplski et al., 2019). Mukherjee and El-Halwagi (2018) developed a mathematical model embracing reliability criteria with source stream uncertainty in the CHOSYN design. Juárez-García et al. (2019) developed an optimization model to design a CHOSYN based on disjunctive programming formulation. Al-Fadhli et al. (2018) introduced the problem of multiperiod operations and developed an optimization model to design a multiperiod CHOSYN. Panu et al. (2019) included the reduction in carbon footprint in the CHOSYN design. Farouk et al. (2021) introduced a multi-objective optimization approach to take into consideration the sustainability, safety and economic criteria during the design of CHOSYN.

The aforementioned studies addressed mass and energy integration only in the CHOSYN design. Thus, there is a lack of research on water integration within the CHOSYN. In general, water and mass (hydrocarbon) networks are designed as two independent networks. Nonetheless, in actual cases, mass and water networks intertwine. In such cases, it is beneficial to include both mass and water networks into the CHOSYN design. For instance, water may exist as a raw material or a product by being part of the mass network, but it also can be part of the water network as a utility for cooling/heating purposes. In this study, a systematic non-linear programming (NLP) model is developed to design an integrated *mass-water carbon-hydrogen-oxygen symbiosis network* (mass-water CHOSYN). The overall objective of the model is to optimize the economic and environmental performance simultaneously for the integrated mass-water CHOSYN. The economic indicators considered for the mass-water CHOSYN are the raw materials costs, freshwater costs, regeneration costs, wastewater treatment costs, capital costs and operating costs, while the environmental indicators are the flowrates of carbon dioxide and wastewater discharged to the environment. The developed model addresses the design of mass and water networks simultaneously in one single step which leads to a coherent mode. The paper is structured as follows. In the following section, a generalized problem statement is shown. This is followed by the model formulation proposed to tackle the problem statement. Afterwards, a case study is solved to show the merits of designing a mass-water CHOSYN, followed by results, discussion and conclusion sections.

3. Methods

3.1. Optimization approach overview

The proposed optimization superstructure in this paper consists of an integrated mass and water networks in the CHOSYN. The objective of this work is to synthesize an optimum network by using a multi-objective optimization approach. The research methodology is divided into three stages. In the first stage, the problem is defined where input parameters and required outputs are defined. The second stage involves mathematical modeling to achieve the required targets. The steps involved in the mathematical modeling are atomic targeting, water separation and mixing, mass and water balanced equations and multi-objective optimization, which incorporates economic and environmental objectives. The outputs of the mathematical modeling are determining the minimum benchmark for external sources, freshwater, wastewater discharge, and carbon dioxide discharge. Moreover, the mass network and water network configurations are generated based on the acquired results. The third stage is to define and solve a case study to show the merits of the developed model. Three CHOSYN schemes are generated in this stage. The first scheme involves the synthesis of separate mass and water networks using minimum external and freshwater sources as an objective function. The second scheme demonstrates the advantages of the developed model by optimizing mass and water networks simultaneously using a multi-objective optimization approach. The final scheme also involves simultaneous mass-water network optimization. However, a single objective of minimum external and freshwater sources was selected to show the difference between multi-objective and single-objective optimization. The proposed optimization approach superstructure is shown in Fig. 1.

3.2. Problem definition

Consider a number of industrial plants $\{p|p = 1,2,\ldots,p^{\text{plant}}\}$ located in the same industrial complex. The plants agreed to share their by-products and wastewater by forming an EIP. The EIP embodies a central facility divided into a mass network (MN) and a water network (WN). Fig. 2 shows the systematic representation of the mass-water CHOSYN.

The mass network receives by-products as internal sources $\{i|i = 1,2,\ldots,i^{\text{internal source}}\}$ that contains a set of chemical species $\{s|s = 1,2,\ldots,s^{\text{species}}\}$ and transforms them into valuable products, i.e., participating plants demand. The molar flowrates of the chemical species within each of the internal sources and the participating plants demand streams are indicated by $F_{s,i,p,}$ and $G_{s,p}$. The mass network may purchase external chemical species sources $\{e|e = 1,2,\ldots,e^{\text{external}}\}$ denoted by $F_{s,e}$ and freshwater denoted by *MD* to satisfy the participating plants demand. The mass network comprises several chemical reactions $\{j|j = 1,2,\ldots,j^{\text{reaction}}\}$ that act as interceptors and transforms the incoming chemical species to the participating plants demand. Additionally, the flowrate of the chemical species discharged $\{d|d = 1,2,\ldots,d^{\text{discharge}}\}$ is indicated by $F_{s,d,}$ while the flowrate of water released from the mass network is indicated by *MW*.

On the other hand, the water network has multiple inputs and outputs of water, each with a certain flowrate and quality. The water network incorporates a series of mixers $\{n|n = 1,2,\ldots,n^{\text{mixer}}\}$ which corresponds to the number of participating plants and mass network water sinks (SK) $\{v|v = 1,2,\ldots,v^{\text{sink}}\}$. The water network receives process water from each participating plant source (SR) $\{q|q = 1,2,\ldots,q^{\text{source}}\}$, each with certain quality denoted by C_q. The wastewater from each q source can be separated to water used in mixer n, untreated water sent to regeneration facility $\{t|t = 1,2,\ldots,t^{\text{regeneration}}\}$ and discharged water sent to treatment fa-

Fig. 1. Optimziation approch framework.

cility $\{l|l = 1,2,\ldots,l^{\text{treatment}}\}$. Additionally, the water network may receive released water from the mass network water source. The water flowrate and quality from the MN are represented by MW and C_m^{in}. The water from the mass network can be separated to water used in mixer n, untreated water sent to regeneration facility t and wastewater sent to treatment facility l. The regeneration and treatment facilities are assumed to be a fixed output quality type. The water network may purchase freshwater $\{f|f = 1,2,\ldots,f^{\text{freshwater}}\}$ with C_f^{overall} water quality to meet the participating plants sinks demand. To satisfy the participating plants and the mass network sinks demand, each mixer n in the water network may receive water from water source q, freshwater source f and regeneration facility t. All the plants participating in the integrated mass-water network have their internal sources, demand and input-output water flowrates and quality identified. The internal water network superstructure is shown in Fig. 3.

The overall aim of this work is to develop a model to design a CHOSYN that incorporates both mass and water networks. The model will select the optimum interceptors in the mass network to convert the input chemical species to the required demand. Additionally, the model will determine the optimum water network configuration simultaneously with the mass network to satisfy the participating plants in such a way that the economic objective is optimized without sacrificing the environmental objective.

3.3. Optimization model

3.3.1. Mass network

3.3.1.1. Atomic targeting. The atomic targeting technique El-Halwagi, 2017a) transforms the participating plants available chemical species from moles to carbon, hydrogen, and oxygen (CHO) atoms using Eqs. (1–(3), where α_s, β_s, γ_s are the atomic coefficients for CHO atoms. Note that $A_{C,p}^{\text{internal}}$, $A_{H,p}^{\text{internal}}$, and $A_{O,p}^{\text{internal}}$ are the total flowrates of the internal sources. Eqs. (4-6) are utilized to determine the flowrates of the participating plants demand in terms of CHO atoms in the same manner as Eqs. (1–3). The terms $F_{s,i,p}$ and $G_{s,p}$ are the molar flowrates of s chemical species in the internal and demand streams.

$$A_{C,p}^{\text{internal}} = \sum_s \left(\sum_i \alpha_s F_{s,i,p} \right); \ \forall p \tag{1}$$

$$A_{H,p}^{\text{internal}} = \sum_s \left(\sum_i \beta_s F_{s,i,p} \right); \ \forall p \tag{2}$$

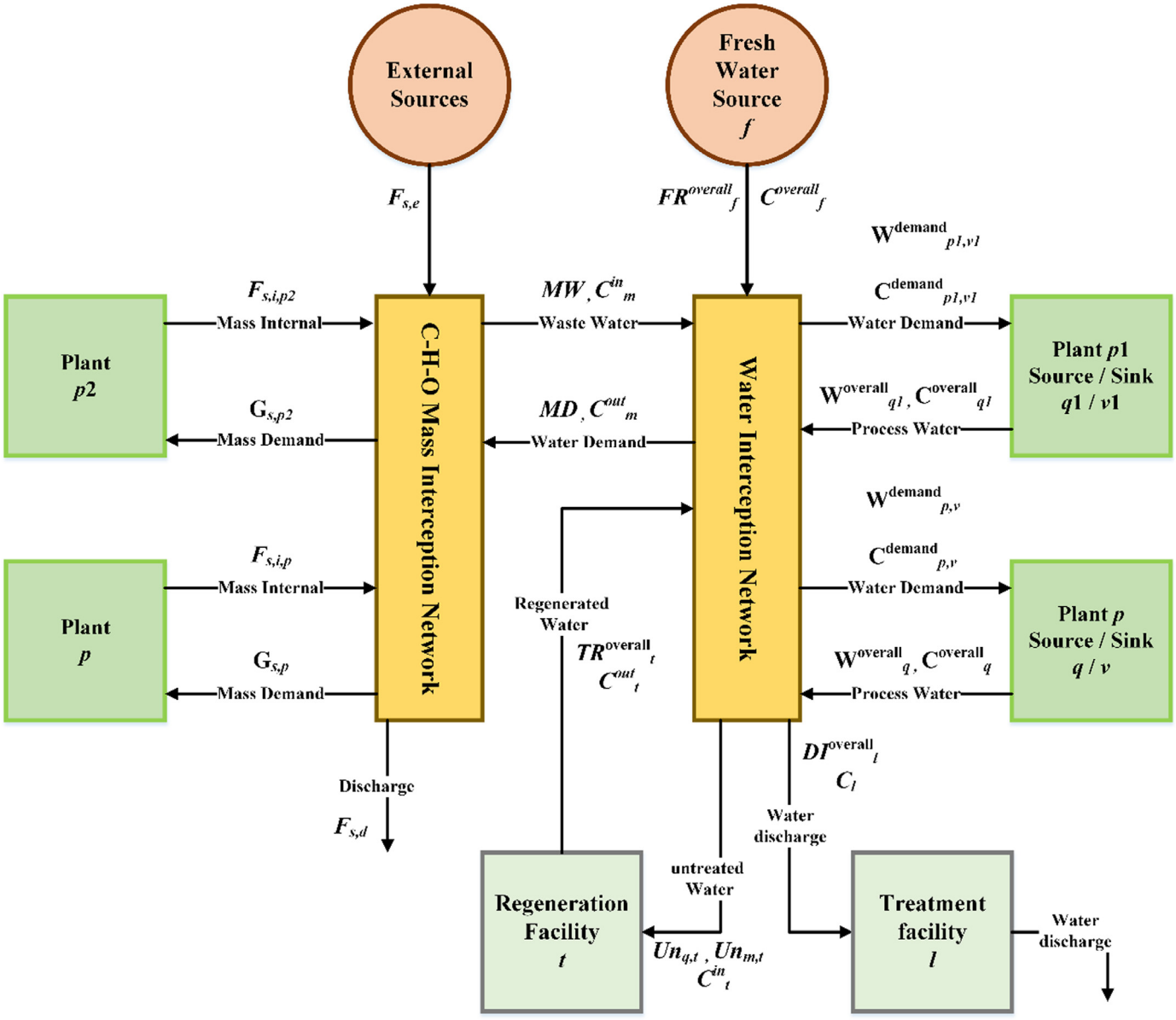

Fig. 2. Systematic representation of the mass-water CHOSYN central facility.

$$A^{internal}_{O,p} = \sum_{s}\left(\sum_{i}\gamma_s F_{s,i,p}\right);\ \forall p \tag{3}$$

$$A^{demand}_{C,p} = \sum_{s}\alpha_s G_{s,p};\ \forall p \tag{4}$$

$$A^{demand}_{H,p} = \sum_{s}\beta_s G_{s,p};\ \forall p \tag{5}$$

$$A^{demand}_{O,p} = \sum_{s}\gamma_s G_{s,p};\ \forall p \tag{6}$$

In Equations (7) – (9), the difference between the total available internal sources and the plants demand represents the total net supply of atoms to the mass network. A positive sign points to a surplus of an atom, which indicates a benchmark for minimum discharge flowrate for that atom. Conversely, a negative sign points to a deficit of an atom, which indicates a benchmark for minimum purchasable external sources.

$$\Delta A^{net}_{C} = \sum_{p} A^{internal}_{C,p} - \sum_{p} A^{demand}_{C,p} \tag{7}$$

$$\Delta A^{net}_{H} = \sum_{p} A^{internal}_{H,p} - \sum_{p} A^{demand}_{H,p} \tag{8}$$

$$\Delta A^{net}_{O} = \sum_{p} A^{internal}_{O,p} - \sum_{p} A^{demand}_{O,p} \tag{9}$$

3.3.1.2. Overall atomic balance. The deficit and surplus of atoms identified by Eqs. (7–9) are satisfied by purchasing external sources and allowing chemical species discharge. The flowrates of external sources ($F_{s,e}$), required water (MD), chemical species discharge ($F_{s,d}$) and released water from MN water source (MW) are determined using Eqs. (10) – (12). Note that the maximum allowable purchased and discharged chemical species are shown in Eqs. (13) – (14).

$$\Delta A^{net}_{C} + \sum_{s}\sum_{e}\alpha_s F_{s,e} + \alpha_{H_2O} MD - \sum_{s}\sum_{d}\alpha_s F_{s,d} - \alpha_{H_2O} MW \tag{10}$$

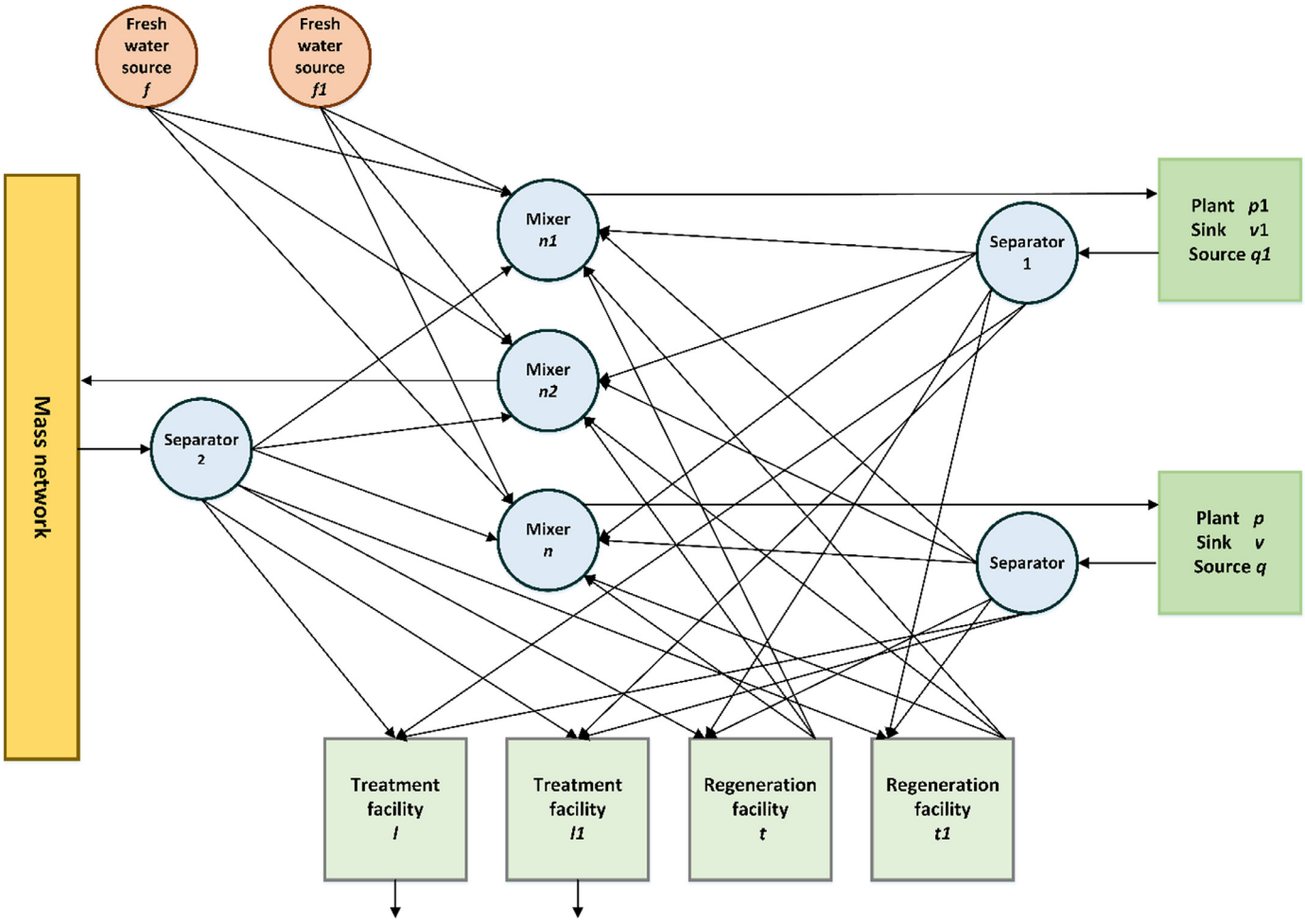

Fig. 3. Water network superstructure.

$$\Delta A_H^{net} + \sum_s \sum_e \beta_s F_{s,e} + \beta_{H_2O} MD - \sum_s \sum_d \beta_s F_{s,d} - \beta_{H_2O} MW \quad (11)$$

$$\Delta A_O^{net} + \sum_s \sum_e \gamma_s F_{s,e} + \gamma_{H_2O} MD - \sum_d \gamma_s \sum_d F_{s,d} - \gamma_{H_2O} MW \quad (12)$$

$$F_{s,e} \le F_{s,e}^{max}; \ \forall s, \ \forall e \quad (13)$$

$$F_{s,d} \le F_{s,d}^{max}; \ \forall s, \ \forall d \quad (14)$$

3.3.1.3. Overall mole balance. The overall stoichiometric Eq. (15) includes all involved chemical species within the mass-water CHOSYN. The molar flowrate coefficient X_j of each chemical reaction j needed to transform the entering chemical species to the required demand is calculated using Eqs. (16) – (17), where $Z_{s,j}$ the stoichiometric coefficient of chemical species s in reaction j.

$$\sum_s \sum_i \sum_p F_{s,i,p} + \sum_s \sum_e F_{s,e} + MD = \sum_s \sum_p G_{s,p} + \sum_e \sum_d F_{s,d} + MW \quad (15)$$

$$\sum_s \sum_i \sum_p F_{s,i,p} + \sum_s \sum_e F_{s,e} + MD - \sum_s \sum_d F_{s,d} - MW = \sum_s \sum_j Z_{s,j} \times \sum_j X_j \quad (16)$$

$$\sum_s \sum_p G_{s,p} = \sum_s \sum_j Z_{s,j} \times \sum_j X_j \quad (17)$$

3.3.2. Water network

3.3.2.1. Participating plants water balances. The input water balances entering the water network from the participating plant water sources are summarized in Eq. (18). The inlet water flowrate from any participating plant water source ($W_q^{overall}$) to the water network using Eq. (18) is separated to water used ($DR_{q,n}$) in mixer n, untreated water ($UN_{q,t}$) to the regeneration facility t and discharged water $DI_{q,l}$ to treatment facility l. The flowrates of the directly used water in the water network can be further separated to multiple inputs to each mixer n inside the water network. The number of mixers in the water network corresponds to the number of participating plants and mass network water sinks. Likewise, the flowrates of untreated and discharged water to the regeneration facility and treatment facility can be further separated to enter several regeneration facilities t and treatment facilities l. Note that the water quality of the separated streams is shown in Eq. (19).

$$W_q^{overall} = \sum_n DR_{q,n} + \sum_t UN_{q,t} + \sum_l DI_{q,l}; \ \forall q \quad (18)$$

$$C_q^{overall} = C_{q,n} = C_{q,t} = C_{q,l}; \ \forall q \quad (19)$$

3.3.2.2. Freshwater balance. Similarly, the purchasable freshwater flowrate ($FR_f^{overall}$) from each freshwater source can be separated to water used ($FR_{f,n}$) in any mixer n in the water network as shown in Eq. (20). The water quality of the separated streams is shown in Eq. (21).

$$FR_f^{overall} = \sum_n FR_{f,n}; \ \forall f \quad (20)$$

$$C_f^{overall} = C_{f,n};\ \forall f \tag{21}$$

3.3.2.3. Mass network water balance. Correspondingly, the flowrate of released water (MW) from the mass network m water source calculated previously using Eq. (10) – (12), is separated to water used ($DR_{m,n}$) in mixer n, untreated water ($UN_{m,t}$) to regeneration facility t and discharged water ($DI_{m,l}$) to the treatment facility l as shown in Eq. (22). $DR_{m,n}$ and $UN_{m,t}$ can be further divided to multiple inputs to mixer n, regeneration facility t and treatment facility l. The water quality is shown in Eq. (23).

$$MW_m = \sum_n DR_{m,n} + \sum_t UN_{m,t} + \sum_l DI_{m,l};\ \forall m \tag{22}$$

$$C_m^{in} = C_{m,n} = C_{m.t} = C_{m,l};\ \forall m \tag{23}$$

3.3.2.4. Regeneration facility water balance. The inputs to the regeneration facility include untreated water from the participating plants water sources and untreated water from the mass network water source, as shown in Eq. (24). After the water undergoes regeneration, the regenerated water can be segregated to multiple inputs to any mixer *n* inside the water network as shown in Eq. (25). The input water concentration (CV_t^{in}) to any regeneration unit is summarized in Eq. (26). The output water concentration ($C_{t,n}^{out}$) depends on the type of water treatment used.

$$TR_t^{overall} = \sum_q UN_{q,t} + \sum_m UN_{m,t};\ \forall t \tag{24}$$

$$TR_t^{overall} = \sum_n TR_{t,n};\ \forall t \tag{25}$$

$$TR_t^{overall} \times CV_t^{in} = \left(\sum_q C_{q,t} \times \sum_q UN_{q,t}\right) + \left(\sum_m C_{m,t} \times \sum_m UN_{m,t}\right);\ \forall t \tag{26}$$

3.3.2.5. Mixers water balance. The inlet flowrate to any mixer *n* in the water network is equal to the summation of the directly used water ($DR_{q,n}$) from any participating plant water source, purchased freshwater ($FR_{f,n}$), released water ($DR_{m,n}$) from the mass network water source and regenerated water ($TR_{t,n}$) from each regeneration facility *t* as summarized in Eq. (27). The mixer's water quality is shown in Eq. (28). The mixer's water flowrate is sent to the participating plants water sinks (Eq. (29)) where the quality constraint at each sink ensures that each plant will only accept input water from the mixer as long as the maximum contaminant concentration specified is not exceeded as summarized in Eq. (30). The number of pariticpating plant sinks corresponds to the number of mixers. If there a mass network sink demand, another mixer is added, where the mass network water demand calculated from Eqs. (10) – (12) can be supplied using Eq. (31). The mass network water demand quality is shown in Eq. (32).

$$W_n = \sum_q DR_{q,n} + \sum_m DR_{m,n} + \sum_f FR_{f,n} + \sum_t TR_{t,n};\ \forall n \tag{27}$$

$$W_n \times C_n = \left(\sum_q C_{q,n} \times \sum_q DR_{q,n}\right) + \left(\sum_m C_{m,n} \times \sum_m DR_{m,n}\right) + \left(\sum_f C_{f,n} \times \sum_f FR_{f,n}\right) + \left(\sum_t C_{t,n}^{out} \times \sum_t TR_{t,n}\right);\ \forall n \tag{28}$$

$$W_{p,v}^{demand} = W_n \tag{29}$$

$$W_{p,v}^{demand} \times C_{p,v}^{demand} \geq W_n \times C_n \tag{30}$$

$$MD = W_n \tag{31}$$

$$MD \times C_m^{out} \geq W_n \times C_n \tag{32}$$

3.3.2.6. Discharge water balance. The water flowrate discharged $DI_l^{overall}$ to the environment through l treatment facility is equal to the flowrate of water discharged from any participating plant water source $DI_{q,l}$ and mass network $DI_{m,l}$ water source as shown in Eq. (33), whereas the pollutant concentration discharged to the environment is determined through Eq. (34). Note that the environmental regulations impose maximum pollutant concentration limits on the water discharged to the environment, as shown in Eq. (35).

$$DI_l^{overall} = \sum_m DI_{m,l} + \sum_q DI_{q,l};\ \forall l \tag{33}$$

$$DI_l^{overall} \times CV_l = \sum_m DI_{m,l} \times \sum_m C_{m,l} + \sum_q DI_{q,l} \times \sum_q C_{q,l};\ \forall l \tag{34}$$

$$CV_l^{max} \geq CV_l \tag{35}$$

3.3.3. Economic analysis

The economics of the mass-water CHOSYN is divided to MN and WN economics. The detailed governing equations are summarized through Eqs. (36–49)

3.3.3.1. Mass network economics. Each reaction involved in the MN represents an interceptor incorporating several types of equipment to convert the inlet chemical species to the demand chemical species. Therefore, the MN economics is divided into three components. First, the equipment costs (EQ) which calculated using Eq. (36) (Farouk et al., 2021). Data for the equipment costs can be extracted from actual plant data, literature review, or simulation programs. Next, the equipment costs are utilized to calculate fixed capital investment (FCI) using the factorial method (El-Halwagi, 2017b; Smith, 2005). The FCI is divided into physical and indirect plant costs which are assumed as a factor of the calculated equipment costs. Subsequently, Work capital investment (*WCI*) is assumed as a percentage of capital investment (15%) where the capital investment is the summation of both FCI and WCI, as shown in Eq. (37). Note that the detailed factorial method is shown in the supporting information Tables A1 - A2. Afterward, the operating costs for the MN are expressed as a function of chemical species products flowrate, as shown in Eq. (39) (Farouk et al., 2021). The operating costs are divided into direct and indirect costs, which are assumed as a factor of FCI and labor. The detailed operating costs are summarized in the supporting information Table A3. The total raw materials costs per year are calculated separately using Eq. (38) and are expressed as a function of purchased chemical species.

$$Equipment\ cost = \sum_j EQ_{j,s} \times \sum_j Z_{s,j} \times \sum_j X_j \times AH \tag{36}$$

$$Capital\ investment = FCI + WCI \tag{37}$$

$$Raw\ material\ cost = \sum_S COST_s \times \sum_s \sum_e F_{s,e} \times AH \tag{38}$$

$$Operating\ cost\ MN = \sum_j \mathrm{OP}_{j,s} \times \sum_j \mathrm{Z}_{s,j} \times \sum_j X_j \times \mathrm{AH} \tag{39}$$

where $\mathrm{EQ}_{j,s}$ is the equipment cost per kg of a product of chemical species s per year, AH is the annual operating hours of the mass-water CHOSYN, X_j is the molar flowrate coefficient of reaction j, $\mathrm{Z}_{s,j}$ is the stoichiometric coefficient of chemical species s in reaction j. $\mathrm{OP}_{j,s}$ is the operating cost per kg of a product of chemical species s in reaction j and COST_s is the cost price of external chemical species.

3.3.3.2. Water network economics. The WN economics is divided into five components. First, the capital piping costs needed to construct the piping between the participating plants, regeneration facilities, freshwater sources, MN, treatment facilities and the WN expressed as a function of distance in meters as shown in Eq. (40). Second, the operating costs for using and maintaining the WN infrastructure are expressed as a function of the input water flowrates within the WN in Eq. (41). The input water is divided into water from the participating plants water sources, water from the MN water source and purchased freshwater. Third, the regeneration costs, which are the costs incurred in water regeneration, are expressed as a function of regenerated water in Eq. (42). Fourth, the cost of purchased freshwater, is expressed as a function of freshwater flowrate in Eq. (43). Lastly, the cost of discharging wastewater through the treatment facility is expressed as a function of discharged water flowrate as shown in Eq. (44).

$$Piping\ cost = \mathrm{PC} \times \left(\sum_f \mathrm{PD}_f + \mathrm{PD}_m + \sum_q \mathrm{PD}_q + \sum_t \mathrm{PD}_t + \sum_l \mathrm{PD}_l \right) \tag{40}$$

$$Operating\ cost\ WN = OC \times \left(\sum_f FR_f^{overall} + MW + \sum_q W_q^{overall} \right) \tag{41}$$

$$Regeneration\ cost = \sum_t TR_t^{overall} \times \sum_t \mathrm{TRC}_t \tag{42}$$

$$Freshwater\ cost = \sum_f FR_f^{\mathrm{overall}} \times \sum_f \mathrm{FRC}_f \tag{43}$$

$$Treatment\ cost = \sum_l DI_l^{\mathrm{overall}} \times \sum_l \mathrm{WWC}_l \tag{44}$$

where PD_f, PD_m, PD_q, PD_t and PD_l are the distance between the WN and fresh source, MN, participating plants water source, regeneration facility, and treatment facility. Note that PC, OC, TRC_t, FRC_f, and WWC_l are the piping costs, operating costs, regeneration costs for each regeneration facility, freshwater costs, and discharged water treatment costs.

3.3.3.3. Total economic costs. The total capital investment expenditures (*CAPEX*) of both the MN and the WN are summarized in Eq. (45), while the total operating cost expenditures (*OPEX*) are shown in Eq. (46). The annualized fixed costs using ten years scheme with negligible salvage value is assumed as 10% of the *CAPEX* as summarized in Eq. (47) (El-Halwagi, 2017b). Eq. (48) shows the annual net profit (*ANP*) for the mass-water CHOSYN (Farouk et al., 2021). The return-on-investment metric (ROI) is calculated using Eq. (49).

$$CAPEX = Capital\ investment + Piping\ cost \tag{45}$$

$$\begin{aligned} OPEX = {} & Raw\ material\ cost + Operating\ cost\ MN \\ & + Operating\ cost\ WN + Regeneration\ cost \\ & + Freshwater\ cost + Treatment\ cost \end{aligned} \tag{46}$$

$$AFC = 0.1 \times CAPEX \tag{47}$$

$$ANP = \left[\left(\sum_S \mathrm{SALE}_s \times \mathrm{G}_s - OPEX - AFC \right) \times (1 - \mathrm{Tax\ rate}) \right] + AFC \tag{48}$$

$$\mathrm{ROI} = ANP/CAPEX \tag{49}$$

where SALE_s is the sale price of the demand of chemical species s, *ANP* is the annual net profit, and *AFC* is the annualized fixed cost.

3.3.4. Sustainability weighted return on investment

The sustainability weighted return on investment metric (SWROIM) is a metric proposed by El-Halwagi (2017c) to quantify several environmental indicators. The SWROIM utilized in this work considers two components. The first component is the flowrate of water discharged to the environment as shown in Eq. (50), i.e., water discharge(*WI*). The second component is the flowrate of discharged carbon dioxide from the MN, i.e., carbon dioxide discharge(*CI*) as summarized in Eq. (51). Finally, the SWROIM is applied using Eq. (52) (El-Halwagi, 2017c).

$$WI = \left(\sum_l DI_l^{overall} \right) \tag{50}$$

$$CI = \sum_d F_{CO_2,d} \tag{51}$$

$$\mathrm{SWROIM} = \frac{ANP}{CAPEX} \times \left[1 + \left(\mathrm{WE}_{wi} \times \frac{WI}{\mathrm{WI}^{\mathrm{target}}} \right) + \left(\mathrm{WE}_{\mathrm{ci}} \times \frac{CI}{\mathrm{CI}^{\mathrm{target}}} \right) \right] \tag{52}$$

where *CAPEX* and *ANP* are total capital expenditures and the annual net profit calculated from Eqs. (45) and (48). $F_{CO_2,d}$ is calculated using Eqs. (10) – (12), while $DI_l^{overall}$ is calculated using Eq. (33). Note that, WE_{wi} and WE_{ci} are a weighting factor in the form of a ratio representing the relative importance of the water and carbon impact as compared to the annual net profit. The weighting factor depends on the participating plants own values and commitment towards sustainability. $\mathrm{WI}^{\mathrm{target}}$ and $\mathrm{CI}^{\mathrm{target}}$ are the target values for the water and carbon impacts. The target values can be obtained from process integration benchmarking or set by the company as a sustainability goal. The ratios $\frac{WI}{\mathrm{WI}^{\mathrm{target}}}$ and $\frac{CI}{\mathrm{CI}^{\mathrm{target}}}$ represent the fractional contribution of water and carbon impact toward meeting the target performance and may be positive, negative, or zero (El-Halwagi, 2017c). The higher the contribution value, the better the sustainability performance of the mass-water CHOSYN.

3.3.5. Objective function

The objective function is set to maximize the SWORIM to perform multi-objective optimization, as shown in Eq. (53). The SWROIM consists of annual net profit and capital return on investment, which summarizes the economic indicators. Moreover, the wastewater and carbon dioxide discharge are quantified and relatively compared with the economic indicators, i.e., environmental

Table 1
Participating plants details (Farouk et al., 2021).

Participating plants	Raw material	Product	By-product	Governing chemical reaction
Propane dehydrogenation (PDH)	Propane	Propylene	CO_2H_2	$C_3H_8 \rightarrow C_3H_6+H_2$
Methanol to propylene (MTP)	Methanol	Propylene	CO_2	$3CH_3OH \rightarrow C_3H_6+H_2O$
Ethylene cracking	Ethane	Ethylene	H_2CH_4	$C_2H_6 \rightarrow C_2H_4+H_2C_2H_6+C_2H_4 \rightarrow C_3H_6+CH_42C_2H_6 \rightarrow C_3H_8+CH_4C_3H_8 \rightarrow C_3H_6+H_2$
Gas to liquid (GTL)	Methane	Syngas	$COCO_2H_2$	$CH_4+H_2O \rightarrow CO+3H_2OCH_4+1.5O_2 \rightarrow CO+2H_2OCO+H_2O \rightarrow CO_2+H_2$
Biodiesel	Palm oil Methanol	Biodiesel	$C_3H_8O_3$	$CH_3(CH_2)_{14}COOH+CH_3OH \rightarrow C_{14}H_{28}+C_3H_8O_3$
Acrolein	Acrolein	Acrylic acid	–	Acrolein → Acrylicacid
Propylene glycol	Propylene glycol	polyester	–	Propyleneglycol → Polyester

Table 2
Molar flowrate (kmole/hr) of the participating plants internal sources (Farouk et al., 2021).

	GTL	Ethylene Cracking	PDH	MTP	Biodiesel	Propylene glycol	Acrolein	Total
CO	930	0	0	0	0	–	–	930
CO_2	2910	0	180	900	0	–	–	3990
H_2	7830	135	2000	0	0	–	–	9965
CH_4	0	39	0	0	0	–	–	39
$C_3H_8O_3$	0	0	0	0	1000	–	–	1000

Table 3
Participating plants demand flowrate (kmole/hr) (Farouk et al., 2021).

Plant	Demand	Flowrate
MTP	Methanol	6500
Biodiesel	Methanol	1000
Propylene glycol	Propylene glycol	1000
Acrolein	Acrolein	1000

indicators. All of the previous indicators are optimized simultaneously to give the optimum mass-water configuration. Alternatively, the objective function can also be set to minimize the use of external sources and freshwater, following Eq. (54).

$$\text{Maximum}\left(\text{SWROIM}=\frac{ANP}{CAPEX}\times\left[1+\left(\text{WE}_{wi}\times\frac{WI}{\text{WI}^{\text{target}}}\right)+\left(\text{WE}_{\text{ci}}\times\frac{CI}{\text{CI}^{\text{target}}}\right)\right]\right) \quad (53)$$

$$\text{Minimum}\left(\sum_s\sum_e F_{s,e}+\sum_f FR_f^{\text{overall}}\right) \quad (54)$$

3.4. Case study

Several industrial plants agreed to utilize their by-products and wastewater through a central facility to convert them to value-added products. The central facility is divided into mass and water networks. The case study mass network participating plants were adapted and modified from El-Halwagi (2017a) and Farouk et al. (2021). On the other hand, the case study water network participating plants were adapted and modified from Tiu and Cruz (2017) and Aviso et al. (2010).

3.4.1. Mass network participating plants

Detailed analysis of the participating plants is summarized in Tables 1 and 2. The plants demands are summarized in Table 3. To meet the plants demand, the central facility will require specific interceptors to convert the internal sources to valuable products. The candidate interceptors are summarized in Table 4. The assumptions and detailed costs for the interceptors are shown in Tables A4 and A5 in the supporting document. The external sources unit cost are shown in Table A6 in the supporting document.

Table 4
Suggested candidate interceptors (Farouk et al., 2021).

Technology	Interceptor
Methanol synthesis	$Xj_1 2H_2+CO \rightarrow CH_3OH$
Methanol synthesis	$Xj_2 3H_2+CO_2 \rightarrow CH_3OH+H_2O$
Steam reforming of methane	$Xj_3 CH_4+H_2O \rightarrow 3H_2+CO$
Steam reforming of methane	$Xj_4 CH_4+2H_2O \rightarrow 4H_2+CO_2$
Glycerol to syngas	$Xj_5 C_3H_8O_3+3H_2O \rightarrow 3CO_2+7H_2$
Water-gas shift reaction	$Xj_6 H_2O+CO \rightarrow H_2+CO_2$
Reverse water-gas shift reaction	$Xj_7 H_2+CO_2 \rightarrow H_2O+CO$
Glycerol to propylene glycol	$Xj_8 C_3H_8O_3+H_2 \rightarrow C_3H_8O_2+H_2O$
Glycerol to acrolein	$Xj_9 C_3H_8O_3 \rightarrow C_3H_4O+2H_2O$

3.4.2. Water network participating sources/sinks

The participating plants water SRs (outputs) and water SKs (demand) flowrate and quality are summarized in Table 5. The participating plants distances from the central facility is shown in Table 6. The water cost parameters and treatment costs are shown in Tables A7 and A8 in the supporting document. All assumed parameters for the mass-water CHOSYN are summarized in Table A9 in the supporting document.

4. Results and discussion

4.1. Scenario analysis

The developed model (Equations (1) – (52)) is used to design a mass-water CHOSYN. The problem formulation is non-linear programming (NLP) and is solved using lingo software with a global solver deployed. Note that the non-linearity originates from the ROI and SWROIM in the model. Three scenarios are evaluated in this section. The first scenario is solved with the objective function of minimum external sources and freshwater (Eq. (54)). Scenario one demonstrates a single objective optimization of the synthesis of separate mass and water networks. The second scenario is solved with the objective function of maximum SWROIM (Eq. (53)) where mass and water networks are synthesized simultaneously. Scenario two represents the multi-objective optimization modeling where SWROIM includes economic indicators (annual sales and capital costs) and environmental indicators (carbon dioxide and wastewater discharge. The third scenario is solved using an objective function of minimum freshwater and external chemical species consumption (Eq. (54)). Scenario three represents single-objective optimization modeling of simultaneous mass and water

Table 5
Water SKs and SRs limiting data for the participating plants (Avisoet al., 2010; Tiu et al., 2017).

Water SR	SR flowrate (ton/day)	SR quality (mg/L)	Water SK	SK flowrate (ton/day)	SK quality (mg/L)
q_1	100	100	v_1	100	10
q_2	20	250	v_2	20	100
q_3	50	80	v_3	80	20
q_4	100	200	v_4	60	50

Table 6
Distances to water network (m).

Distance	Distance from	Distance to Water Network (m)
PD_{q1}	v_1/ q_1	300
PD_{q2}	v_2/ q_2	200
PD_{q3}	v_3/ q_3	150
PD_{q4}	v_4/ q_4	150
PD_f	Freshwater source	200
PD_m	Mass network	50
PD_t	Regeneration facility	200
PD_l	Treatment facility	200

Table 7
Flowrates of external and discharged chemical species for the first scenario.

Mass network (kmole/hr)						Water network (kmole/hr)	
$C_3H_8O_3$	CH_4	H_2	CO	H_2O	CO_2	Freshwater	Wastewater discharge
3153	0	−2626	0	−3031	−3920	292	315

Table 8
Economic and environmental analysis for the first scenario.

ANP ($/yr)	*OPEX* ($/yr)	*CAPEX* ($)	ROI (%/yr)	SWROIM (%/yr)
112×10^7	258×10^7	630×10^7	17	23

network optimization where only purchased chemical species are minimized.

4.1.1. First scenario

To synthesize the separate water and mass networks, Eqs. (1-17) and (36–39) were solved to obtain the mass network, while Eqs. (18-35) and 40–(44) were solved to optimize the water network. The objective function of minimum external sources (Eq. (54)) for the mass network and minimum freshwater for the water network was selected to obtain the optimum separate mass and water network. The first scenario is utilized to show the difference between simultaneous and separate optimization of mass and water networks. The results of mass and water networks are tabulated in Tables 7,8 and 9. Based on Table 7, the optimum mass network selected reactions that utilized $C_3H_8O_3$ and minimized the usage of other external sources like CH_4 and H_2. From Table 8, the ROI and SWROIM reached 17 and 23%/yr. The low SWROIM is due to the discharge of 3920 and 315 kmole/hr of CO_2 and H_2O. From Table 9, we can conclude the operating costs breakdown analysis where the raw materials and freshwater costs were significantly lowered. Based on Fig. 4, it can be observed that five interceptors were selected where no methane was consumed while wastewater was discharged. Concurrently, from Fig. 5, not all available wastewater was integrated, leading to a significant wastewater discharge.

4.1.2 Second scenario

In the second scenario, the model is solved with the objective function of maximum SWROIM (Eqn. (53)). The scenario demonstrates the results of simultaneous optimization of mass and water networks using multi-objective optimization. The model indicated the minimum benchmark for purchased chemical species, which included 1000 and 6461 kmole/hr of $C_3H_8O_3$ and CH_4 for the mass network. Although the mass-water CHOSYN required 543 kmole/hr of H_2O, there were no additional costs incurred in purchasing the H_2O. This is because the required flowrates of H_2O were supplied by the mass-water CHOSYN. Additionally, the resulting mass-water CHOSYN has all water sources being integrated with the water network. Hence, the integrated mass water CHOSYN discharges zero wastewater. This is due to the incorporation of the multi-objective optimization approach where the discharged wastewater and carbon dioxide are minimized. The water network requires the purchase of a minimum flowrate of 521 kmole/hr of H_2O to fulfill the water sinks requirements. The flowrates of external and discharged species for the integrated mass-water CHOSYN are summarized in Table 10. Fig. 6 illustrates a schematic representation of the optimum mass-water CHOSYN, where only five interceptors were used since the multi-objective optimization approach led to minimum capital costs. The overall network performance of the mass-water CHOSYN is evaluated in economic and environmental aspects in Table 11. The economic performance is evaluated based on overall annual sales, operating cost, and capital cost for the mass-water CHOSYN, while the environmental indicators are based on wastewater and carbon dioxide discharge. The optimal integrated mass-water CHOSYN solution showed that the maximum *ANP* attained is 160×10^7 $/yr, which leads to an ROI of 29%/yr, as shown in Table 11. Moreover, the SWROIM, which combines the economic and environmental aspects and optimizes them simultaneously, reached 36%/yr. The ROI and SWROIM were notably higher compared to scenario one. This is due to the adoption of the multi-objective optimization approach. Note that the breakdown of the *OPEX* is shown in Table 12. where the *OPEX* in scenario two is lower by 47×10^7 $/yr compared to scenario one. This is due to zero treatment costs and lower MN operating costs due to choosing interceptors with less operating costs (interceptor 3).

4.1.3. Third scenario

The third scenario is solved with the objective function of minimum purchased freshwater and external chemical species (Eqn (54)). The scenario is solved to showcase the difference between multi-objective and single-objective optimization of simultaneous mass-water CHOSYN. The model provides a different network configuration than the second scenario network since a single-objective optimization approach was adopted. The stream data results for external and discharged chemical species used for this scenario analysis are given in Table 13, which determines the minimum flowrate of external and discharged chemical species needed for the overall mass-water CHOSYN. Due to choosing minimum purchased freshwater and external chemical species as an objective function, the purchased CH_4 and H_2O flowrates are lower by 5429 and 229 kmole/hr, respectively, as shown in Table 13. Furthermore, the H_2 and CO discharge are lower by 6161 and 2886 kmole/hr. Howbeit, the CO_2 and the wastewater discharged to the environment increased by 2887 and 2314 kmole/hr. To achieve the intended objective function, reactions that produced wastewater in the mass network were selected. The wastewater from the mass network was utilized in the water network. Therefore, the overall freshwater flowrate for the water network decreased. The optimum mass-water CHOSYN is illustrated in Fig. 7, where regeneration facility one was utilized in contrast with regeneration facility two

Table 9
OPEX breakdown analysis for the first scenario.

Total mass network operating costs ($/yr)		Total water network operating costs ($/yr)			
Raw material cost	Operating cost MN	Freshwater cost	Treatment cost	Regeneration cost	Operating cost WN
$27{,}200\times10^3$	207×10^7	159×10^3	82×10^3	38×10^3	595×10^3

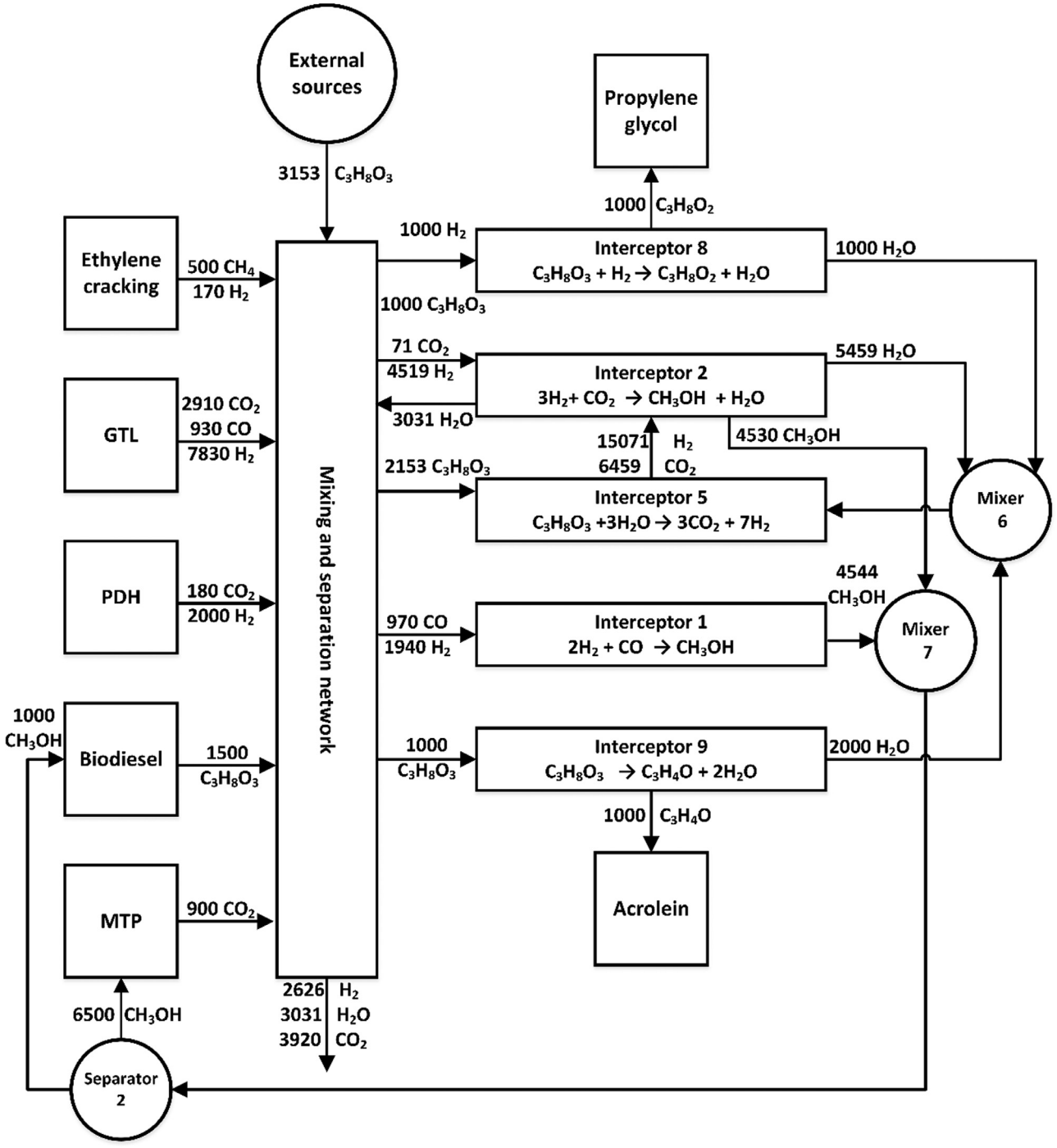

Fig. 4. Optimum mass network representation for scenario one.

Table 10
Flowrates of external and discharged chemical species for the second scenario.

Mass network (kmole/hr)						Water network (kmole/hr)	
$C_3H_8O_3$	CH_4	H_2	CO	H_2O	CO_2	Freshwater	Wastewater discharge
1000	6461	−10,508	−2886	543	−1033	521	0

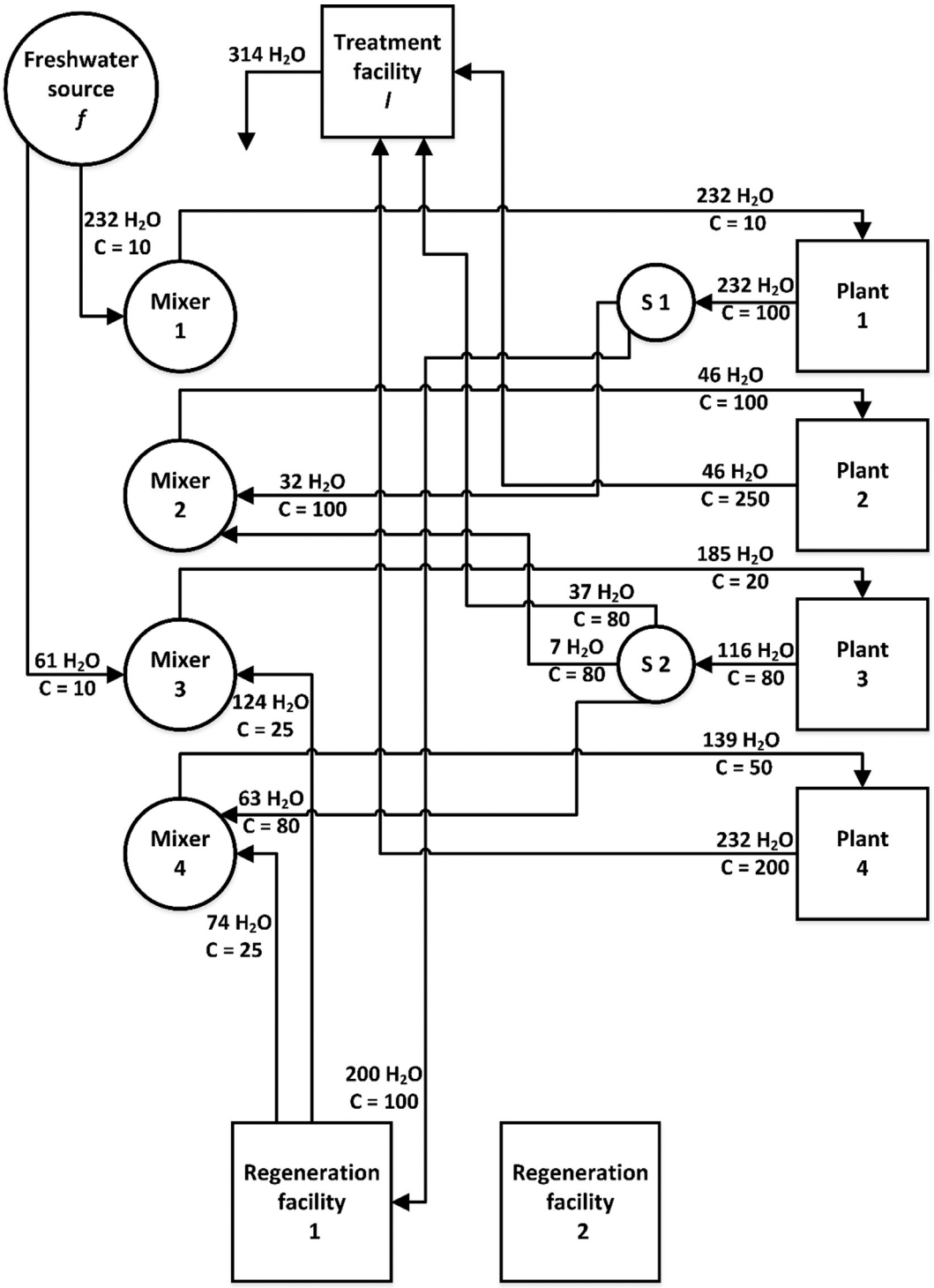

Fig. 5. Optimum water network representation for scenario one.

Table 11
Economic and environmental analysis for the second scenario.

ANP ($/yr)	*OPEX* ($/yr)	*CAPEX* ($)	ROI%/yr)	SWROIM (%/yr)
160×10^7	211×10^7	556×10^7	29	36

in scenario one. From Fig. 7, six interceptors were used instead of five to achieve the intended objective function of minimum external source, which led to higher *CAPEX*. The total purchased external species for the mass-water CHOSYN are lower than scenario one by $23{,}500\times10^3$ $/yr as shown in Table 15. Nevertheless, the lower raw material costs incurred higher operating costs and *CAPEX* leading to an ROI of 18%/yr. This is due to choosing reactions that incurred higher capital costs and lower chemical species flowrates, as shown in Fig. 7. Moreover, the SWROIM reached 25%/yr only due to the discharging of 3920 and 2314 kmole/hr of CO_2 and H_2O to the environment. Additionally, from Table 15, we can deduce that the operating costs for the mass-water CHOSYN are higher due to the extra costs incurred in discharging wastewater. Although scenario

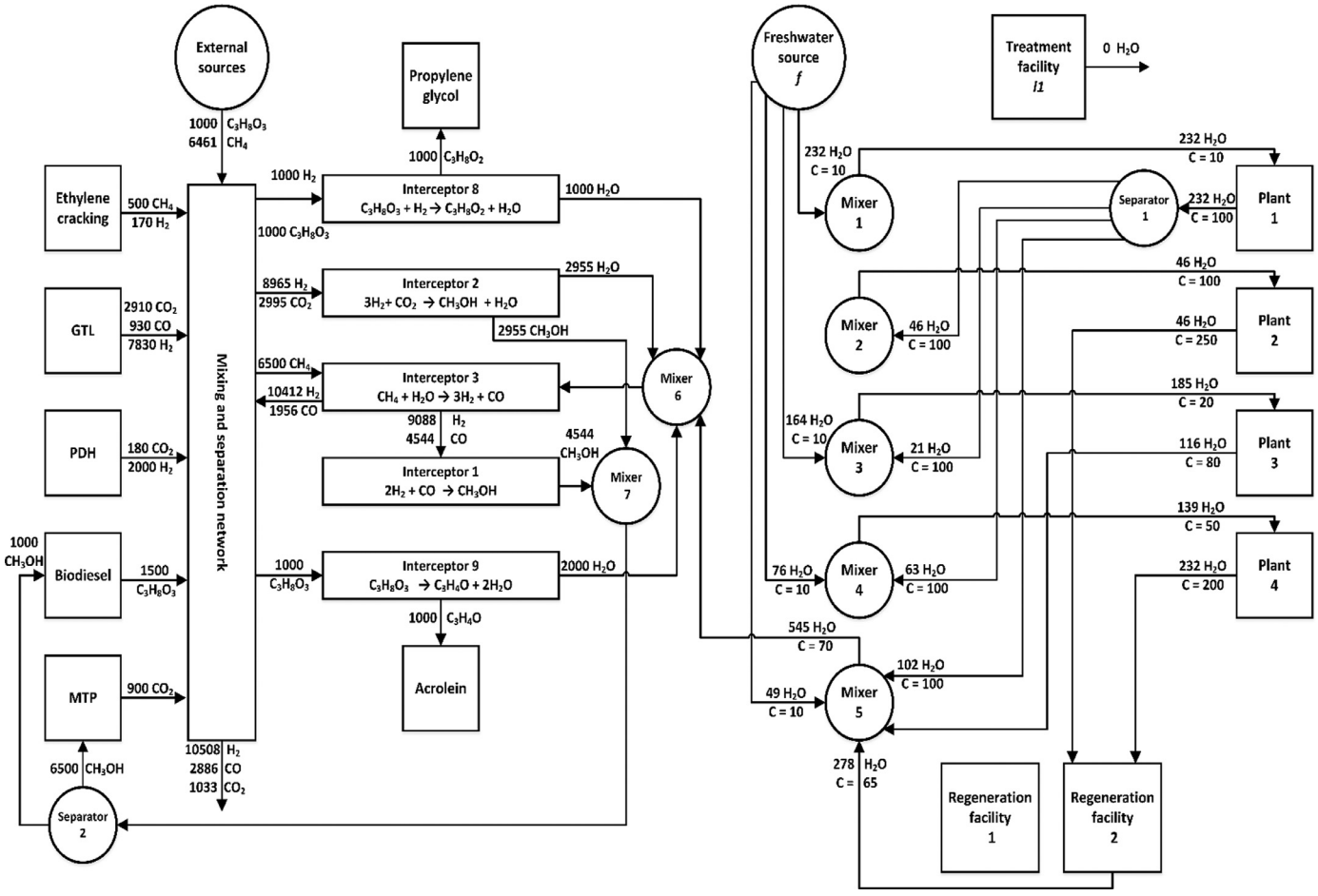

Fig. 6. Optimum mass-water CHOSYN representation for scenario two.

Table 12
OPEX breakdown analysis for the second scenario.

Total mass network operating costs ($/yr)		Total water network operating costs ($/yr)			
Raw material cost	Operating cost MN	Freshwater cost	Treatment cost	Regeneration cost	Operating cost WN
$55{,}200\times10^3$	205×10^7	67×10^3	0	41×10^3	223×10^3

Table 13
Flowrates of external and discharged chemical species for the third scenario.

Mass network (kmole/hr)						Water network (kmole/hr)	
$C_3H_8O_3$	CH_4	H_2	CO	H_2O	CO_2	Freshwater	Wastewater discharge
2809	1032	−4347	0	−1998	−3920	292	2314

Table 14
Economic and environmental analysis for the third scenario.

ANP ($/yr)	*OPEX* ($/yr)	*CAPEX* ($)	ROI (%/yr)	SWROIM (%/yr)
115×10^7	258×10^7	662×10^7	18	25

two economic and environmental performance is better, scenario one and three objective function and results are crucial in the case of low availability of external sources and freshwater.

4.2. Results implications

The developed model was solved for three scenarios. Scenario one was solved with a single-objective optimization approach to synthesize separate mass and water networks. Scenario two was solved with a multi-objective optimization approach, while scenario three was solved with an single-objective function of minimum external sources to synthesize simultaneous mass-water

Table 15
OPEX breakdown analysis for the third scenario.

Total mass network operating costs ($/yr)		Total water network operating costs ($/yr)			
Raw material cost	Operating cost MN	Freshwater cost	Treatment cost	Regeneration cost	Operating cost WN
$31{,}700\times10^3$	255×10^7	38×10^3	599×10^3	60×10^3	179×10^3

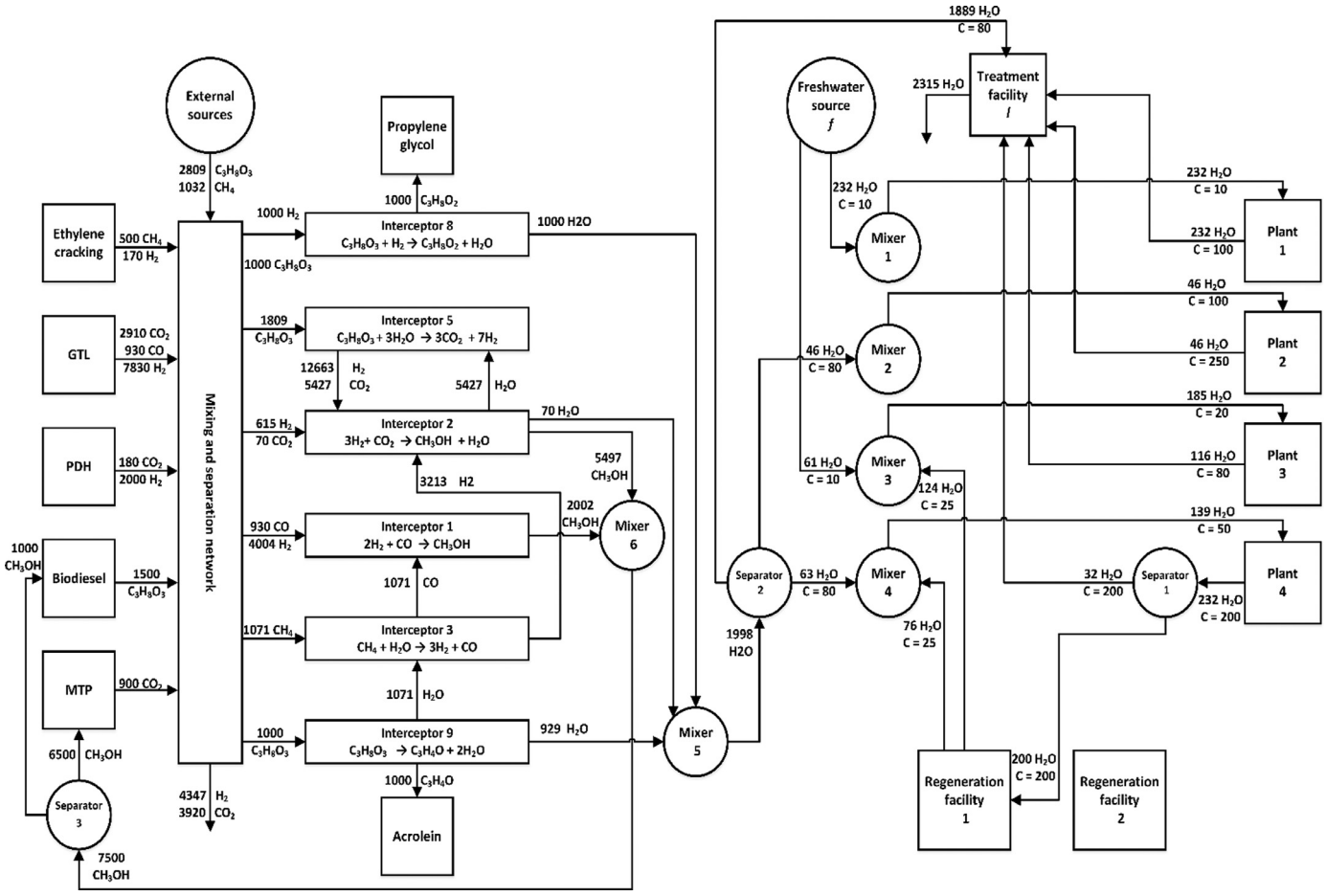

Fig. 7. Optimum mass-water CHOSYN representation for scenario three.

Table 16
Economic and environmental indicators of scenarios one, two and three.

Scenarios	ROI (%/yr)	SWROIM (%/yr)	CO_2 discharge (kmole/hr)	H_2O discharge (kmole/hr)	Contribution
Scenario one	17	23	3920	3346	• Single-objective function • Separate mass and water network optimization
Scenario two	29	36	1033	0	• Multi-objective function • Simultaneous mass-water CHOSYN optimization
Scenario three	18	25	3920	2314	• Single-objective function • Simultaneous mass-water CHOSYN optimization

CHOSYN. From the results, we can observe that scenario two was superior to scenario one in terms of ROI and SWROIM. The results also showed that scenario two configuration has achieved 2887 and 2314 kmole/hr reduction on CO_2 and wastewater discharge as compared to Scenario three. The adoption of the multi-objective optimization using the SWROIM further decreased the capital and operating costs of scenario two by 106×10^7 \$/yr and 47×10^7 \$/yr as compared to scenario three. The ROI and SWROIM in scenario two reached 29%/yr and 36%/yr, which is higher than both scenarios one and three. The important economic and environmental indicators of the three scenarios is summarized in Table 16 to emphasize on the advantage of the multi-objective optimization of simultaneous mass-water CHOSYN.

Overall, the proposed second scenario network excels in the aspect of economic and environmental performance; it reflects the ultimate objective of EIP development, where the participating plants collaborate to seek cost and environmental benefits, as well as business excellence. Furthermore, its implementation can improve the sustainability of participating plants and assist them in fulfilling corporate social responsibility. All scenarios show various design parameters and offer several vital benchmarks such as minimum benchmarks for external sources, discharges, environmental and economic aspects. As a preliminary tool, the model can assist engineers during the detailed design phase by mapping the environmental design opportunities and giving various essential infor-

mation and benchmarks. The model requires minimal data to solve, which makes it an ideal preliminary tool.

5. Conclusion

In this study, a systematic methodology for the design of a mass-water CHOSYN is developed. A mass-water CHOSYN model is introduced to integrate both water and mass networks in the CHOSYN, where the model is formulated and solved as MINLP model. The model maximizes the mass-water CHOSYN economic aspects while accounting for the environmental performance simultaneously using SWROIM. The prominence of the mass-water CHOSYN is accentuated through a case study involving several hydrocarbon plants. Three scenarios were investigated to highlight the robustness of the model. Each scenario manifested clear results to address different circumstances that may eventuate during the mass-water CHOSYN design. From scenario one, a single objective optimization was utilized to synthesize separate mass and water networks. It was found that the flowrate of wastewater discharged to the environment from the mass network and water network increased as compared to scenario two. This is due to ignoring the possibility of integrating wastewater discharged the mass network in the water network. Scenario two was solved to demonstrate the advantages of the multi-objective optimization of simultaneous mass-water CHOSYN integration. Based on scenario two results, the multi-objective optimization approach is able to elevate the economic and environmental performance of the mass-water CHOSYN. This configuration reduced the system's overall costs and network complexity by utilizing only five interceptors in the mass network and discharging zero wastewater from the mass-water network. On the other hand, scenario three provided a solution to the case where the purchase of external chemical species might be arduous. In scenario three, the raw material and freshwater costs were lower compared to scenario two.

In conclusion, performing multi-objective optimization of a simultaneous mass-water CHOSYN has proven to be more advantageous in terms of economic and environmental capabilities compared to single-objective optimization or separate mass and water network integration. Future works should consider integrating energy in the water network by incorporating the water temperature in the process parameters to achieve maximum integration. Besides, it is also proposed to consider multiple containment concentrations instead of single containments in the mass-water CHOSYN.

Notes

The authors declare no competing financial interest.
All Figures and Tables are original works of the authors.

Synopsis

This work introduces a simultaneous mass-water network optimization model to synthesize a robust eco-industrial park considering both economic and environmental criteria.

Declaration of Competing Interest

The authors declare no competing financial interest.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.spc.2021.06.004.

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Development of a Simultaneous Mass-Water Carbon-Hydrogen-Oxygen Symbiosis Network

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Supporting document

Total capital investment is divided to fixed capital investment (FCI) and working capital investment (WCI). FCI is divided to physical plant cost (PPC) and in-direct plant cost (IPC)[1-2]. Equipment costs are utilized to calculate the PPC. WCI is taken as 15% of the total capital investment (Smith, 2005; El-Halwagi, 2017).

Table A1: Physical plant cost (PPC) factorial method

(Smith, 2005; El-Halwagi, 2017)

Items of physical plant cost (PPC)	Fraction of the equipment cost
Equipment	1
Installation	0.4
Piping	0.7
Instrumentation	0.2
Electrical	0.1
Buildings	0.15
Storage	0.17
Utilities	0.5
Site development	0.1
Auxiliary buildings	0.15

Table A2: In-direct plant cost (IPC) factorial method

(Smith, 2005; El-Halwagi, 2017)

Items of in-direct plant cost (IPC)	Fraction of the physical plant cost (PPC)
Design and engineering	0.3
Contractor's fee	0.05
Contingency	0.1

Table A3: Operating costs factorial method

(Smith, 2005; El-Halwagi, 2017)

Direct costs		In-direct costs
Variable	Fixed	
Raw materials	Labor	Sales (10%)
Miscellaneous (10% of maintenance)	Supervision (20% of labor)	Research and development (5%)
Utilities	Plant overhead (50% of labor)	General overhead (5%)
-	Interest (2% of fixed capital investment)	-
-	Insurance (1% of fixed capital investment)	-
-	Rent (1% of fixed capital investment)	-
-	Royalties (1% of fixed capital investment)	-
-	Maintenance (10% of fixed capital investment)	-
Direct costs = Variable costs + Fixed costs		-
Operating costs = Direct costs + In-direct costs		

Table A4: OPEX assumptions

(Farouk et al., 2021)

Items of in-direct plant cost (IPC)	Assumptions
Cost of electricity	0.078 $/kWh
Labor	120 persons are needed for each technology, with 300 working days, and an average working salary of 350 $/month
Raw materials	Calculated in a separate step using Equation (40)

Table A5: Proposed technologies for the CHOSYN

(Farouk et al., 2021)

Technology	Equipment costs per kg product per year	OPEX per kg product
Methanol synthesis from syngas	0.31	0.61
Methanol synthesis from CO_2 and hydrogen	0.49	1.01
Steam reforming of methane to H_2 and CO	0.29	0.66
Steam reforming of methane to H_2 and CO_2	0.29	0.66
Glycerol to syngas overall reaction	0.66	2.6
Water-gas shift reaction	0.1	0.1
Reverse reaction of water gas shift reaction	0.1	0.1
Glycerol to propylene glycol	0.28	0.85
Glycerol to Acrolein	0.21	0.42

Table A6: Available feedstock costs ($/kmole)

Available feedstock	Price
$C_3H_8O_3$	1.2
CH_4	1
H_2	2
CO	1

Table A7: Water network cost parameters

(Aviso et al., 2010; Tiu et al., 2017)

Cost component	Value
Pipe cost ($/m)	5
Water network operating costs ($/ton)	1.5
Water treatment costs ($/ton)	1
Freshwater costs ($/ton)	1

Table A8: Water network regeneration costs

(Aviso et al., 2010; Tiu et al., 2017)

Regeneration process	Regeneration cost ($/ton)	Output water quality (mg/L)
1	1.5	25

2	0.7	65

Table A9: Assumed parameters values

Paremeter	Value	Paremeter	Value
$F_{H_2,i}$	9965 kmole/hr	$W_{q1}^{overall}$	100 ton/day
$F_{CO,i}$	930 kmole/hr	$W_{q2}^{overall}$	20 ton/day
$F_{CO_2,i}$	3990 kmole/hr	$W_{q3}^{overall}$	50 ton/day
$F_{CH_4,i}$	39 kmole/hr	$W_{q4}^{overall}$	100 ton/day
$F_{C_3H_8O_3,i}$	1000 kmole/hr	$W_{p1,v1}^{demand}$	100 ton/day
G_{CH_3OH}	7500 kmole/hr	$W_{p2,v2}^{demand}$	20 ton/day
$G_{C_3H_8O_2}$	1000 kmole/hr	$W_{p3,v3}^{demand}$	80 ton/day
$G_{C_3H_4O}$	1000 kmole/hr	$W_{p4,v4}^{demand}$	60 ton/day
EQ_{j1,CH_3OH}	0.31 $/kg/yr	$C_{q1}^{overall}$	100 mg/l
EQ_{j2,CH_3OH}	0.49 $/kg/yr	$C_{q2}^{overall}$	250 mg/l
EQ_{j3,H_2}	0.29 $/kg/yr	$C_{q3}^{overall}$	80 mg/l
EQ_{j4,H_2}	0.29 $/kg/yr	$C_{q4}^{overall}$	200 mg/l
EQ_{j5,H_2}	0.66 $/kg/yr	$C_{p1,v1}^{demand}$	10 mg/l
EQ_{j6,H_2}	0.1 $/kg/yr	$C_{p2,v2}^{demand}$	100 mg/l
$EQ_{j7,CO}$	0.1 $/kg/yr	$C_{p3,v3}^{demand}$	20 mg/l
$EQ_{j8,C_3H_8O_2}$	0.28 $/kg/yr	$C_{p4,v4}^{demand}$	50 mg/l
EQ_{j9,C_3H_4O}	0.21 $/kg/yr	$C_{f1}^{overall}$	10 mg/l
OP_{j1,CH_3OH}	0.61 $/kg	C_{t1}^{out}	25 mg/l
OP_{j2,CH_3OH}	1.01 $/kg	C_{t2}^{out}	65 mg/l
OP_{j3,H_2}	0.66 $/kg	C_{m}^{out}	70 mg/l
OP_{j4,H_2}	0.66 $/kg	PD_{q1}	300 m
OP_{j5,H_2}	2.6 $/kg	PD_{q2}	200 m
OP_{j6,H_2}	0.1 $/kg	PD_{q3}	150 m
$OP_{j7,CO}$	0.1 $/kg	PD_{q4}	150 m
$OP_{j8,C_3H_8O_2}$	0.85 $/kg	PD_{f}	200 m
OP_{j9,C_3H_4O}	0.42 $/kg	PD_{m}	50 m
$COST_{H_2}$	2 $/kmole	PD_{t}	200 m
$COST_{CO}$	1 $/kmole	PD_{l}	200 m
$COST_{CH_4}$	1 $/kmole	PC	5 $/m
$COST_{C_3H_8O_3}$	1.2 $/kmole	OC	1.5 $/ton

AH	300 days	TRC_{t1}	1.5 \$/ton
$SALE_{CH_3OH}$	55 \$/kmole	TRC_{t2}	0.7 \$/ton
$SALE_{C_3H_8O_2}$	85 \$/kmole	FRC_{f1}	1 \$/ton
$SALE_{C_3H_4O}$	75 \$/kmole	WWC_{l1}	2 \$/ton
Tax rate	25%		
WE_{wi}	0.1		
WE_{ci}	0.1		
WI^{target}	10000 kmole/hr		
CI^{target}	10000 kmole/hr		

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Chapter 5 Incorporation of a Storage and Dispatch System in Multiperiod C-H-O Symbiosis Network

5.1 Introduction

Sustainability can be achieved through the integration of multiple plants, i.e., eco-industrial park (EIP). The EIP integration, also known as industrial symbiosis (IS) can be in the form of mass, water, or energy. A plethora of research has addressed two types of EIPs, i.e., water and hydrocarbon networks. Towards the first particular case of water networks, Chew et al. [46] analyzed direct and indirect water integration schemes via a mixed-integer programming model. The same authors later studied the interaction of the participating plants within the EIP using the game theory approach [47]. Lovelady et al. [48] further investigated the integration of the water networks by focusing on recycling, reuse, and separation strategies. Considering that the participating firms in the EIP have their own individual fuzzy cost goals, a bi-level optimization model was developed to study the interaction between the fees for the purchase of fresh water and the treatment of wastewater in optimizing the water networks in the EIP [57]. A follow-up work was later reported using a fuzzy mixed-integer linear programming to incorporate further design aspects like incomplete information regarding the process data of the participating plants and the possibility of existing topologically constraints on the number of links connecting different plants [49]. To further bring forth the optimization and complexity of the water networks within the EIP, the environmental impact of industrial effluents discharged into watersheds [53] and piping expenses [54] were incorporated in the water network design. Although most of the above research assumed steady-state operations, this may not be the actual case for some plants whose operations may vary with time. Nonetheless, numerous optimization frameworks were suggested to utilize the available resources efficiently to address multiperiod operations in the water networks within an EIP. Liao et al. [88] synthesized a multi-period water network considering seasonal variations of plant production rates to increase the flexibility of the water networks. Later, a robust optimization model was developed to address the optimal water network design subject to multiple probable scenarios [60]. Subsequently, Bishnu et al. [89] developed a mathematical model using a multiperiod planning approach for direct water reuse. Thereafter, the same authors further developed their model to account for centralized and decentralized water regeneration

units [90]. Later on, Leong et al. [91] integrated a set of multiperiod chilled and cooling water networks. Additionally, a recent review of industrial symbiosis summarized the main tools for the design of EIPs [92].

Within the context of hydrocarbons, Noureldin et al. [78] introduced the novel problem of synthesizing *carbon-hydrogen-oxygen symbiosis networks* (CHOSYNs) and proposed a multi-scale targeting approach that starts with atomic targeting and proceeds through various stages to the final EIP design. A follow-up work by El-Halwagi [79] introduced a shortcut algebraic approach for employing atomic benchmarks for the design of CHOSYNs. The design of CHOSYN under uncertainties of source streams due to the variability in the performance of the participating plants was investigated by Mukherjee et al. [86]. Carbon footprint reduction in CHOSYN was addressed by Panu et al. [87]. Topolski et al. [80] devised a systematic approach for the integration of grassroots plants in addition to existing plants during the design of CHOSYN. A follow-up work by Topolski et al. [81] enhancing the anchor-tenant approach to further account for both mass and energy within a CHOSYN. Al-Fadhli [82] designed a multiperiod CHOSYN to account for variations in demand and feed sources. A disjunctive programming approach has been proposed by Juárez-García et al. [85] to automate the synthesis of CHOSYNs.

Despite the value of the previous contributions in designing CHOSYNs, there is an implicit assumption of a steady-state operation. In some cases, integration opportunities may be significantly enhanced by enabling the storage and dispatch of raw materials and intermediate products. This is particularly important for plants that operate in multiple modes and for raw materials whose availability varies over time. For instance, biorefineries, which depend on the availability of biomass feedstocks. Some oil refineries may have a summer and winter modes of operation to produce either more gasoline or more diesel. In such cases, the incorporation of storage and dispatch can provide valuable degrees of freedom for design and operation. Thus, the objective of this work is to introduce a systematic approach for the incorporation of storage and dispatch systems in the design of CHOSYNs. An integrated multiperiod CHOSYN with optimal storage and dispatch system is proposed to account for the various operational modes of industrial facilities and the seasonal variability, and availability of raw materials.

5.2 Problem Statement:

Given a set of plants $\{p|p = 1,2,\ldots..,p^{\text{plant}}\}$ within a certain region. Each plant may have multiple operation periods. The plants have a set of internal sources $\{i|i = 1,2,\ldots..,i^{\text{internal source}}\}$ during each operation period $\{t|t = 1,2,\ldots..,t^{\text{operation period}}\}$. Each of these sources comprises a set of chemical species $\{s|s = 1,2,\ldots..,s^{th}$ species$\}$. The flow rate of the internal chemical species *s* during each operation period *t* is denoted by $W_{s,i,t,}$. The flowrate of each external chemical species $\{e|e = 1,2,\ldots..,e^{\text{external}}\}$ during each operation period *t* as denoted by $F_{s,e,t}$. These external sources can be purchased when internal sources are exhausted. The purpose of the EIP is to convert the incoming chemical species to plants demand given by $G_{s,p,t}$ for each operation period. Additionally, chemical species *s* can be stored or dispatched during each operation period, as denoted by $N_{s,t}^{\text{Total}}$. $F_{s,m,t}$ is the flow rate of chemical species *s* dispatched $\{m|m = 1,2,\ldots..,m^{\text{dispatch}}\}$ from storage, while, $F_{s,u,t}$ is the flow rate of chemical species *s* to storge $\{u|u = 1,2,\ldots..,u^{\text{storage}}\}$ during *t* operation period.

As shown in Figure 5.1, an interception network facility is situated to receive internal sources from various plants, accommodate external sources, satisfy the participating plant demands and discharge chemical species. The discharged chemical species $\{d|d = 1,2,\ldots..,d^{\text{discharge}}\}$ flowrates are indicated by $F_{s,d,t}$. The received external and internal chemical species are converted to product streams through the usage of a set of reactions $\{j|j = 1,2,\ldots..,j^{\text{reaction}}\}$ which act as interceptors. The overall aim of this research to develop a mathematical model that accommodates multi-operation periods within a CHOSYN through the designing of an optimal storage and dispatch system as shown in Figure 5.1.

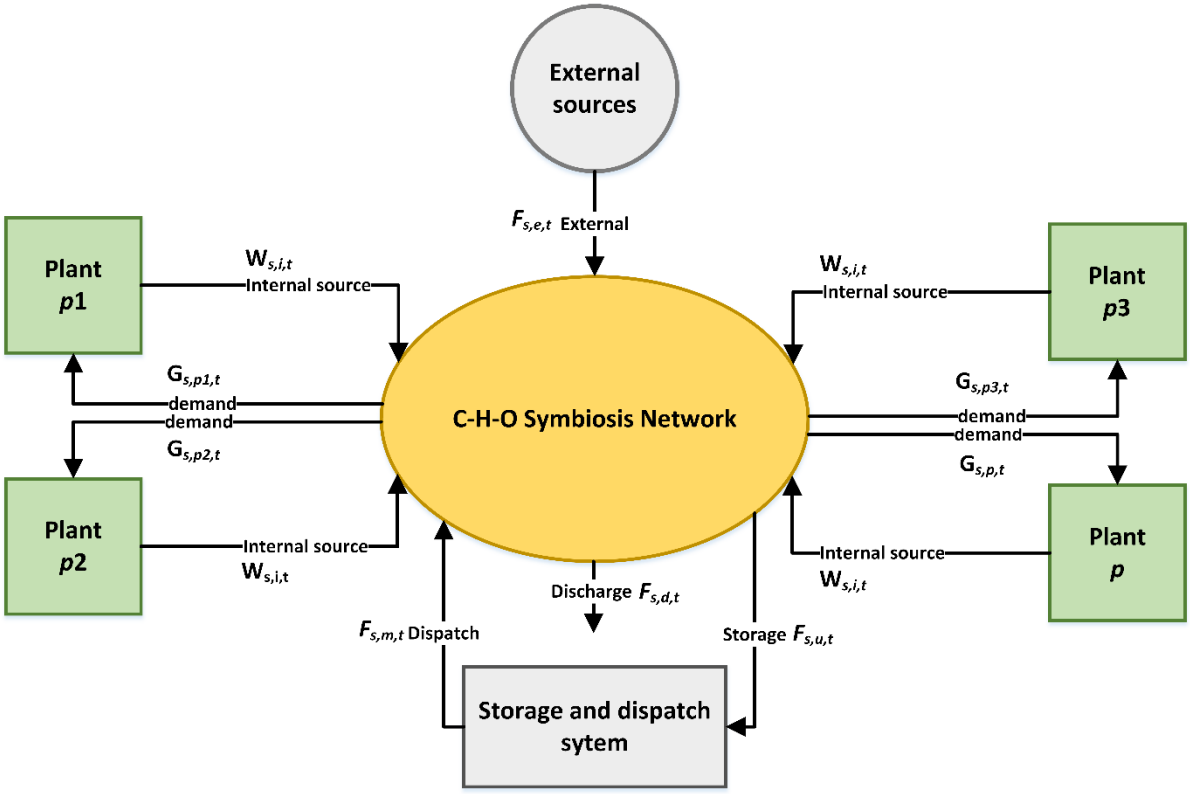

Figure 5.1: Schematic representation of the CHOSYN with storage and dispatch system.

5.3 Mathematical formulation

In this part, the mathematical modeling equations for the proposed approach are demonstrated. The optimization algorithm is shown in Figure 5.2.

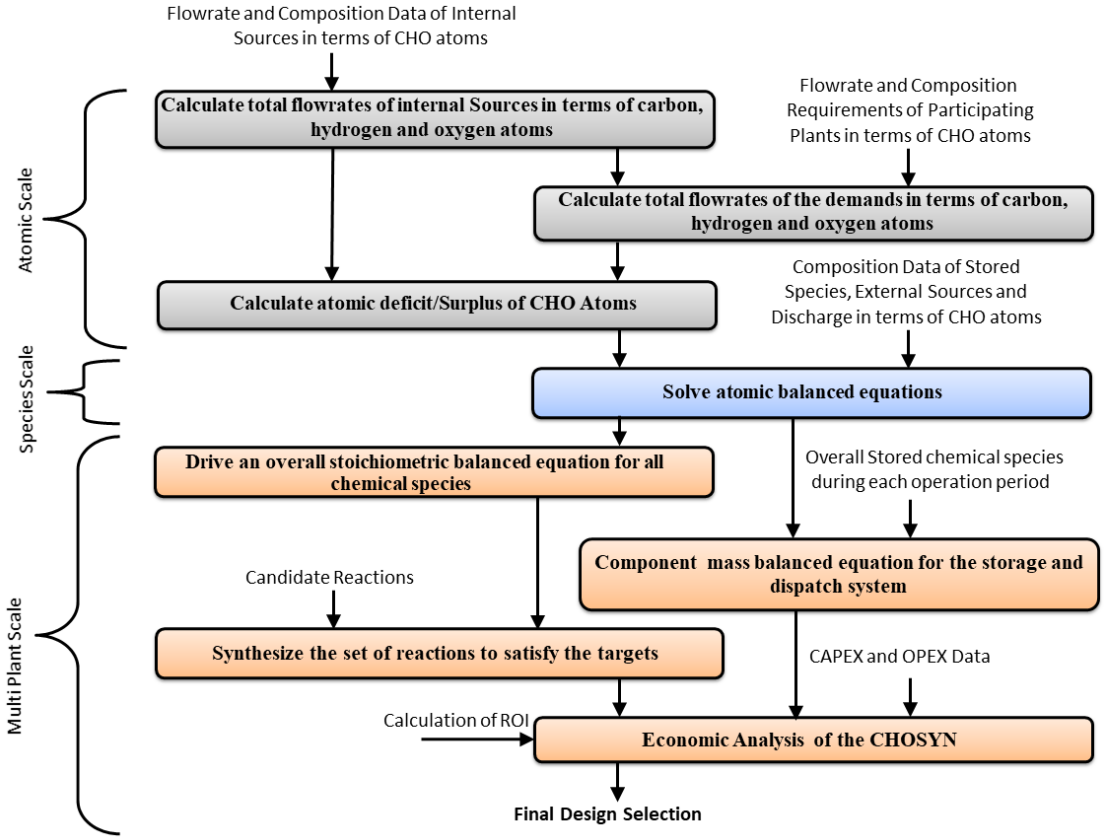

Figure 5.2: Multiperiod CHOSYN with storage and dispatch system optimization algorithm

5.3.1 Atomic targeting

The flow rates of the internal sources of all plants for each operational period are indicated by $A_{C,t}^{internal}$, $A_{H,t}^{internal}$, and $A_{O,t}^{internal}$. The flow rates are calculated in terms of carbon, hydrogen, and oxygen atoms through Equations (1) - (3), where α_s, β_s, γ_s are the atomic coefficients for CHO atoms for chemical species s.

$$A_{C,t}^{internal} = \sum_i \left(\sum_s \alpha_s W_{s,i,t} \right) \quad \forall t \tag{1}$$

$$A_{H,t}^{internal} = \sum_i \left(\sum_s \beta_s W_{s,i,t} \right) \quad \forall t \tag{2}$$

$$A_{O,t}^{internal} = \sum_i \left(\sum_s \gamma_s W_{s,i,t} \right) \quad \forall t \tag{3}$$

The atomic flow rates of the demand of the participating plants are calculated using Equations (4) - (6) for each operation period. $A_{C,t}^{demand}$, $A_{H,t}^{demand}$ and $A_{O,t}^{demand}$ are the atomic flow rates of CHO atoms of the participating plants during operational period *t*.

$$A_{C,t}^{demand} = \sum_p \sum_s \alpha_s G_{s,p,t} \quad \forall t \tag{4}$$

$$\mathrm{A}_{\mathrm{H},t}^{\mathrm{demand}} = \sum_p \sum_s \beta_s \mathrm{G}_{s,p,t} \quad \forall t \tag{5}$$

$$\mathrm{A}_{\mathrm{O},t}^{\mathrm{demand}} = \sum_p \sum_s \gamma_s \mathrm{G}_{s,p,t} \quad \forall t \tag{6}$$

Next, Equations (7) - (9) are employed to calculate the surplus or deficits of CHO atoms, which represents the net supply of atoms to the EIP. A positive sign of an atom implies a surplus, which represents a benchmark for the minimum target of discharge. On the other hand, a negative sign means a deficit of that atom, which indicates minimum target of external sources.

$$\Delta\mathrm{A}_{\mathrm{C},t}^{\mathrm{net}} = \mathrm{A}_{\mathrm{C},t}^{\mathrm{internal}} - \mathrm{A}_{\mathrm{C},t}^{\mathrm{demand}} \quad \forall t \tag{7}$$

$$\Delta\mathrm{A}_{\mathrm{H},t}^{\mathrm{net}} = \mathrm{A}_{\mathrm{H},t}^{\mathrm{internal}} - \mathrm{A}_{\mathrm{H},t}^{\mathrm{demand}} \quad \forall t \tag{8}$$

$$\Delta\mathrm{A}_{\mathrm{O},t}^{\mathrm{net}} = \mathrm{A}_{\mathrm{O},t}^{\mathrm{internal}} - \mathrm{A}_{\mathrm{O},t}^{\mathrm{demand}} \quad \forall t \tag{9}$$

An overall atomic balanced equation for the CHOSYN is written to overcome the deficit of certain atoms identified by the previous Equations. In this case, external chemical species and excess stored chemical species could be utilized to supply the deficit atoms. Equations (10) - (12) represent the overall atomic balanced Equation for each operation period. Equations (13) - (14) represent the maximum allowable discharge and maximum purchasable external chemical species.

$$\Delta\mathrm{A}_{\mathrm{C},t}^{\mathrm{net}} + \sum_e \alpha F_{s,e,t} + \sum_m \alpha F_{s,m,t} - \sum_u \alpha F_{s,u,t} - \sum_d \alpha F_{s,d,t} = 0 \quad \forall s, \forall t \tag{10}$$

$$\Delta\mathrm{A}_{\mathrm{H},t}^{\mathrm{net}} + \sum_e \beta F_{s,e,t} + \sum_m \beta F_{s,m,t} - \sum_u \beta F_{s,u,t} - \sum_d \beta F_{s,d,t} = 0 \quad \forall s, \forall t \tag{11}$$

$$\Delta\mathrm{A}_{\mathrm{O},t}^{\mathrm{net}} + \sum_e \gamma F_{s,e,t} + \sum_m \gamma F_{s,m,t} - \sum_u \gamma F_{s,u,t} - \sum_d \gamma F_{s,d,t} = 0 \quad \forall s, \forall t \tag{12}$$

$$F_{s,d}^{max} \geq F_{s,d} \tag{13}$$

$$F_{s,e}^{max} \geq F_{s,e} \tag{14}$$

where $F_{s,e,t}$, $F_{s,d,t}$ are the flow rates of external and discharged chemical species during t operation period. Note that $F_{s,m,t}$ is the flow rate of chemical species s in the m dispatched stream from the storage system, while $F_{s,u,t}$ is the flow rate of chemical species s in the u stream supplied to the storage system.

5.3.2 Candidate reactions

Next, an overall mass balanced Equation (15) that environ all chemical species within the CHOSYN for each operation period is written. Subsequently, Equations (16) - (17) are employed for each operation period to identify the set of candidate reactions needed to convert the involved chemical species to the plants demand. Note that, left-hand side of Equation (16) represents the overall balance of all chemical species involved in the CHOSYN, while plants demand flowrates are described by the left-hand side of Equation (17). The stoichiometric coefficient of species *s* in reaction *j* is denoted by $Z_{s,j,t,}$ while the molar flow rate coefficient of reaction *j* is represented by $X_{j,t}$

$$\sum_i W_{s,i,t} + \sum_e F_{s,e,t} + \sum_m F_{s,m,t} = \sum_p G_{s,p,t} + \sum_d F_{s,d,t} - \sum_u F_{s,u,t} \quad \forall s, \forall t \qquad (15)$$

$$\sum_i W_{s,i,t} + \sum_e F_{s,e,t} + \sum_m F_{s,m,t} - \sum_u F_{s,u,t} - \sum_d F_{s,d,t} = \sum_j Z_{s,j,t} \times X_{j,t} \quad \forall s, \forall t \qquad (16)$$

$$\sum_p G_{s,p,t} = \sum_j Z_{s,j,t} \times X_{j,t} \quad \forall s, \forall t \qquad (17)$$

5.3.3 Storage and dispatch system

Thereafter, material balanced Equations are written for the storage and dispatch system during operation period *t.* In the special case of two operational periods only, Equations (18) – (20) are used where any stored species in the first period are dispatched in the second period and vice versa. On the other hand, if the operational periods exceed two periods, Equation (21) is utilized where chemical species are only stored in the first period. Subsequently, a portion of the chemical species can be dispatched or stored in the second period and so forth and so on for the next periods until the end of the operation cycle, where all stored chemical species are consumed. Thereafter, the first period starts again with storing chemical species only. All the previous Equations are limited by maximum storage capacity, as indicated in Equation (22). Note that the $N_{s,t}^{\text{Total}}$ is the total stored species during operational period *t*, N_s^{max} is the maximum capacity of stored species.

$$\sum_u F_{s,u,t} = \sum_m F_{s,mt+1} \quad \forall t \qquad (18)$$

$$\sum_u F_{s,u,t+1} = \sum_m F_{s,m,t} \quad \forall t \qquad (19)$$

$$N_{s,t}^{\text{Total}} = \sum_u F_{s,u,t} + \sum_u F_{s,u,t+1} - \sum_m F_{s,m,t} - \sum_m F_{s,m,t+1} \quad \forall t \qquad (20)$$

$$N_{s,t+1}^{\text{Total}} = \sum_u F_{s,u,t} + \sum_u F_{s,u,t+1} - \sum_m F_{s,m,t+1} \quad \forall t \tag{21}$$

$$N_{s,t}^{\text{Total}} \leq N_s^{max} \ \forall t \tag{22}$$

5.3.4 Economics

Economic analysis tools are incorporated to determine the optimum configuration of the CHOSYN. The capital cost expenditure (*CAPEX*) can be estimated using Equation (23), where *FCI* and *WCI* are the fixed and working capital investments, respectively. *WCI* is taken as 15% of CAPEX. *FCI* is calculated using the factorial method based on delivered equipment cost. Since the proposed model is a preliminary tool, the storage costs are assumed as a factor of the *FCI*. Equations (24) - (25) are binary equations to take into consideration the largest equipment sizing to accommodate all operating periods where $l_{j,t}$ is a binary variable

$$CAPEX = FCI + WCI \tag{23}$$

$$X_{j,t} \geq X_{j+1,t+1} \times l_{j,t} \tag{24}$$

$$X_{j,t} \times (1 - l_{j,t}) \leq X_{j+1,t+1} \tag{25}$$

Next, the operating cost expenditures (*OPEX*) are calculated using the factorial method. Afterwards, the *CAPEX* is used to determine the annualized fixed costs (*AFC*) in Equation (26), which is the depreciation of the capital cost. Using a 10-year linear scheme with negligible salvage, the value is assumed to be 10% of the overall capital cost. Subsequently, the annualized net profit (*ANP*) is calculated through Equation (27) where V_t is used to represent the weightage of the duration of each operational period with respect to a whole year. Finally, the return-on-investment metric (*ROI*) in Equation (28) is evaluated to determine project feasibility in terms of costs.

$$AFC = 0.1 \times CAPEX \tag{26}$$

$$ANP = \langle \left[\left(\sum_s \text{SALE}_s \times \sum_t \sum_s \text{G}_{s,t} \times \sum_t V_t \right) - \left(\sum_s \text{COST}_s \times \sum_t \sum_e \sum_s F_{s,e,t} \times \sum_t V_t \right) - \left(\sum_t OPEX_t \times \sum_t V_t \right) - (AFC) \right] \times (1 - \text{Tax rate}) \rangle + AFC \tag{27}$$

$$ROI = ANP \times CAPEX \tag{28}$$

where

AFC: annualized fixed costs

SALE_s: sale price of product of chemical species *s*

COST_s: cost price of external chemical species s

$OPEX$: annual operating cost expenditures

V_t: the weightage of each operating period with respect to a whole year

5.3.5 Objective function

The objective function utilized in the proposed optimization model is maximum *ANP* and minimum CO_2 and H_2O discharge. The first and second scenarios are solved with the objective function of maximum *ANP* using Equation (29). On the other hand, the third scenario is solved with minimum CO_2 and H_2O discharges using Equation (30).

$$\text{Maximum}(ANP) = \langle\left[\left(\sum_s \mathrm{SALE}_s \times \sum_t \sum_s \mathrm{G}_{s,t} \times \sum_t V_t\right) - \left(\sum_s \mathrm{COST}_s \times \sum_t \sum_e \sum_s F_{s,e,t} \times \sum_t V_t\right) - \left(\sum_t OPEX_t \times \sum_t V_t\right) - (AFC)\right] \times (1 - \text{Tax rate})\rangle + AFC \quad (29)$$

$$\text{Minimum}\left(\sum_d F_{s,d,t}\right) \quad \forall s, \forall t \quad (30)$$

5.4 Case study

5.4.1 Participating plants

The merits of the proposed model are shown through the following case study. Seven chemical plants desire the formation of an EIP to maximize the utilization of available resources to induce synergism. The participating plants are:

1) Gas to Liquid (GTL) plant: The GTL converts methane to syngas, followed by Fischer-Tropsch reaction [93].

$$\mathrm{CH_4 + H_2O \rightarrow CO + 3H_2O}$$

$$\mathrm{CH_4 + 1.5O_2 \rightarrow CO + 2H_2O}$$

$$\mathrm{CO + H_2O \rightarrow CO_2 + H_2}$$

$$\mathrm{nCO + (2n+1)H_2 \rightarrow H(CH_2)_nH + nH_2O}$$

2) Ethylene plant: The plant uses steam cracking of ethane to produce ethylene. The plant consumes ethane (C_2H_6) and produces CH_4 and H_2 as by-products [94].

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$C_2H_6 + C_2H_4 \rightarrow C_3H_6 + CH_4$$

$$2C_2H_6 \rightarrow C_3H_8 + CH_4$$

$$C_3H_8 \rightarrow C_3H_6 + H_2$$

3) Propane dehydrogenation (PDH) plant: In the PDH plant, propane is converted to propylene using catalytic dehydrogenation, where H_2 and CO_2 are generated as by-products [95].

$$C_3H_8 \rightarrow C_3H_6 + H_2$$

4) Methanol to propylene (MTP) plant: Methanol is converted to propylene in two steps, where methanol is converted to dimethyl ether, followed by the conversion of dimethyl ether to propylene leading to the following overall reaction [96].

$$3CH_3OH \rightarrow C_3H_6 + H_2O$$

5) Biodiesel plant: Biodiesel is produced using palm oil through transesterification, where glycerol is generated as a by-product:

$$CH_3(CH_2)_{14}COOH + CH_3OH \rightarrow C_{14}H_{28} + C_3H_8O_3$$

Note that, the last three plants, propylene glycol, acrolein and power station plants, are considered as a black box, where only the plants demand are known. The participating plants may have multiple operation periods where the molar flowrate of their by-products and wastes vary according to different seasons. In this case study, each plant has two operation periods, each last for half a year. The participating plants available by-products molar composition and molar flowrate for each operational period are summarized in Tables 5.1 and 5.2. The available purchasable external chemical species prices are summarized in Table 5.3. The prices are available for individual chemical species only.

Table 5.1: Molar composition and total flowrates of the participating plants by-products for the first operation period

Plants	Molar composition (%)					Total Molar flowrate (kmole/hr)
	CO	CO_2	H_2	CH_4	$C_3H_8O_3$	
GTL	8	25	67	0	0	11670
Ethylene	0	0	25	75	0	670
PDH	0	18	82	0	0	2180
MTP	0	100	0	0	0	900
Biodiesel	0	0	0	0	100	1500
Propylene glycol	0	0	0	0	0	0
Acrolein	0	0	0	0	0	0

Table 5.2: Molar composition and total flowrates of the participating plants by-products for the second operation period

Plants	Molar composition (%)					Total Molar flowrate (kmole/hr)
	CO	CO_2	H_2	CH_4	$C_3H_8O_3$	
GTL	6	15	79	0	0	9860
Ethylene	0	0	7	93	0	2170
PDH	0	0	100	0	0	7000
MTP	0	100	0	0	0	500
Biodiesel	0	0	0	0	100	4000
Propylene glycol	0	0	0	0	0	0
Acrolein	0	0	0	0	0	0

Table 5.3: Available external sources and their corresponding prices [97]

Available feedstock	Price ($/kmole)
$C_3H_8O_3$	1.2
CH_4	7.24
H_2	3
CO	4

The chemical species demands in each operation period are shown in Table 5.4. These demands are met by utilizing the available internal sources, minimum external chemical species, and stored chemical species. The maximum allowable discharge is subject to

the geographical location and environmental regulations of each country. The overall objective is to set atomic benchmarks, determine the reaction pathways to reach minimum resource consumption through utilizing a storage and dispatch system to meet the plants demand during each operational period. The project's feasibility during the preliminary design is determined in a one-stage model using the return-on-investment metric.

Table 5.4: Participating plants demands flowrates (kmole/hr) during the first and second operation period.

Plant	Demand	First operation period	Second operation period
MTP	Methanol	7500	6500
Biodiesel	Methanol	2500	1000
Propylene glycol	Propylene glycol	2000	1000
Acrolein	Acrolein	2000	1000
Power production	H_2	5000	11000

5.4.2 Candidate interceptors

In order to meet the plants demand, the EIP will require specific chemical reactions to transform the internal sources to the required products. The suggested chemical reactions, which are considered as interceptors, are summarized in Table 5.5. The equipment costs and operating costs of the mentioned interceptors are summarized in Table 5.6.

. Table 5.5: Candidate interceptors description.

Technology	Interceptor number	Reaction
Methanol synthesis	X_{j1}	$2H_2 + CO \rightarrow CH_3OH$
Methanol synthesis	X_{j2}	$3H_2 + CO_2 \rightarrow CH_3OH + H_2O$
Steam reforming of methane	X_{j3}	$CH_4 + H_2O \rightarrow 3H_2 + CO$
Steam reforming of methane	X_{j4}	$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$
Glycerol to syngas	X_{j5}	$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$
Water-gas shift reaction	X_{j6}	$H_2O + CO \rightarrow H_2 + CO_2$

Reverse water-gas shift reaction	X_{j7}	$H_2 + CO_2 \rightarrow H_2O + CO$
Glycerol to propylene glycol	X_{j8}	$C_3H_8O_3 + H_2 \rightarrow C_3H_8O_2 + H_2O$
Glycerol to acrolein	X_{j9}	$C_3H_8O_3 \rightarrow C_3H_4O + 2H_2O$

Table 5.6: Equipment costs and operating costs of different reactions used in the EIP [97].

Interceptor	Equipment costs $ / kg product / year	Operating costs $ / kg product
Interceptor 1	0.31	0.61
Interceptor 2	0.49	1.01
Interceptor 3	0.29	0.66
Interceptor 4	0.29	0.66
Interceptor 5	0.66	2.6
Interceptor 6	0.1	0.1
Interceptor 7	0.1	0.1
Interceptor 8	0.28	0.85
Interceptor 9	0.21	0.42

5.5 Results and Discussion

The previous model with Equations (1) – (28)) is solved using LINGO v13.0 with a Global Solver invoked to obtain an optimum CHOSYN configuration. The model is formulated as a mixed-integer non-linear program (MINLP). Three scenarios are conceived in this section. The first scenario is the multiperiod CHOSYN without storage and dispatch system while the second scenario is the multiperiod CHOSYN with a storage and dispatch system, both using the global objective function of maximum *ANP* using Equation (29). Third scenario is multiperiod CHOSYN with a storage and dispatch system with the global objective function of minimum CO_2 and H_2O discharges using Equation (30).

5.5.1 First scenario

The first scenario is considered the base case scenario where no storage of chemical species occurs. The first scenario is solved using Equations (1) – (17) and (23) – (28) where the variables $F_{s,m,t}$ and $F_{s,u,t}$ are set to zero since there is no storage and dispatch system. The objective function (Equation (29)) of maximum *ANP* is selected to solve the model. In the first period, the optimum CHOSYN integrated all the streams from internal sources, in addition to consuming 3000, 4000 and 1570 kmole/hr of CH_4, $C_3H_8O_3$ and H_2 as shown in Table 5.7. On the other hand, the CHOSYN discharged 500 kmole/hr of $C_3H_8O_3$, because it received sufficient $C_3H_8O_3$ from the internal sources in the second operation period. The discharge of $C_3H_8O_3$ may incur additional charges for disposal. The overall network economic performance is summarized in Table 5.8. Note that, the total capital investment is the lower as compared to the scenario two due to the unavailability of storage and dispatch system. Nonetheless, the *ROI* reached 19 %/yr. The resulted CHOSYN configurations for both operational periods for scenario one is shown in Figures 5.3 and 5.4. The CHOSYN discharged a total of 4450 and 5040 kmole/hr of CO_2 and H_2O during the two operational periods.

Table 5.7: Flow rates (kmole/hr) of external, stored and discharged species in the CHOSYN for the first scenario

Streams	Operation period one			Operation period two		
	External sources	Stored species	Discharged species	External sources	Stored species	Discharged species
CH_4	3000	0	0	0	0	0
$C_3H_8O_3$	4000	0	0	0	0	500
H_2	1570	0	0	470	0	0
CO	0	0	0	0	0	0
CO_2	0	0	2920	0	0	1530
H_2O	0	0	3570	0	0	1470

Table 5.8: Economic analysis of the first scenario CHOSYN

Economic aspects	Operation period one	Operation period two
OPEX ($x10^6$ \$/yr)	2403	711
ANP ($x10^6$ \$/yr)	1570	

CAPEX ($x10^6$ \$)	8479
ROI (%/yr)	19

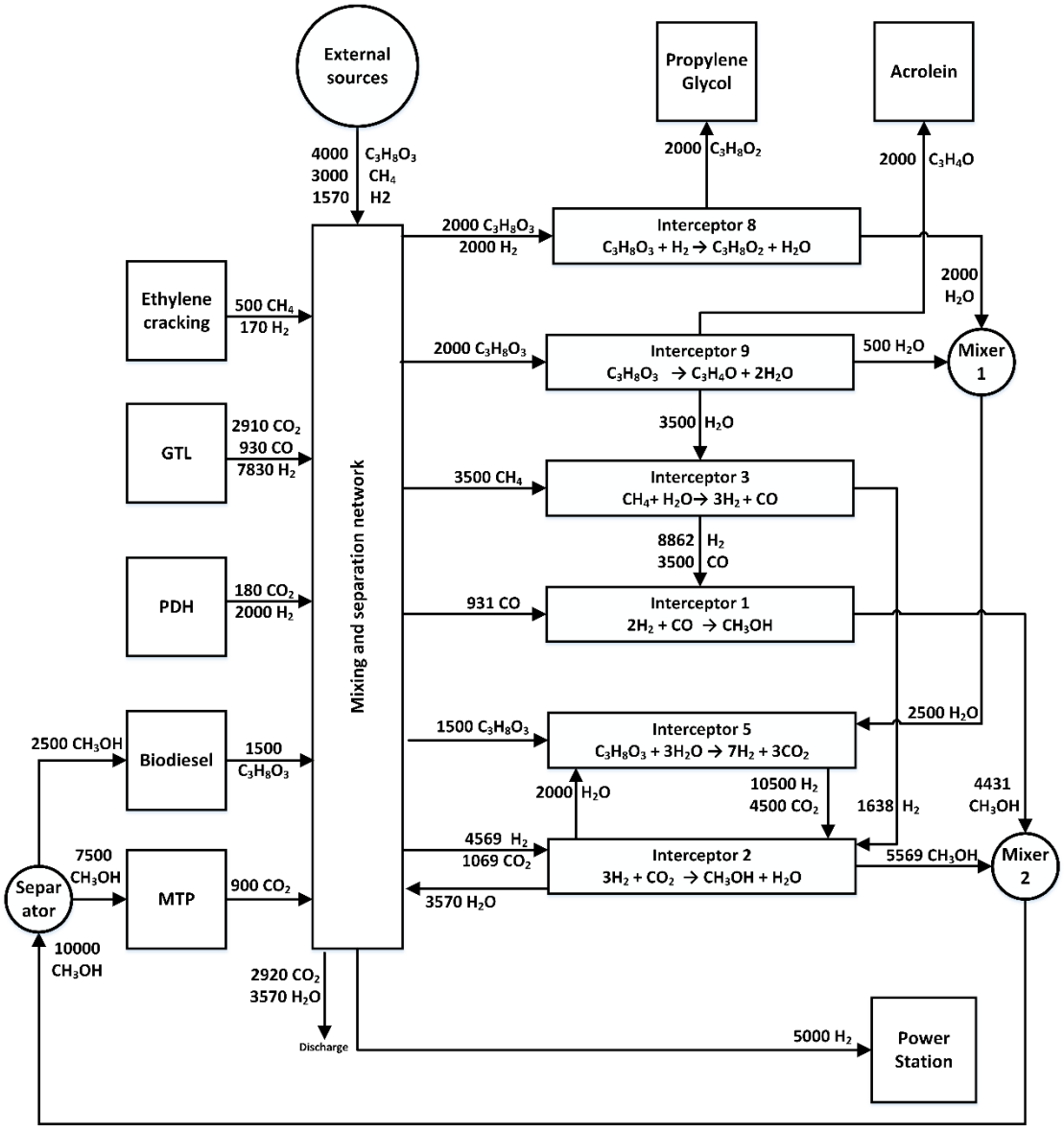

Figure 5.3: An optimum CHOSYN for the first operational period in scenario one

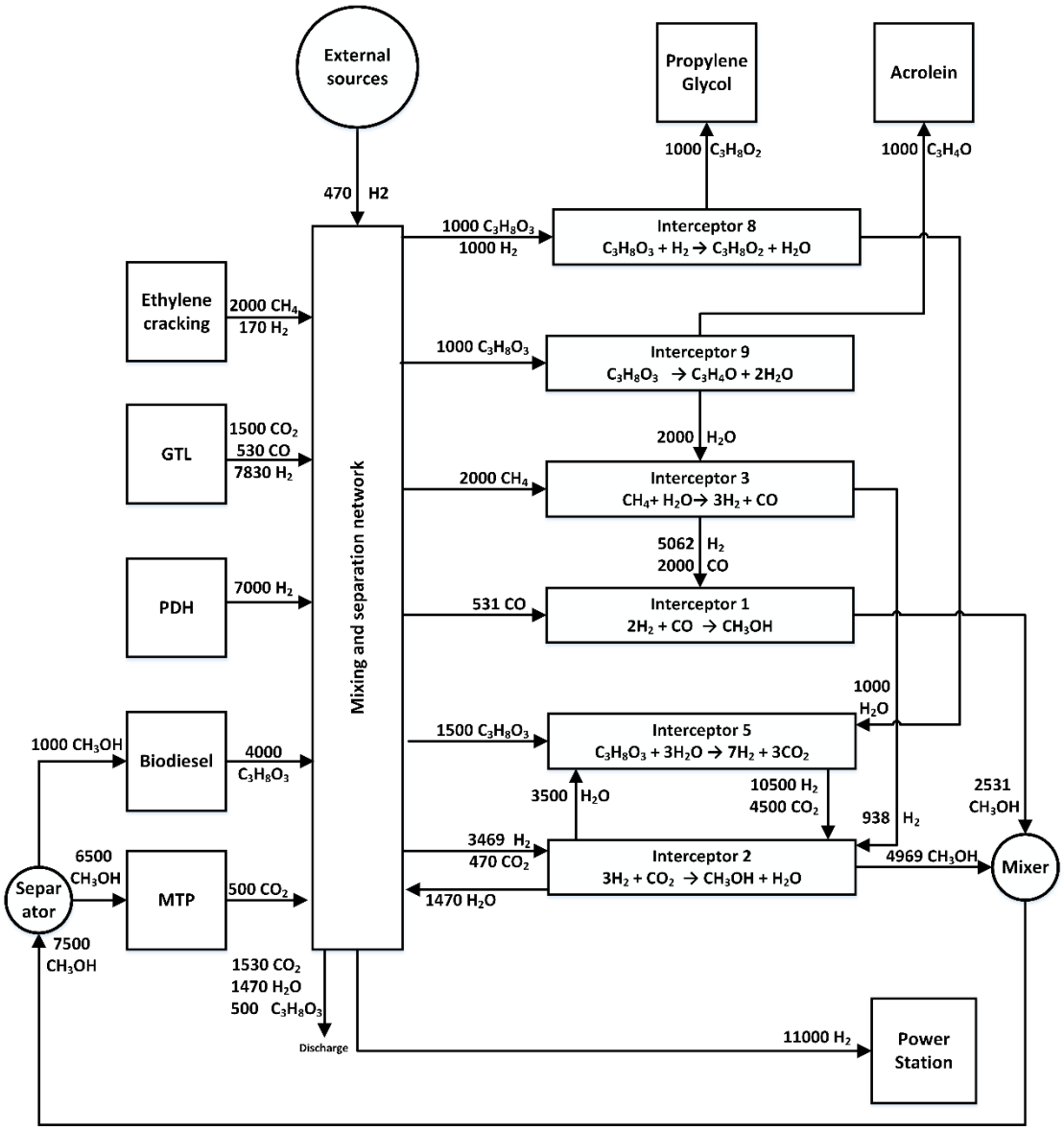

Figure 5.4: An optimum CHOSYN for the second operational period in scenario one

5.5.2 Second scenario

The second scenario is solved using Equations (1) – (28) in which the storage and dispatch system is integrated in the CHOSYN design. The objective function of maximum *ANP* (Equation (29))) is selected to solve the model. Table 5.10 shows that 4500 kmole/hr $C_3H_8O_3$ is purchased compared to 4000 kmole/hr $C_3H_8O_3$ and 3000 kmole of CH_4 in the first scenario (Table 5.7). This is due to the surplus of 500 kmole/hr $C_3H_8O_3$ in the second period is stored and consumed in the next period instead of being discharged. Note that the stored and purchased $C_3H_8O_3$ is consumed by interceptor 5 in contrast to the selection of interceptor 3 that consumed the purchased CH_4 in scenario

one (zero CH4 external source as shown in Table 5.9). Despite having high capital investment, Table 5.10 shows that the ROI reached 26 %/yr.. This is due to the fact the storage and dispatch system decreased the *OPEX* by 30 x 10^6 $/yr which overcome the high *CAPEX* leading to 7%/yr increase in ROI compared to scenario one. The resulted CHOSYN configurations for both operational periods for scenario two is shown in Figures 5.5 and 5.6 where 4450 and 8040 kmole/hr of CO_2 and H_2O are discharged. The H_2O discharge is higher by 3000 kmole/hr as compared to scenario one. This is because interceptor 5 molar flowrate increased which led to increasing interceptor 2 molar flowrate leading to higher H_2O discharge. Additionally, from Figures 5.5 and 5.6, no external sources are needed for the second period because the required chemical species are provided by the storage and dispatch system.

Table 5.9: Flow rates (kmole/hr) of external, stored and discharged species in the CHOSYN for the second scenario

Streams	Operation period one			Operation period two		
	External sources	Stored species	Discharged species	External sources	Stored species	Discharged species
CH_4	0	0	0	0	0	0
$C_3H_8O_3$	4500	0	0	0	500	0
H_2	7040	2000	0	0	0	0
CO	0	0	0	0	1530	0
CO_2	0	0	4450	0	0	0
H_2O	0	0	5040	0	0	3000

Table 5.10: Economic analysis of second scenario CHOSYN

Economic aspects	Operation period one	Operation period two
OPEX (x10^6 $/yr)	1828	1256
ANP (x10^6 $/yr)	2571	
CAPEX (x10^6 $)	9889	
ROI (%/yr)	26	

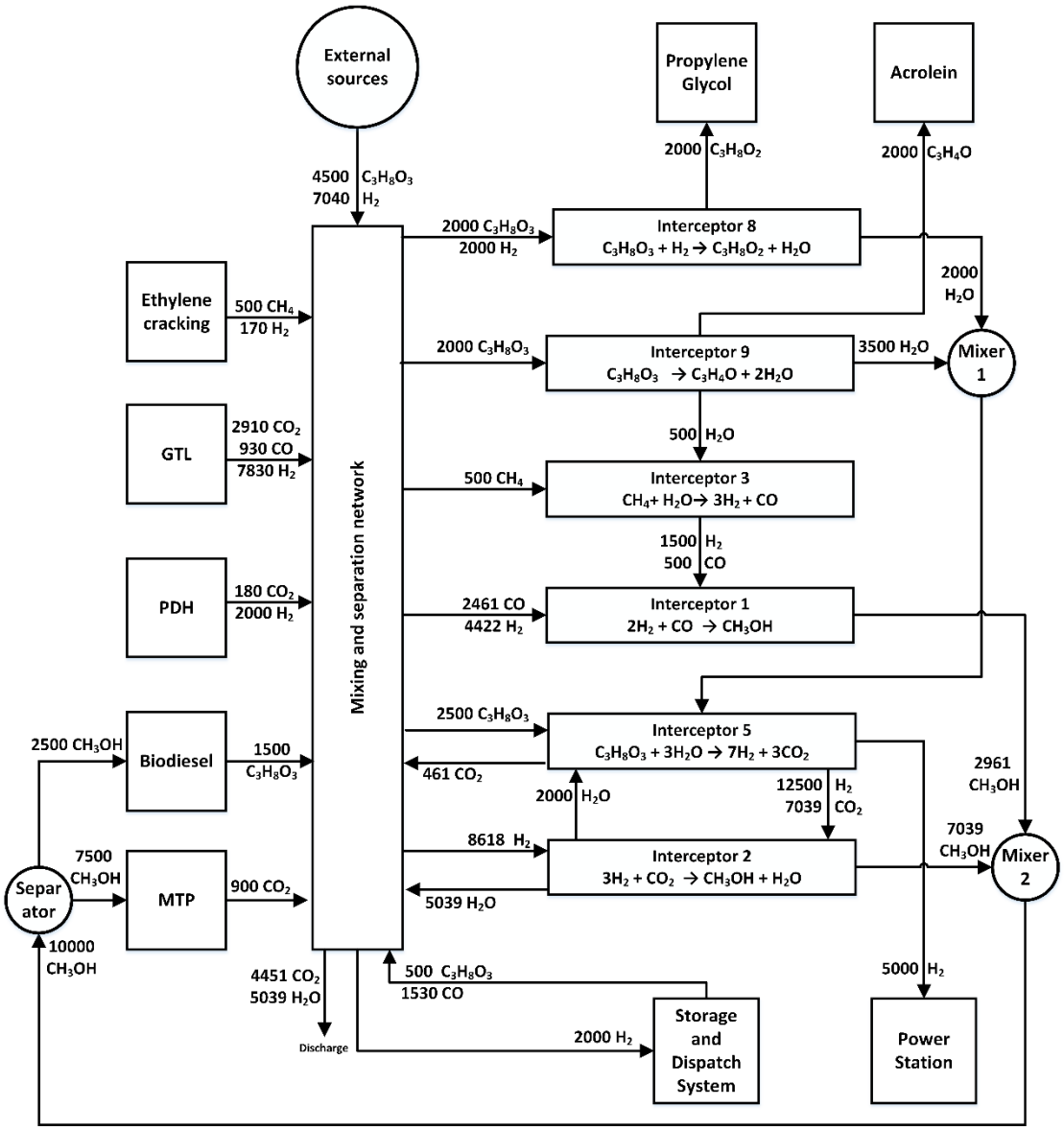

Figure 5.5: An optimum CHOSYN for the first operational period in scenario two

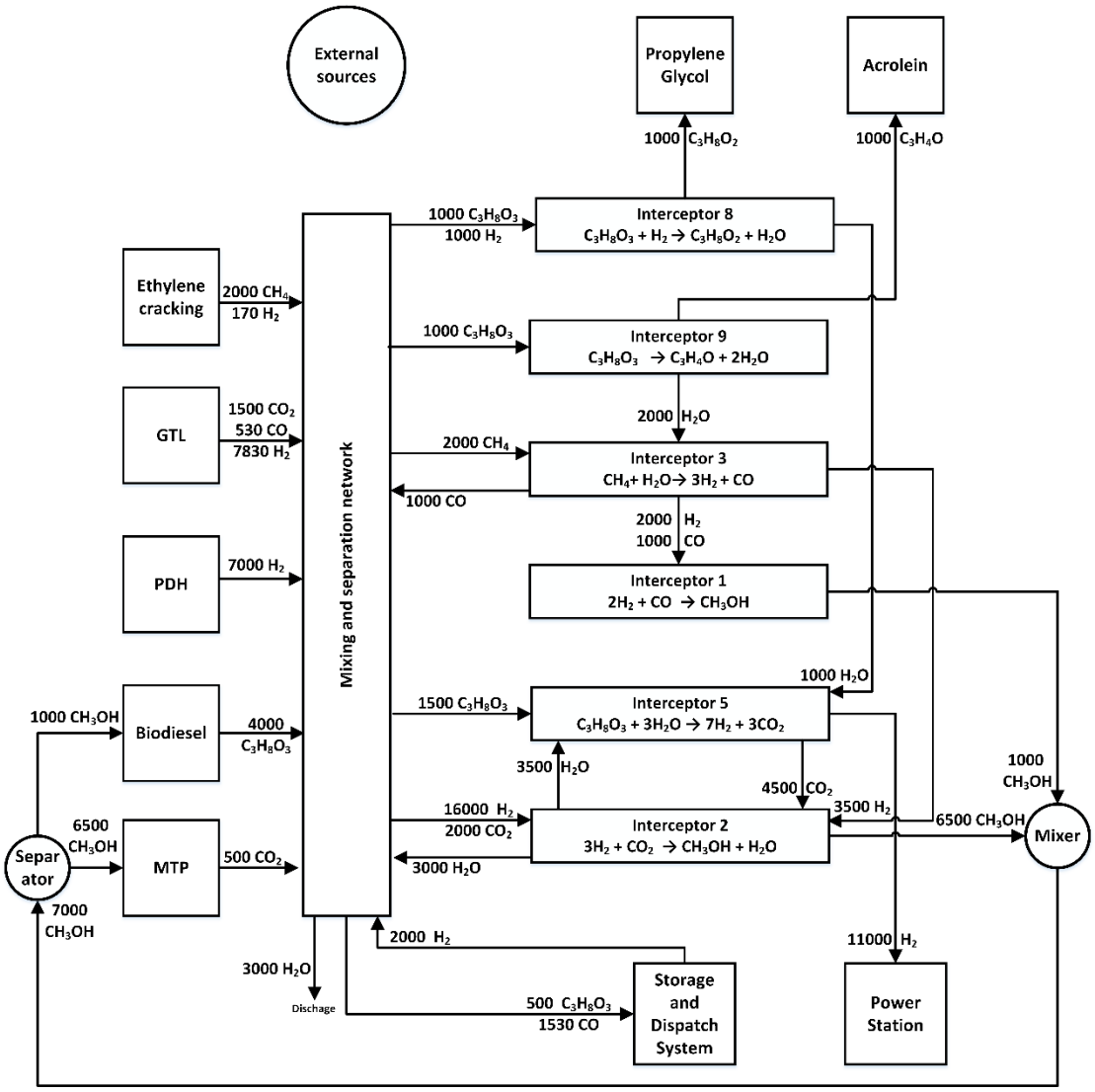

Figure 5.6: An optimum CHOSYN for the second operational period in scenario two

5.5.3 Third scenario

The second scenario is solved using Equations (1) – (28) with the objective function of minimum CO_2 and H_2O discharge (Equation (30)). The flowrates of external, stored and discharged chemical species for scenario three are summarized in Table 5.11. From Table 5.11, scenario three has the lowest CO_2 and H_2O discharges since the global objective function of minimizing CO_2 and H_2O discharge was employed. However, from Table 5.12, scenario three has the lowest ROI of 15 %/yr. This is because the purchased raw materials costs are the highest because the CHOSYN selected reactions that prioritized producing less CO_2 and H_2O as a by-product, i.e., interceptors 1 and 3. Although scenario three is more environmentally friendly, it is not very economic as

compared to the other scenarios. The resulted CHOSYN configurations for both operational periods for scenario one is shown in Figures 5.7 and 5.8 where only 3059 and 3547 kmole of CO_2 and H_2O are discharge.

Table 5.11: Flow rates (kmole/hr) of external, stored and discharged species in the CHOSYN for the third scenario

Streams	Operation period one			Operation period two		
	External sources	Stored species	Discharged species	External sources	Stored species	Discharged species
CH_4	5465	0	0	2465	0	0
$C_3H_8O_3$	1856	0	0	0	1321	0
H_2	0	0	4787	0	2643	0
CO	0	0	1389	0	995	0
CO_2	0	0	2525	0	0	534
H_2O	0	0	1499	170	0	2048

Table 5.12: Economic analysis of third scenario CHOSYN

Economic aspects	Operation period one	Operation period two
OPEX ($x10^6$ \$/yr)	1585	1081
ANP ($x10^6$ \$/yr)	1242	
CAPEX ($x10^6$ \$)	8282	
ROI (%/yr)	15	

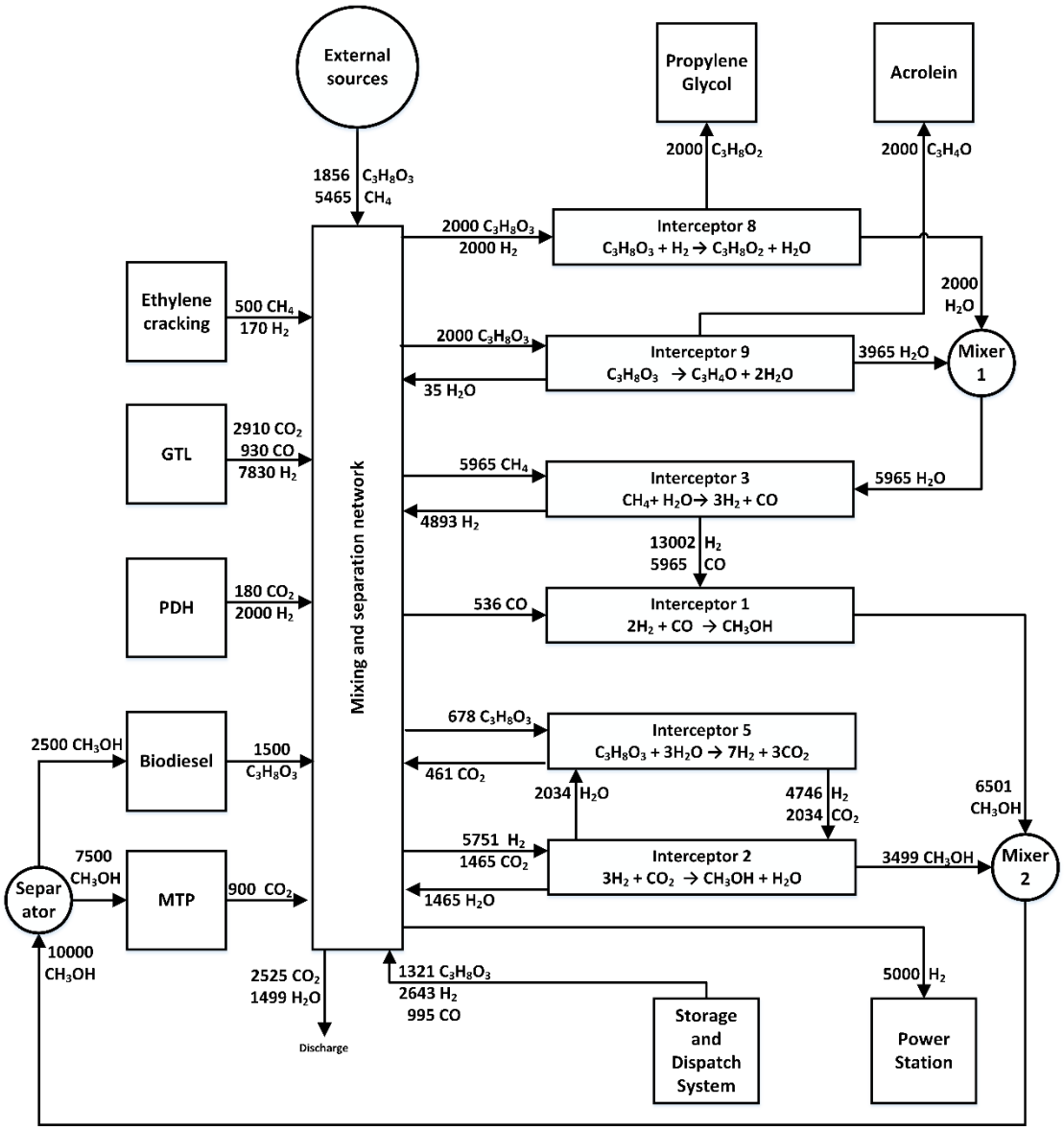

Figure 5.7: An optimum CHOSYN for the first operational period in scenario three

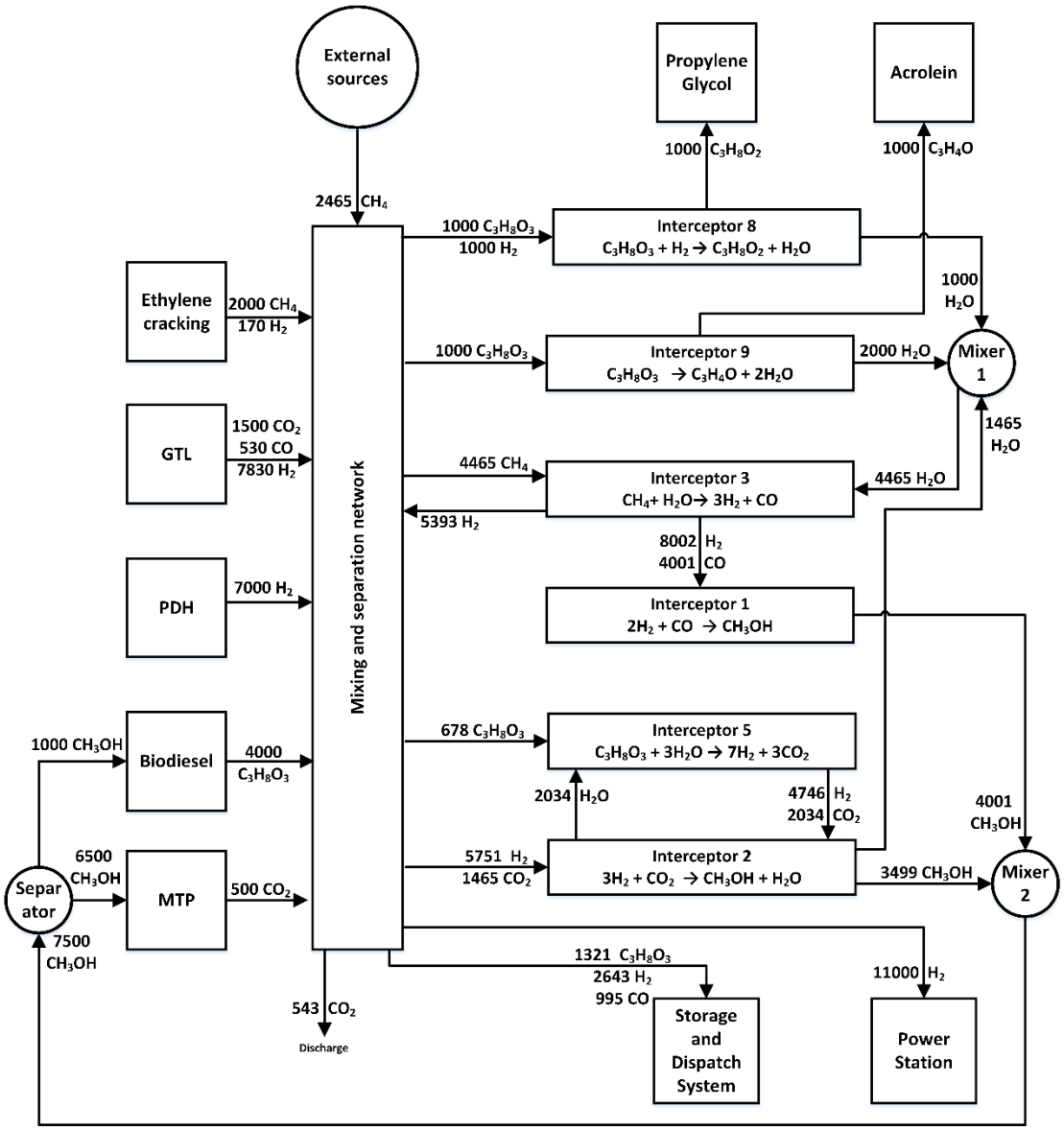

Figure 5.8: An optimum CHOSYN for the second operational period in scenario three

5.5.4 Sensitivity analysis

Next, a sensitivity analysis is carried out with respect to the external sources costs on the second scenario. Scenario two was selected from an economic viewpoint because of the highest *ROI* the scenario achieved. The effects of altering the feedstock market prices of all available raw materials during t_1 period are shown in Figure 5.9. Three cases are conceived in this part. First case is infinite storage capacity, where there is a little change in the ROI with respect to feedstock price. This is due to the availability of the storage and dispatch system, where the required feedstock is purchased during the t_2 period, when the prices are low. Subsequently, the stocked raw materials are

dispatched during the next period leading to small change in the ROI of the CHOSYN due to the increase in capital cost. The second case is no change in storage capacity with respect to the increase in raw materials prices leading to a huge decrease in ROI. Third case is the storage capacity increases by 100%, which represents an extension to the existing storage and dispatch system. Figure 5.9 shows that the decrease in ROI in the third case is lower as compared to the second case.

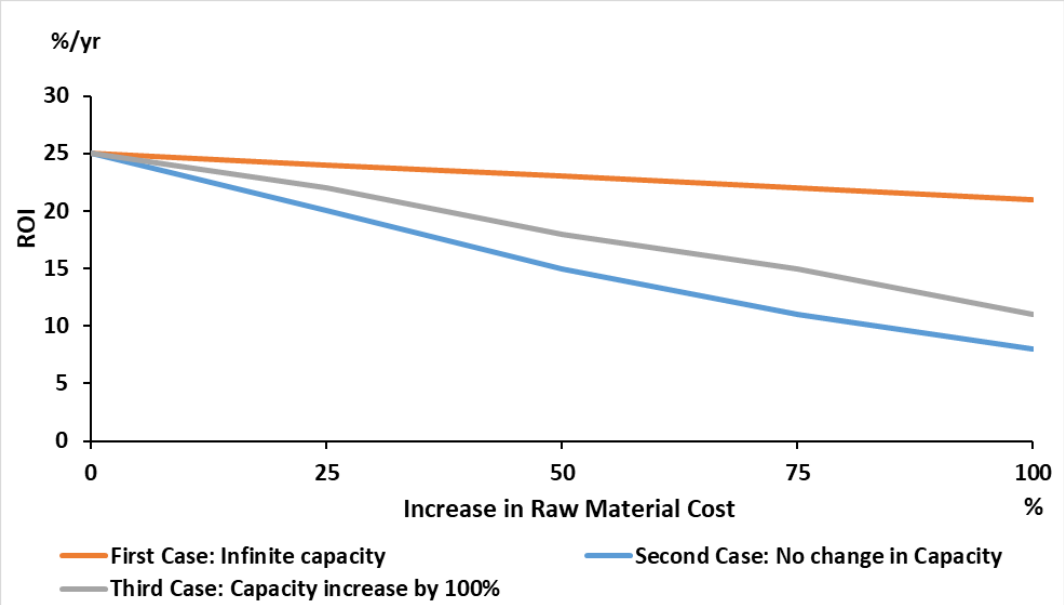

Figure 5.9: Sensitivity analysis of the increase in raw material costs on ROI

5.6 Conclusion:

A multi-period CHOSYN optimization model embedded with a storage and dispatch system has been successfully developed. The approach devised in this work was simulated in LINGO to obtain the required atomic benchmarks, determine necessary chemical reactions and satisfy the plant's demand with the aid of the storage and dispatch system driven by economical objectives, in addition to a significant reduction in the carbon and water discharge. The newly developed model was applied to a case study based on glycerol valorization along with other chemical plants. A comparison between the newly proposed model and the conventional multiperiod CHOSYN has been conceived to showcase the merits of the storage and dispatch system. Subsequently, a sensitivity analysis with respect to feedstock market price was carried out, which proved the model advantageous. As a preliminary tool, this methodology can be coupled with decision-making tools due to the complex nature of the EIP and the large number of stakeholders involved.

Chapter 6 Conclusion and future work

Despite numerous studies in the area of sustainable EIPs, there remain significant gaps in the EIPs design and formulation. In this research, a sustainable type of EIPs named CHOSYN was synthesized using mathematical optimization methodologies.

Firstly (chapter 3), an optimization model was formulated to design a sustainable CHOSYN with consideration to economic, sustainability and safety criteria. A recycling framework was integrated in the model. Several scenarios were obtained to showcase the features of the formulated model. It was found that safety and sustainability criteria is critical in the CHOSYN initial design stages as it directly affects the economic criteria the CHOSYN configuration. By optimizing the CHOSYN based on multi-criteria, the mathematical model was able to report the most feasible sustainable CHOSYN pathways and compare them.

Later (chapter 4), mass and water networks were synthesized simultaneously in the CHOSYN. A model was developed to design a simultaneous mass-water CHOSYN since water integration was not covered before in the CHOSYN design. Additionally, multi-criteria optimization was performed based on economic and sustainability aspects. A quantitative metric termed sustainability weighted return on investment metric was utilized to quantify the sustainability performance of the mass-water CHOSYN. The metric above is embedded along with the economic performance of the CHOSYN into the mathematical model. Although mass and water networks are often designed separately, the results show that it is more advantageous to design both of them simultaneously.

Following this (chapter 5), the time element was taken into consideration to design multiperiod CHOSYN. Previous research assumed steady-state operations and single operation mode. A multiperiod framework incorporating a storage and dispatch system was implemented. The storage and dispatch system allowed the storage of certain chemical species during an operation period to be dispatched in another operation period. It was found the incorporation of the storage and dispatch system elevated the economic performance of the resulting multiperiod CHOSYN.

Next, future recommendations of the research project could consider integrating other criteria in the CHOSYN design. Recommended criteria are resilience, reliability and social. This will add an additional complexity layer to the CHOSYN design. Moving on, the research project explored the simultaneous integration of mass and water networks. Thus it is paramount for future initiatives to consider heat integration along with mass and water integration. The incorporation of heat integration will capture a more broad picture and realism in the CHOSYN design.

Besides, other areas of studies should incorporate multi-criteria decision-making frameworks in the CHOSYN design due to the number of participating plants and decision-makers involved. Suggested frameworks are gaming theories, including non-cooperative games, cooperative games, and the Stackelberg game. These games should help in reaching a mutually agreeable sustainable CHOSYN design.

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Appendix

Appendix 1: LINGO model formulation for chapter 3

Appendix 1(a): LINGO mathematical modeling codes for case 1

```
!objective function ;
!Maximum annual sales);


max = sales;

!Atomic Targeting
!IS STANDS FOR INTERNAL SOURCES INSIDE EIP (kmole/hr);
!Calculation of number of CHO atoms in internal streams;

IS_CO       = 930;
IS_CO2      = 3990;
IS_H2       = 9965;
IS_CH4      = 39;
IS_C3H8O3   = 1000;

AC_SRC      = IS_CO * 1 + IS_CO2 * 1 + IS_CH4 * 1 + IS_C3H8O3 * 3;
AH_SRC      =              IS_H2 * 2 + IS_CH4 * 4 + IS_C3H8O3 * 8;
AO_SRC      = IS_CO * 1 + IS_CO2 * 2              + IS_C3H8O3 * 3;

!Atomic Targeting
!DMD STANDS FOR DEMAND BY FACTORIES (kmole/hr);
!Calculation of number of CHO atoms in demand streams;

CH3OH_DEMAND      = 7500;
H2_Demand         = 5000;
C3H8O2_DEMAND     = 1000;
C3H4O_DEMAND      = 1000;


AC_DMD      = CH3OH_DEMAND * 1                  + 3 * C3H8O2_DEMAND  + 3 * C3H4O_DEMAND ;
AH_DMD      = CH3OH_DEMAND * 4 + 2 * H2_DEMAND + 8 * C3H8O2_DEMAND  + 4 * C3H4O_DEMAND ;
AO_DMD      = CH3OH_DEMAND * 1                  + 2 * C3H8O2_DEMAND  + 1 * C3H4O_DEMAND ;

!Atomic Targeting
!NET STANDS FOR NET RESULT BETWEEN INTERNAL AND DEMAND streams (kmole/hr);

AC_NET      = AC_SRC - AC_DMD;
AH_NET      = AH_SRC - AH_DMD;
AO_NET      = AO_SRC - AO_DMD;

!Atomic Targeting - overall atomic balanced equation;
!calculation of external, recycled, discharged species in the CHOSYN (kmole/hr);
!Equations (10-12);

AC_NET + 3 * EX_C3H8O3  - 3 * Di_C3H8O3  + 1 * EX_CH4   - 1 * Di_CH4 + 0 * EX_H2   - 0 *
Di_H2 + 1 * EX_CO   - 1 * Di_CO + 0 * EX_H2O - 0 * DI_H2O - 1 * D_CO2 = 0;
AH_NET + 8 * EX_C3H8O3  - 8 * Di_C3H8O3  + 4 * EX_CH4   - 4 * Di_CH4 + 2 * EX_H2   - 2 *
Di_H2 + 0 * EX_CO   - 0 * Di_CO + 2 * EX_H2O - 2 * DI_H2O - 0 * D_CO2 = 0;
AO_NET + 3 * EX_C3H8O3  - 3 * Di_C3H8O3  + 0 * EX_CH4   - 0 * Di_CH4 + 0 * EX_H2   - 0 *
Di_H2 + 1 * EX_CO   - 1 * Di_CO + 1 * EX_H2O - 1 * DI_H2O - 2 * D_CO2 = 0;

!maximum allowable purchased and discharged chemical species if need;
!DI_H2O < 5000 ;
!D_CO2 < 13000;
!EX_C3H8O3 < 15000;
!EX_CH4 < 15000;
!EX_H2 < 15000;
!EX_CO < 15000;

@FREE(AC_NET);
@FREE(AH_NET);
@FREE(AO_NET);
```

```
@FREE(EX_C3H8O3);
@FREE(EX_CH4);
@FREE(EX_H2O);
@FREE(D_CO2);
@FREE(EX_H2);
@FREE(EX_CO);



!Overall mass balanced equation (kmole/hr);

IN_C3H8O3  = (IS_C3H8O3 + EX_C3H8O3 ) ;
Out_C3H8O3 = (DI_C3H8O3) ;

IN_CH4     = (IS_CH4 + EX_CH4 );
Out_CH4    = (DI_Ch4);

IN_H2      = (IS_H2 + EX_H2 );
Out_H2     = (DI_h2);

IN_CO      = (IS_CO + EX_CO ) ;
Out_CO     = (DI_Co);

D_CO2 >  0;
EX_H2O > 0;
DI_H2O > 0;

EX_C3H8O3 > 0;
DI_C3H8O3 > 0;

EX_CO > 0;
DI_CO > 0;

EX_H2 > 0;
DI_H2 > 0;

EX_CH4 > 0;
DI_CH4 > 0;

(IN_C3H8O3 - Out_C3H8O3 ) + (IN_CH4 - Out_CH4) + (IS_CO2 - D_CO2) + (IN_H2 - Out_H2 - H2
_DEMAND) + (IN_CO - Out_CO) + (EX_H2O - DI_H2O) = CH3OH_DEMAND + C3H8O2_DEMAND +
C3H4O_DEMAND;

OVR_C3H8O3        = (IN_C3H8O3 - Out_C3H8O3)     ;
OVR CO            = (IN CO - Out CO)             ;
OVR CO2           = (IS CO2    - D CO2)          ;
OVR H2            = (IN H2 - Out H2 - H2 DEMAND);
OVR_CH4           = (IN_CH4 - Out_CH4)           ;
OVR H2O           = (EX H2O - DI H2O)            ;
!OVR C3H8O2  = (C3H8O2 DEMAND)                                    ;
!OVR_C3H40   = C3H4O_DEMAND                                       ;

@FREE(OVR_C3H8O3);
@FREE(OVR_CO);
@FREE(OVR_CO2);
@FREE(OVR_H2);
@FREE(OVR_CH4);
@FREE(OVR_H2O);
@FREE(CH3OH_DEMAND);
@FREE(H2_DEMAND);
@FREE(OVR_C3H8O2);
@FREE(C3H8O2_DEMAND);




! Calculation of reaction flowrates
```

```
! X_old STANDS FOR theoretical STOICHMETRIC COFFICIENT FOR A SET OF EQUATIONS DETERMINED
BY THE CHOSYN AND the PARTICIPATING plants;

(x5_old   + x8_old   + x9_old  )                                                    =
OVR_C3H8O3 ;
(x1_old   - x3_old   + x6_old   - x7_old  )                                         =
OVR_CO ;
(x2_old   - x4_old   - 3*x5_old - x6_old   + x7_old  )                              =
OVR_CO2;
(2*x1_old + 3*x2_old - 3*x3_old - 4*x4_old - 7*x5_old - x6_old   + x7_old + x8_old ) =
OVR_H2;
(-1*x2_old+ x3_old   + 2*x4_old + 3*x5_old + x6_old   - x7_old  - x8_old - 2*x9_old) =
OVR_H2O;
(x3_old   + x4_old          )                                                       =
OVR_CH4;
(x1_old   + x2_old        )                                                         =
CH3OH_DEMAND;
(x8_old            )                                                              =
C3H8O2_DEMAND;
(x9_old           )                                                                =
C3H4O_DEMAND;

!reaction conversion calculations, all reactions are assumed having 80% conversion rate;
!Equations (18);

X1 = 1.2*X1_old;
X2 = 1.2*X2_old;
X3 = 1.2*X3_old;
X4 = 1.2*X4_old;
X5 = 1.2*X5_old;
X6 = 1.2*X6_old;
X7 = 1.2*X7_old;
X8 = 1.2*X8_old;
X9 = 1.2*X9_old;

H2_x1 = 2* X1 ;
H2_X2 = 3* X2 ;
H2_x7 =    X7 ;
H2_x8 =    X8 ;
CO_x1 =    X1 ;
CO_x6  =   X6  ;
CH4_x3  =   X3  ;
CH4_x4  =   X4  ;
C3H8O3_x5 =X5 ;
C3H8O3_x8 =X8 ;
C3H8O3_x9 =X9 ;

!Since the conversion is not 100%, the extra discharged chemical species mass balance are
shown here;
Extra_H2     =  H2_x1     + H2_X2     + H2_x7     + H2_x8 - 2*x1_old - 3*x2_old - x7_old -
x8_old ;
Extra_CO     =  CO_x1     + CO_x6     - x1_old    - x6_old
;
Extra_CH4    =  CH4_x3    + CH4_x4    - x3_old    - x4_old
;
Extra_C3H8O3 =  C3H8O3_x5 + C3H8O3_x8 + C3H8O3_x9 - x5_old - x8_old   - x9_old
;



x1>0;
x2>0;
x3>0;
x4>0;
x5>0;
```

```
x6>0;
x7 > 0;
x6 + x7 < 1;
x8>0;
x9>0;

x1_old>0;
x2_old>0;
x3_old>0;
x4_old>0;
x5_old>0;
x6_old>0;
x7_old > 0;
x6_old + x7_old < 1;
x8_old>0;
x9_old>0;

!Economics calculations ;
!raw materials and sales calculations ($/hr) ;
!each species flowrate is multiplied first by molecular weight to convert to KG/hr, then
multiplied by the price in $/kg;
COST_C3H8O3       = (EX_C3H8O3 + Extra_C3H8O3) * 92 * 1.09 ;
COST_CH4          = (EX_CH4 + Extra_CH4)     * 16 * 7.25 ;
COST_H2           = (EX_H2 + Extra_H2)      * 1  * 3      ;
COST_CO           = (EX_CO + Extra_CO  )      * 28 * 0.18    ;

PROFIT_CH3OH      = CH3OH_DEMAND  * 32 * 1.5 ;
PROFIT_C3H8O2     = C3H8O2_DEMAND * 76  * 5 ;
PROFIT_C3H4O      = C3H4O_DEMAND  * 56  * 3 ;

!production costs ($/hr);
!the number of moles of each species is multiplied by flowrate and then multiplied by
molecular weight to convert to KG/hr, then multiplied by the price in $/kg;
! production costs 6/7 are assumed small numbers because they are water-gas shift
reactions, which occur as side reactions;
!Equation (21);

Production_cost_1 = 1 * 32 * 0.61 * x1  ;
Production_cost_2 = 1 * 32 * 1.01 * x2  ;
Production_cost_3 = 3 * 1  * 0.66 * x3  ;
Production_cost_4 = 4 * 1  * 0.66 * x4  ;
Production_cost_5 = 7 * 1  * 2.6  * x5  ;
Production_cost_6 = 0.1           * x6  ;
Production_cost_7 = 0.1           * x7  ;
Production_cost_8 = 1 * 76 * 0.85 * x8  ;
Production_cost_9 = 1 * 56 * 0.42 * x9  ;
Total_production_cost = Production_cost_1 + Production_cost_2 + Production_cost_3 +
Production_cost_4 + Production_cost_5 + Production_cost_6 + Production_cost_7 +
Production_cost_8+Production_cost_9;

!Capital costs ;
!the number of moles of each species is multiplied by flowrate and then multiplied by
molecular weight to convert to KG/hr, then multiplied by the price in $/kg;
!Equation (22) and (24) + factorial method;

EQUIP_cost_1 = (0.31 * (x1)  * 1 * 32) ;
EQUIP_cost_2 = (0.49  * (x2) * 1 * 32) ;
EQUIP_cost_3 = (0.29 * (x3)  * 3 * 1)  ;
EQUIP_cost_4 = (0.29 * (x4)  * 4 * 1)  ;
EQUIP_cost_5 = (0.66 * (x5)  * 7 * 1)  ;
EQUIP_cost_6 = (0.1  * (x6))           ;
EQUIP_cost_7  =  (0.1   *  (x7)  )     ;
EQUIP_cost_8 = (0.28 * (x8) * 1 * 76)  ;
EQUIP_cost_9 = (0.21 * (x9) * 1 * 56)  ;

PPC_1 = 3.47*EQUIP_cost_1;
```

```
IPC_1 = 0.45* PPC_1;
Fixed_cost_1 = PPC_1+IPC_1;
Capital_cost_1 = Fixed_cost_1*1.18;

PPC_2 = 3.47*EQUIP_cost_2;
IPC_2 = 0.45* PPC_2;
Fixed_cost_2 = PPC_2+IPC_2;
Capital_cost_2 = Fixed_cost_2*1.18;

PPC_3          = 3.47*       EQUIP_cost_3;
IPC 3          = 0.45*              PPC 3;
Fixed cost 3   =        PPC 3+      IPC 3;
Capital_cost_3 = Fixed_cost_3*1.18;

PPC_4          = 3.47*       EQUIP_cost_4;
IPC 4          = 0.45*              PPC 4;
Fixed cost 4   =        PPC 4+      IPC 4;
Capital_cost_4 = Fixed_cost_4*1.18;

PPC_5          = 3.47*       EQUIP_cost_5;
IPC_5          = 0.45*              PPC_5;
Fixed cost 5   =        PPC 5+      IPC 5;
Capital_cost_5 = Fixed_cost_5*1.18;

PPC_6          = 3.47*       EQUIP_cost_6;
IPC 6          = 0.45*              PPC 6;
Fixed cost 6   =        PPC 6+      IPC 6;
Capital_cost_6 = Fixed_cost_6*1.18;

PPC_7          = 3.47*       EQUIP_cost_7;
IPC 7          = 0.45*              PPC 7;
Fixed cost 7   =        PPC 7+      IPC 7;
Capital_cost_7 = Fixed_cost_7*1.18;


PPC_8          = 3.47*       EQUIP_cost_8;
IPC 8          = 0.45*              PPC 8;
Fixed cost 8   =        PPC 8+      IPC 8;
Capital_cost_8 = Fixed_cost_8*1.18;

PPC_9          = 3.47*       EQUIP_cost_9;
IPC 9          = 0.45*              PPC 9;
Fixed cost 9   =        PPC 9+      IPC 9;
Capital_cost_9 = Fixed_cost_9*1.18;

capital_cost = Capital_cost_1 + Capital_cost_2 + Capital_cost_3 + Capital_cost_4 +
Capital_cost_5 + Capital_cost_6 + Capital_cost_7 + Capital_cost_8 + Capital_cost_9 ;


!annualized fixed costs and annual sales calculations;
!Equations (25-26);

AFC          = 0.1 * capital_cost  ;
sales = ((PROFIT_CH3OH + PROFIT_C3H8O2 + PROFIT_C3H4O - COST_C3H8O3 - COST_CH4 - COST_H2 -
COST_CO -(Total_production_cost+AFC))*(1-0.25)) + AFC ;
Annual_sales_final = sales * 300 * 24 ;
Total_Capital_cost_final = Capital_cost * 24 * 300;
ROI > 10;


!metrics calculation;
!Equations (27, 34-35);
ROI          = ( Annual_sales_final/ Total_Capital_cost_final) * 100  ;
```

Appendix 1(b): LINGO mathematical modeling codes for case 2

```
!objective function ;
!Maximum annual sales);


max = sales;

!Atomic Targeting
!IS STANDS FOR INTERNAL SOURCES INSIDE EIP (kmole/hr);
!Calculation of number of CHO atoms in internal streams;

IS_CO       = 930;
IS_CO2      = 3990;
IS_H2       = 9965;
IS_CH4      = 39;
IS_C3H8O3   = 1000;

AC_SRC  = IS_CO * 1 + IS_CO2 * 1 + IS_CH4 * 1 + IS_C3H8O3 * 3;
AH_SRC      =              IS_H2 * 2 + IS_CH4 * 4 + IS_C3H8O3 * 8;
AO_SRC      = IS_CO * 1 + IS_CO2 * 2              + IS_C3H8O3 * 3;

!Atomic Targeting
!DMD STANDS FOR DEMAND BY FACTORIES (kmole/hr);
! Calculation of number of CHO atoms in demand streams;

CH3OH_DEMAND      = 7500;
H2_Demand         = 5000;
C3H8O2_DEMAND     = 1000;
C3H4O_DEMAND      = 1000;


AC_DMD      = CH3OH_DEMAND * 1                  + 3 * C3H8O2_DEMAND  + 3 * C3H4O_DEMAND ;
AH_DMD  = CH3OH_DEMAND * 4 + 2 * H2_DEMAND + 8 * C3H8O2_DEMAND  + 4 * C3H4O_DEMAND ;
AO_DMD      = CH3OH_DEMAND * 1                  + 2 * C3H8O2_DEMAND  + 1 * C3H4O_DEMAND ;

!Atomic Targeting
!NET STANDS FOR NET RESULT BETWEEN INTERNAL AND DEMAND streams (kmole/hr);

AC_NET      = AC_SRC - AC_DMD;
AH_NET      = AH_SRC - AH_DMD;
AO_NET      = AO_SRC - AO_DMD;

!Atomic Targeting - overall atomic balanced equation;
!calculation of external, recycled, discharged species in the CHOSYN (kmole/hr);
!Equations (10-12);


AC_NET + 3 * EX_C3H8O3 + 3 * RE_C3H8O3 - 3 * Di_C3H8O3  + 1 * EX_CH4 + 1 * RE_CH4  - 1 *
Di_CH4 + 0 * EX_H2 + 0 * RE_H2  - 0 * Di_H2 + 1 * EX_CO + 1 * RE_CO  - 1 * Di_CO + 0 *
EX_H2O - 0 * DI_H2O - 1 * D_CO2 = 0;
AH_NET + 8 * EX_C3H8O3 + 3 * RE_C3H8O3 - 8 * Di_C3H8O3  + 4 * EX_CH4 + 1 * RE_CH4  - 4 *
Di_CH4 + 2 * EX_H2 + 0 * RE_H2  - 2 * Di_H2 + 0 * EX_CO + 0 * RE_CO  - 0 * Di_CO + 2 *
EX_H2O - 2 * DI_H2O - 0 * D_CO2 = 0;
AO_NET + 3 * EX_C3H8O3 + 3 * RE_C3H8O3 - 3 * Di_C3H8O3  + 0 * EX_CH4 + 1 * RE_CH4  - 0 *
Di_CH4 + 0 * EX_H2 + 0 * RE_H2  - 0 * Di_H2 + 1 * EX_CO + 1 * RE_CO  - 1 * Di_CO + 1 *
EX_H2O - 1 * DI_H2O - 2 * D_CO2 = 0;

!maximum allowable purchased and discharged chemical species if need;
!Equations (13-14);

!DI_H2O < 5000 ;
!D_CO2 < 13000;
!EX_C3H8O3 < 15000;
!EX_CH4 < 15000;
!EX_H2 < 15000;
!EX_CO < 15000;
```

```
@FREE(AC_NET);
@FREE(AH_NET);
@FREE(AO_NET);
@FREE(EX_C3H8O3);
@FREE(EX_CH4);
@FREE(EX_H2O);
@FREE(D_CO2);
@FREE(EX_H2);
@FREE(EX_CO);

!total discharged species can be divided to recycled species and final discharged species;

Discharge_C3H8O3 = RE_C3H8O3 + DI_C3H8O3 ;
Discharge_Ch4 = RE_Ch4 + DI_Ch4 ;
Discharge_Co = RE_Co + DI_Co ;
Discharge_h2 = RE_h2 + DI_h2 ;

!Overall mass balanced equation (kmole/hr);
!Equation (15);

IN_C3H8O3  = (IS_C3H8O3 + EX_C3H8O3 + RE_C3H8O3) ;
Out_C3H8O3 = (Discharge_C3H8O3) ;

IN_CH4     = (IS_CH4 + EX_CH4 + RE_CH4);
Out_CH4    = (Discharge_Ch4);

IN_H2      = (IS_H2 + EX_H2 + RE_H2);
Out_H2     = (Discharge_h2);

IN_CO      = (IS_CO + EX_CO + RE_CO) ;
Out_CO     = (Discharge_Co);

D_CO2 >  0;
EX_H2O > 0;
DI_H2O > 0;

RE_C3H8O3 > 0;
EX_C3H8O3 > 0;
DI_C3H8O3 > 0;

RE_CO > 0;
EX_CO > 0;
DI_CO > 0;

RE_H2 > 0;
EX_H2 > 0;
DI_H2 > 0;

RE_CH4 > 0;
EX_CH4 > 0;
DI_CH4 > 0;


(IN_C3H8O3 - Out_C3H8O3 ) + (IN_CH4 - Out_CH4) + (IS_CO2 - D_CO2) + (IN_H2 - Out_H2 - H2
_DEMAND) + (IN_CO - Out_CO) + (EX_H2O - DI_H2O) = CH3OH_DEMAND + C3H8O2_DEMAND +
C3H4O_DEMAND;

OVR_C3H8O3        = (IN_C3H8O3 - Out_C3H8O3)     ;
OVR_CO            = (IN_CO - Out_CO)             ;
OVR CO2           = (IS CO2    - D CO2)          ;
OVR H2            = (IN H2 - Out H2 - H2 DEMAND);
OVR_CH4           = (IN_CH4 - Out_CH4)           ;
OVR_H2O           = (EX_H2O - DI_H2O)            ;
!OVR C3H8O2  = (C3H8O2 DEMAND)                                  ;
!OVR_C3H40   = C3H4O_DEMAND                                     ;
```

```
@FREE(OVR_C3H8O3);
@FREE(OVR_CO);
@FREE(OVR_CO2);
@FREE(OVR_H2);
@FREE(OVR_CH4);
@FREE(OVR_H2O);
@FREE(CH3OH_DEMAND);
@FREE(H2_DEMAND);
@FREE(OVR_C3H8O2);
@FREE(C3H8O2_DEMAND);

! Calculation of reaction flowrates
! X_old STANDS FOR theoretical STOICHMETRIC COFFICIENT FOR A SET OF EQUATIONS DETERMINED
BY THE CHOSYN AND the PARTICIPATING plants;
!Equations (16-17);

(x5_old   + x8_old   + x9_old  )                                                    =
OVR_C3H8O3 ;
(x1_old   - x3_old   + x6_old   - x7_old  )                                         =
OVR_CO ;
(x2_old   - x4_old   - 3*x5_old - x6_old   + x7_old  )                              =
OVR_CO2;
(2*x1_old + 3*x2_old - 3*x3_old - 4*x4_old - 7*x5_old - x6_old   + x7_old + x8_old ) =
OVR_H2;
(-1*x2_old+ x3_old   + 2*x4_old + 3*x5_old + x6_old   - x7_old  - x8_old - 2*x9_old) =
OVR_H2O;
(x3_old   + x4_old          )                                                       =
OVR_CH4;
(x1_old   + x2_old        )                                                         =
CH3OH_DEMAND;
(x8_old             )                                                               =
C3H8O2_DEMAND;
(x9_old           )                                                                 =
C3H4O_DEMAND;

!reaction conversion calculations, all reactions are assumed having 80% conversion rate;
!Equations (18);

X1 = 1.2*X1_old;
X2 = 1.2*X2_old;
X3 = 1.2*X3_old;
X4 = 1.2*X4_old;
X5 = 1.2*X5_old;
X6 = 1.2*X6_old;
X7 = 1.2*X7_old;
X8 = 1.2*X8_old;
X9 = 1.2*X9_old;

H2_x1 = 2* X1 ;
H2_X2 = 3* X2 ;
H2_x7 =    X7 ;
H2_x8 =    X8 ;
CO_x1 =    X1 ;
CO_x6  =   X6  ;
CH4_x3 =   X3  ;
CH4_x4 =   X4  ;
C3H8O3_x5 =X5 ;
C3H8O3_x8 =X8 ;
C3H8O3_x9 =X9 ;

!Recycling mass balance equations;
!Total recycled chemical species ( Unreacted raw materials + By-products) ;
!Equation (19);

REE_H2     =  H2_x1     + H2_X2     + H2_x7     + H2_x8 - 2*x1_old - 3*x2_old - x7_old -
x8 old ;
REE_CO     =  CO_x1     + CO_x6     - x1_old    - x6_old
```

```
;
REE_CH4    =  CH4_x3    + CH4_x4    - x3_old    - x4_old
;
REE_C3H8O3 =  C3H8O3_x5 + C3H8O3_x8 + C3H8O3_x9 - x5_old - x8_old    - x9_old
;
Reycled_H2     = REE_H2 + RE_H2 ;
Reycled_CO     = REE_CO + RE_CO ;
Reycled_CH4    = REE_Ch4 + RE_Ch4 ;
Reycled_C3H8O3 = REE_C3H8O3 + RE_C3H8O3 ;



x1>0;
x2>0;
x3>0;
x4>0;
x5>0;
x6>0;
x7 > 0;
x6 + x7 < 1;
x8>0;
x9>0;

x1_old>0;
x2_old>0;
x3_old>0;
x4_old>0;
x5_old>0;
x6_old>0;
x7_old > 0;
x6_old + x7_old < 1;
x8_old>0;
x9_old>0;

!Economics calculations ;
!raw materials and sales calculations ($/hr) ;
!each species flowrate is multiplied first by molecular weight to convert to KG/hr, then
multiplied by the price in $/kg;
!part of Equation (26);
COST_C3H8O3       = EX_C3H8O3 * 92 * 1.09 ;
COST_CH4          = EX_CH4    * 16 * 7.25 ;
COST_H2           = EX_H2     * 1  * 3      ;
COST_CO           = EX_CO     * 28 * 0.18    ;

PROFIT_CH3OH      = CH3OH_DEMAND  * 32 * 1.5 ;
PROFIT_C3H8O2     = C3H8O2_DEMAND * 76  * 5 ;
PROFIT_C3H4O      = C3H4O_DEMAND  * 56  * 3 ;

!production costs ($/hr);
!the number of moles of each species is multiplied by flowrate and then multiplied by
molecular weight to convert to KG/hr, then multiplied by the price in $/kg;
! production costs 6/7 are assumed small numbers because they are water-gas shift
reactions, which occur as side reactions;
!Equation (21);

Production_cost_1 = 1 * 32 * 0.61 * x1  ;
Production_cost_2 = 1 * 32 * 1.01 * x2  ;
Production_cost_3 = 3 * 1  * 0.66 * x3  ;
Production_cost_4 = 4 * 1  * 0.66 * x4  ;
Production_cost_5 = 7 * 1  * 2.6  * x5  ;
Production_cost_6 = 0.1           * x6  ;
Production_cost_7 = 0.1           * x7  ;
Production_cost_8 = 1 * 76 * 0.85 * x8  ;
Production_cost_9 = 1 * 56 * 0.42 * x9  ;
Total_production_cost = Production_cost_1 + Production_cost_2 + Production_cost_3 +
Production_cost_4 + Production_cost_5 + Production_cost_6 + Production_cost_7 +
Production_cost_8+Production_cost_9;
```

```
!Capital costs ;
!the number of moles of each species is multiplied by flowrate and then multiplied by
molecular weight to convert to KG/hr, then multiplied by the price in $/kg;
!Equation (22) and (24) + factorial method;

EQUIP_cost_1 = (0.31 * (x1)  * 1 * 32) ;
EQUIP_cost_2 = (0.49  * (x2) * 1 * 32) ;
EQUIP_cost_3 = (0.29 * (x3)  * 3 * 1)  ;
EQUIP_cost_4 = (0.29 * (x4)  * 4 * 1)  ;
EQUIP_cost_5 = (0.66 * (x5)  * 7 * 1)  ;
EQUIP_cost_6 = (0.1  * (x6))           ;
EQUIP_cost_7  =  (0.1   *  (x7)  )     ;
EQUIP_cost_8 = (0.28 * (x8) * 1 * 76)  ;
EQUIP_cost_9 = (0.21 * (x9) * 1 * 56)  ;

PPC_1 = 3.47*EQUIP_cost_1;
IPC_1 = 0.45* PPC_1;
Fixed_cost_1 = PPC_1+IPC_1;
Capital_cost_1 = Fixed_cost_1*1.18;

PPC_2 = 3.47*EQUIP_cost_2;
IPC_2 = 0.45* PPC_2;
Fixed_cost_2 = PPC_2+IPC_2;
Capital_cost_2 = Fixed_cost_2*1.18;

PPC_3          = 3.47*       EQUIP_cost_3;
IPC 3          = 0.45*              PPC 3;
Fixed cost 3   =        PPC 3+      IPC 3;
Capital_cost_3 = Fixed_cost_3*1.18;

PPC_4          = 3.47*       EQUIP_cost_4;
IPC_4          = 0.45*              PPC_4;
Fixed cost 4   =        PPC 4+      IPC 4;
Capital_cost_4 = Fixed_cost_4*1.18;

PPC_5          = 3.47*       EQUIP_cost_5;
IPC_5          = 0.45*              PPC_5;
Fixed cost 5   =        PPC 5+      IPC 5;
Capital_cost_5 = Fixed_cost_5*1.18;

PPC_6          = 3.47*       EQUIP_cost_6;
IPC 6          = 0.45*              PPC 6;
Fixed cost 6   =        PPC 6+      IPC 6;
Capital_cost_6 = Fixed_cost_6*1.18;

PPC_7          = 3.47*       EQUIP_cost_7;
IPC 7          = 0.45*              PPC 7;
Fixed cost 7   =        PPC 7+      IPC 7;
Capital_cost_7 = Fixed_cost_7*1.18;


PPC_8          = 3.47*       EQUIP_cost_8;
IPC 8          = 0.45*              PPC 8;
Fixed cost 8   =        PPC 8+      IPC 8;
Capital_cost_8 = Fixed_cost_8*1.18;

PPC_9          = 3.47*       EQUIP_cost_9;
IPC 9          = 0.45*              PPC 9;
Fixed cost 9   =        PPC 9+      IPC 9;
Capital_cost_9 = Fixed_cost_9*1.18;

capital_cost = Capital_cost_1 + Capital_cost_2 + Capital_cost_3 + Capital_cost_4 +
Capital_cost_5 + Capital_cost_6 + Capital_cost_7 + Capital_cost_8 + Capital_cost_9 ;


!annualized fixed costs and annual sales calculations;
```

```
!Annual sales/capital cost calculations;

AFC          = 0.1 * capital_cost  ;
sales = ((PROFIT_CH3OH + PROFIT_C3H8O2 + PROFIT_C3H40 - COST_C3H8O3 - COST_CH4 - COST_H2 -
COST_CO -(Total_production_cost+AFC))*(1-0.25)) + AFC ;
Annual_sales_final = sales * 300 * 24 ;
Total_Capital_cost_final = Capital_cost * 24 * 300;
ROI > 10;


!metrics calculation;
!Equations (27, 34-35);
ROI          = ( Annual_sales_final/ Total_Capital_cost_final) * 100 ;
```

Appendix 1(c): LINGO mathematical modeling codes for case 2 – scenario one

```
!objective function   ;
!maximum annual sales;

max = sales;

!Atomic Targeting
!IS STANDS FOR INTERNAL SOURCES INSIDE EIP (kmole/hr);
! Calculation of number of CHO atoms in internal streams;

IS_CO       = 930;
IS_CO2      = 3990;
IS_H2       = 9965;
IS_CH4      = 39;
IS_C3H8O3   = 1000;

AC_SRC  = IS_CO * 1 + IS_CO2 * 1 + IS_CH4 * 1 + IS_C3H8O3 * 3;
AH_SRC      =             IS_H2 * 2 + IS_CH4 * 4 + IS_C3H8O3 * 8;
AO_SRC      = IS_CO * 1 + IS_CO2 * 2             + IS_C3H8O3 * 3;

!Atomic Targeting
!DMD STANDS FOR DEMAND BY FACTORIES (kmole/hr);
! Calculation of number of CHO atoms in demand streams;

CH3OH_DEMAND      = 7500;
H2_Demand         = 5000;
C3H8O2_DEMAND     = 1000;
C3H4O_DEMAND      = 1000;


AC_DMD      = CH3OH_DEMAND * 1                 + 3 * C3H8O2_DEMAND  + 3 * C3H4O_DEMAND ;
AH_DMD  = CH3OH_DEMAND * 4 + 2 * H2_DEMAND + 8 * C3H8O2_DEMAND  + 4 * C3H4O_DEMAND ;
AO_DMD      = CH3OH_DEMAND * 1                 + 2 * C3H8O2_DEMAND  + 1 * C3H4O_DEMAND ;

!Atomic Targeting
!NET STANDS FOR NET RESULT BETWEEN INTERNAL AND DEMAND streams(kmole/hr);
!Equations (7-9);

AC_NET      = AC_SRC - AC_DMD;
AH_NET      = AH_SRC - AH_DMD;
AO_NET      = AO_SRC - AO_DMD;

!Atomic Targeting - overall atomic balanced equation;
!calculation of external, recycled, discharged species in the CHOSYN (kmole/hr);
!Equations (10-12);


AC_NET + 3 * EX_C3H8O3 + 3 * RE_C3H8O3 - 3 * Di_C3H8O3  + 1 * EX_CH4 + 1 * RE_CH4  - 1 *
Di_CH4 + 0 * EX_H2 + 0 * RE_H2  - 0 * Di_H2 + 1 * EX_CO + 1 * RE_CO  - 1 * Di_CO + 0 *
EX_H2O - 0 * DI_H2O - 1 * D_CO2 = 0;
AH_NET + 8 * EX_C3H8O3 + 3 * RE_C3H8O3 - 8 * Di_C3H8O3  + 4 * EX_CH4 + 1 * RE_CH4  - 4 *
Di_CH4 + 2 * EX_H2 + 0 * RE_H2  - 2 * Di_H2 + 0 * EX_CO + 0 * RE_CO  - 0 * Di_CO + 2 *
EX_H2O - 2 * DI_H2O - 0 * D_CO2 = 0;
AO_NET + 3 * EX_C3H8O3 + 3 * RE_C3H8O3 - 3 * Di_C3H8O3  + 0 * EX_CH4 + 1 * RE_CH4  - 0 *
Di_CH4 + 0 * EX_H2 + 0 * RE_H2  - 0 * Di_H2 + 1 * EX_CO + 1 * RE_CO  - 1 * Di_CO + 1 *
EX_H2O - 1 * DI_H2O - 2 * D_CO2 = 0;
!maximum allowable purchased and discharged chemical species if need;
!Equations (13-14);
!DI_H2O < 5000 ;
!D_CO2 < 13000;
!EX_C3H8O3 < 15000;
!EX_CH4 < 15000;
!EX_H2 < 15000;
!EX_CO < 15000;

@FREE(AC_NET);
```

```
@FREE(AH_NET);
@FREE(AO_NET);
@FREE(EX_C3H8O3);
@FREE(EX_CH4);
@FREE(EX_H2O);
@FREE(D_CO2);
@FREE(EX_H2);
@FREE(EX_CO);

!total discharged species can be divided to recycled species and final discharged species;

Discharge_C3H8O3 = RE_C3H8O3 + DI_C3H8O3 ;
Discharge_Ch4 = RE_Ch4 + DI_Ch4 ;
Discharge_Co = RE_Co + DI_Co ;
Discharge_h2 = RE_h2 + DI_h2 ;

!Overall mass balanced equation (kmole/hr);
!Equation (15);

IN_C3H8O3  = (IS_C3H8O3 + EX_C3H8O3 + RE_C3H8O3) ;
Out_C3H8O3 = (Discharge_C3H8O3) ;

IN_CH4     = (IS_CH4 + EX_CH4 + RE_CH4);
Out_CH4    = (Discharge_Ch4);

IN_H2      = (IS_H2 + EX_H2 + RE_H2);
Out_H2     = (Discharge_h2);

IN_CO      = (IS_CO + EX_CO + RE_CO) ;
Out_CO     = (Discharge_Co);

D_CO2 >  0;
EX_H2O > 0;
DI_H2O > 0;

RE_C3H8O3 > 0;
EX_C3H8O3 > 0;
DI_C3H8O3 > 0;

RE_CO > 0;
EX_CO > 0;
DI_CO > 0;

RE_H2 > 0;
EX_H2 > 0;
DI_H2 > 0;

RE_CH4 > 0;
EX_CH4 > 0;
DI_CH4 > 0;


(IN_C3H8O3 - Out_C3H8O3 ) + (IN_CH4 - Out_CH4) + (IS_CO2 - D_CO2) + (IN_H2 - Out_H2 - H2
_DEMAND) + (IN_CO - Out_CO) + (EX_H2O - DI_H2O) = CH3OH_DEMAND + C3H8O2_DEMAND +
C3H4O_DEMAND;

OVR_C3H8O3        = (IN_C3H8O3 - Out_C3H8O3)     ;
OVR_CO            = (IN_CO - Out_CO)             ;
OVR_CO2           = (IS_CO2    - D_CO2)          ;
OVR_H2            = (IN_H2 - Out_H2 - H2_DEMAND);
OVR_CH4           = (IN_CH4 - Out_CH4)           ;
OVR_H2O           = (EX_H2O - DI_H2O)            ;
!OVR_C3H8O2   = (C3H8O2_DEMAND)                                    ;
!OVR_C3H4O    = C3H4O_DEMAND                                       ;


@FREE(OVR_C3H8O3);
```

```
@FREE(OVR_CO);
@FREE(OVR_CO2);
@FREE(OVR_H2);
@FREE(OVR_CH4);
@FREE(OVR_H2O);
@FREE(CH3OH_DEMAND);
@FREE(H2_DEMAND);
@FREE(OVR_C3H8O2);
@FREE(C3H8O2_DEMAND);

! Calculation of reaction flowrates
! X_old STANDS FOR theoretical STOICHMETRIC COFFICIENT FOR A SET OF EQUATIONS DETERMINED
BY THE CHOSYN AND the PARTICIPATING plants;
!Equations (16-17);

(x5_old   + x8_old   + x9_old  )                                                    =
OVR_C3H8O3 ;
(x1_old   - x3_old   + x6_old   - x7_old  )                                         =
OVR_CO ;
(x2_old   - x4_old   - 3*x5_old - x6_old   + x7_old  )                              =
OVR_CO2;
(2*x1_old + 3*x2_old - 3*x3_old - 4*x4_old - 7*x5_old - x6_old   + x7_old + x8_old ) =
OVR_H2;
(-1*x2_old+ x3_old   + 2*x4_old + 3*x5_old + x6_old   - x7_old  - x8_old - 2*x9_old) =
OVR_H2O;
(x3_old   + x4_old          )                                                       =
OVR_CH4;
(x1_old   + x2_old        )                                                         =
CH3OH_DEMAND;
(x8_old             )                                                               =
C3H8O2_DEMAND;
(x9_old           )                                                                 =
C3H4O_DEMAND;

!reaction conversion calculations, all reactions are assumed having 80% conversion rate;
!Equations (18);

X1 = 1.2*X1_old;
X2 = 1.2*X2_old;
X3 = 1.2*X3_old;
X4 = 1.2*X4_old;
X5 = 1.2*X5_old;
X6 = 1.2*X6_old;
X7 = 1.2*X7_old;
X8 = 1.2*X8_old;
X9 = 1.2*X9_old;

H2_x1 = 2* X1 ;
H2_X2 = 3* X2 ;
H2_x7 =    X7 ;
H2_x8 =    X8 ;
CO_x1 =    X1 ;
CO_x6  =   X6  ;
CH4_x3 =   X3  ;
CH4_x4 =   X4  ;
C3H8O3_x5 =X5 ;
C3H8O3_x8 =X8 ;
C3H8O3_x9 =X9 ;

!Recycling mass balance equations;
!Total recycled chemical species ( Unreacted raw materials + By-products) ;
!Equation (19);

REE_H2     =  H2_x1     + H2_X2     + H2_x7     + H2_x8 - 2*x1_old - 3*x2_old - x7_old -
x8 old ;
REE CO     =  CO x1     + CO x6     - x1 old    - x6 old
;
```

```
REE_CH4    =  CH4_x3    + CH4_x4    - x3_old    - x4_old
;
REE_C3H8O3 =  C3H8O3_x5 + C3H8O3_x8 + C3H8O3_x9 - x5_old - x8_old    - x9_old
;
Reycled_H2      = REE_H2 + RE_H2 ;
Reycled_CO      = REE_CO + RE_CO ;
Reycled_CH4     = REE_Ch4 + RE_Ch4 ;
Reycled_C3H8O3 = REE_C3H8O3 + RE_C3H8O3 ;

x1>0;
x2>0;
x3>0;
x4>0;
x5>0;
x6>0;
x7 > 0;
x6 + x7 < 1;
x8>0;
x9>0;

x1_old>0;
x2_old>0;
x3_old>0;
x4_old>0;
x5_old>0;
x6_old>0;
x7_old > 0;
x6_old + x7_old < 1;
x8_old>0;
x9_old>0;

!Economics calculations ;
!raw materials and sales calculations ($/hr) ;
!each species flowrate is multiplied first by molecular weight to convert to KG/hr, then
multiplied by the price in $/kg;
!part of Equation (26);
COST_C3H8O3       = EX_C3H8O3 * 92 * 1.09 ;
COST_CH4          = EX_CH4    * 16 * 7.25 ;
COST_H2           = EX_H2     * 1  * 3      ;
COST_CO           = EX_CO     * 28 * 0.18    ;

PROFIT_CH3OH      = CH3OH_DEMAND  * 32 * 1.5 ;
PROFIT_C3H8O2     = C3H8O2_DEMAND * 76  * 5 ;
PROFIT_C3H4O      = C3H4O_DEMAND  * 56  * 3 ;

!production costs ($/hr);
!the number of moles of each species is multiplied by flowrate and then multiplied by
molecular weight to convert to KG/hr, then multiplied by the price in $/kg;
! production costs 6/7 are assumed small numbers because they are water-gas shift
reactions, which occur as side reactions;
!Equation (21);

Production_cost_1 = 1 * 32 * 0.61 * x1  ;
Production_cost_2 = 1 * 32 * 1.01 * x2  ;
Production_cost_3 = 3 * 1  * 0.66 * x3  ;
Production_cost_4 = 4 * 1  * 0.66 * x4  ;
Production_cost_5 = 7 * 1  * 2.6  * x5  ;
Production_cost_6 = 0.1           * x6  ;
Production_cost_7 = 0.1           * x7  ;
Production_cost_8 = 1 * 76 * 0.85 * x8  ;
Production_cost_9 = 1 * 56 * 0.42 * x9  ;
Total_production_cost = Production_cost_1 + Production_cost_2 + Production_cost_3 +
Production_cost_4 + Production_cost_5 + Production_cost_6 + Production_cost_7 +
Production_cost_8+Production_cost_9;

!Capital costs ;
!the number of moles of each species is multiplied by flowrate and then multiplied by
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molecular weight to convert to KG/hr, then multiplied by the price in $/kg;
!Equation (22) and (24) + factorial method;

EQUIP_cost_1 = (0.31 * (x1)  * 1 * 32) ;
EQUIP_cost_2 = (0.49  * (x2) * 1 * 32) ;
EQUIP_cost_3 = (0.29 * (x3)  * 3 * 1)  ;
EQUIP_cost_4 = (0.29 * (x4)  * 4 * 1)  ;
EQUIP_cost_5 = (0.66 * (x5)  * 7 * 1)  ;
EQUIP_cost_6 = (0.1  * (x6))           ;
EQUIP_cost_7  =  (0.1   *  (x7)  )     ;
EQUIP_cost_8 = (0.28 * (x8) * 1 * 76)  ;
EQUIP_cost_9 = (0.21 * (x9) * 1 * 56)  ;

PPC_1 = 3.47*EQUIP_cost_1;
IPC_1 = 0.45* PPC_1;
Fixed_cost_1 = PPC_1+IPC_1;
Capital_cost_1 = Fixed_cost_1*1.18;

PPC_2 = 3.47*EQUIP_cost_2;
IPC_2 = 0.45* PPC_2;
Fixed_cost_2 = PPC_2+IPC_2;
Capital_cost_2 = Fixed_cost_2*1.18;

PPC_3          = 3.47*       EQUIP_cost_3;
IPC 3          = 0.45*              PPC 3;
Fixed cost 3   =        PPC 3+      IPC 3;
Capital_cost_3 = Fixed_cost_3*1.18;

PPC_4          = 3.47*       EQUIP_cost_4;
IPC_4          = 0.45*              PPC_4;
Fixed cost 4   =        PPC 4+      IPC 4;
Capital_cost_4 = Fixed_cost_4*1.18;

PPC_5          = 3.47*       EQUIP_cost_5;
IPC 5          = 0.45*              PPC 5;
Fixed cost 5   =        PPC 5+      IPC 5;
Capital_cost_5 = Fixed_cost_5*1.18;

PPC_6          = 3.47*       EQUIP_cost_6;
IPC 6          = 0.45*              PPC 6;
Fixed cost 6   =        PPC 6+      IPC 6;
Capital_cost_6 = Fixed_cost_6*1.18;

PPC_7          = 3.47*       EQUIP_cost_7;
IPC_7          = 0.45*              PPC_7;
Fixed cost 7   =        PPC 7+      IPC 7;
Capital_cost_7 = Fixed_cost_7*1.18;


PPC_8          = 3.47*       EQUIP_cost_8;
IPC 8          = 0.45*              PPC 8;
Fixed cost 8   =        PPC 8+      IPC 8;
Capital_cost_8 = Fixed_cost_8*1.18;

PPC_9          = 3.47*       EQUIP_cost_9;
IPC_9          = 0.45*              PPC_9;
Fixed cost 9   =        PPC 9+      IPC 9;
Capital_cost_9 = Fixed_cost_9*1.18;

capital_cost = Capital_cost_1 + Capital_cost_2 + Capital_cost_3 + Capital_cost_4 +
Capital_cost_5 + Capital_cost_6 + Capital_cost_7 + Capital_cost_8 + Capital_cost_9 ;


!annualized fixed costs and annual sales calculations;
!Equations (25-26);

AFC          = 0.1 * capital_cost  ;
```

```
sales = ((PROFIT_CH3OH + PROFIT_C3H8O2 + PROFIT_C3H40 - COST_C3H8O3 - COST_CH4 - COST_H2 -
COST_CO -(Total_production_cost+AFC))*(1-0.25)) + AFC ;
Annual_sales_final = sales * 300 * 24 ;
Total_Capital_cost_final = Capital_cost * 24 * 300;
ROI > 10;

!binary equations;
!Equation (22-23);
(x1) >= 1*I1;
(x1) <= 100000*(I1);
(x2) >= 1*I2;
(x2) <= 100000*(I2);
(x3) >= 1*I3;
(x3) <= 100000*(I3);
(x4)>= 1*I4;
(x4)<= 100000*(I4);
(x5)>= 1*I5;
(x5)<= 100000*(I5);
(x6)>= 1*I6;
(x6)<= 100000*(I6);
(x7)>= 1*I7;
(x7)<= 100000*(I7);
(x8)>= 1*I8;
(x8)<= 100000*(I8);
(x9)>= 1*I9;
(x9)<= 100000*(I9);
!I1+I2+I3+I4+I5+I6+I7+I8+I9 = 5;


@BIN(I1);
@BIN(I2);
@BIN(I3);
@BIN(I4);
@BIN(I5);
@BIN(I6);
@BIN(I7);
@BIN(I8);
@BIN(I9);

! SAFETY pressure calculations;
!Equation (31);

P1 = 98.5*I1;
P2 = 75*I2;
P3 = 30*I3;
P4 = 30*I4;
P5 = 2*I5;
P6 = 1*I6;
P7 = 1 * I7;
P8 = 19.7*I8;
P9 = 0.98*I9;
Sum_pressure = (P1)+(P2)+(P3)+(P4)+(P5)+ P6 +(P7)+(P8)+(P9);
P1_new_normalized = P1/Sum_pressure;
P2_new_normalized = P2/Sum_pressure;
P3_new_normalized = P3/Sum_pressure;
P4_new_normalized = P4/Sum_pressure;
P5_new_normalized = P5/Sum_pressure;
P6_new_normalized = P6/Sum_pressure;
P7_new_normalized = P7/Sum_pressure;
P8_new_normalized = P8/Sum_pressure;
P9_new_normalized = P9/Sum_pressure;

! SAFETY Temperture calculations;
!Equation (32);

T1 = 573*I1;
T2 = 483*I2;
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T3 = 1152*I3;
T4 = 1152*I4;
T5 = 900*I5;
T6 = 100*I6;
T7 = 100*I7;
T8 = 478*I8;
T9 = 683.15*I9;
Sum_tempruture = (T1)+(T2)+(T3)+(T4)+(T5)+(T6) + T7 +(T8)+(T9);
T1_new_normalized = T1/Sum_tempruture;
T2_new_normalized = T2/Sum_tempruture;
T3_new_normalized = T3/Sum_tempruture;
T4_new_normalized = T4/Sum_tempruture;
T5_new_normalized = T5/Sum_tempruture;
T6_new_normalized = T6/Sum_tempruture;
T7_new_normalized = T7/Sum_tempruture;
T8_new_normalized = T8/Sum_tempruture;
T9_new_normalized = T9/Sum_tempruture;

! Heating value calculations;
!Equation (30);

AVERAGE_HEATING_VALUE_REACTION_1 = I1*((283   *x1)       + (x1*282.8)   + (x1*723.2))/3;
AVERAGE_HEATING_VALUE_REACTION_2 = I2*((424.5*x2)       + (x2*723.2))/4;
AVERAGE_HEATING_VALUE_REACTION_3 = I3*((880   *x3)       + (x3*282.8)   + (x3*424.5))/4;
AVERAGE_HEATING_VALUE_REACTION_4 = I4*((880   *x4)       + (x4*566))/4;
AVERAGE_HEATING_VALUE_REACTION_5 = I5*((990.5*x5)       + (x5*1652.32))/4;
AVERAGE_HEATING_VALUE_REACTION_6 = I6*((141.5*x6)       + (x6*282.8))/4;
AVERAGE_HEATING_VALUE_REACTION_7 = I7*((141.5*x7)       + (x7*282.8))/4;
AVERAGE_HEATING_VALUE_REACTION_8 = I8*((141.5*x8) + (x8*1824)         + (x8*1652.32))/4;
AVERAGE_HEATING_VALUE_REACTION_9 = I9*((1624   *x9) + (x9*1652.32))/3;
SUM_AVERAGE_HEATING_VALUE = AVERAGE_HEATING_VALUE_REACTION_1 +
AVERAGE_HEATING_VALUE_REACTION_2 + AVERAGE_HEATING_VALUE_REACTION_3 +
AVERAGE_HEATING_VALUE_REACTION_4 + AVERAGE_HEATING_VALUE_REACTION_5 +
AVERAGE_HEATING_VALUE_REACTION_6 + AVERAGE_HEATING_VALUE_REACTION_7 +
AVERAGE_HEATING_VALUE_REACTION_8 + AVERAGE_HEATING_VALUE_REACTION_9 ;
HEATING_VALUE_1_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_1/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_2_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_2/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_3_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_3/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_4_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_4/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_5_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_5/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_6_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_6/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_7_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_7/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_8_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_8/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_9_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_9/SUM_AVERAGE_HEATING_VALUE;


!DENSITY OF MIXTURE Calculations;
!Equation (29);

DENSITY_MIXTURE_REACTION_1 = I1*1/(0.001 + ((2*x1*H2_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_1*H2_DENSITY))+ (x1*CO_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_1
*CO_DENSITY))+(x1*CH3OH_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_1*CH3OH_DENSITY))));
DENSITY_MIXTURE_REACTION_2 = I2*1/(0.001 +((3*x2*H2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_
2*H2_DENSITY)) + (x2*CO2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_2*CO2_DENSITY)) + (x2
*CH3OH_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_2*CH3OH_DENSITY)) + (x2*H2O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_2*H2O_DENSITY))));
DENSITY_MIXTURE_REACTION_3 = I3*1/(0.001 +((x3*CH4_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_3
*CH4_DENSITY)) + (x3*CO_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_3*CO_DENSITY) ) + (3*x3*H2
_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_3*H2_DENSITY)) + (x3*H2O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_3*H2O_DENSITY))));
DENSITY_MIXTURE_REACTION_4 = I4*1/(0.001 +((x4*CH4_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_4
*CH4_DENSITY)) + (x4*CO2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_4*CO2_DENSITY) ) + (4*x4*H2
_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_4*H2_DENSITY)) + (2*x4*H2O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_4*H2O_DENSITY))));
DENSITY_MIXTURE_REACTION_5 = I5*1/(0.001 +((7*x5*H2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_
5*H2_DENSITY)) + (3*x5*CO2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_5*CO2_DENSITY) ) + (x5
*C3H8O3_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_5*C3H8O3_DENSITY)) + (3*x5
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*H2O_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_5*H2O_DENSITY))));
DENSITY_MIXTURE_REACTION_6 = I6*1/(0.001 +((x6*H2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_6
*H2_DENSITY)) + (x6*CO2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_6*CO2_DENSITY) ) + (x6
*CO_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_6*CO_DENSITY)) + (x6*H2O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_6*H20_DENSITY))));
DENSITY_MIXTURE_REACTION_7 = I7*1/(0.001 +((x7*H2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_7
*H2_DENSITY)) + (x7*CO2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_7*CO2_DENSITY) ) + (x7
*CO_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_7*CO_DENSITY)) + (x7*H2O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_7*H20_DENSITY))));
DENSITY_MIXTURE_REACTION_8 = I8*1/(0.001 +((x8*H2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_8
*H2_DENSITY)) + (x8*C3H8O2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_8*C3H8O2_DENSITY) ) + (x8
*C3H8O3_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_8*C3H8O3_DENSITY)) + (x8
*H2O_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_8*H2O_DENSITY))));
DENSITY_MIXTURE_REACTION_9 = I9*1/(0.001 +((x9*C3H4O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_9*C3H4O_DENSITY) ) + (x9*C3H8O3_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_9*C3H8O3_DENSITY)) + (2*x9*H2O_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_
9*H2O_DENSITY))));
SUM_DENSITY_MIXTURE = DENSITY_MIXTURE_REACTION_1 + DENSITY_MIXTURE_REACTION_2 +
DENSITY_MIXTURE_REACTION_3 + DENSITY_MIXTURE_REACTION_4 + DENSITY_MIXTURE_REACTION_5 +
DENSITY_MIXTURE_REACTION_6 +DENSITY_MIXTURE_REACTION_7+ DENSITY_MIXTURE_REACTION_8 +
DENSITY_MIXTURE_REACTION_9;
DENSITY_MIXTURE_REACTION_1_NORMALIZED  =  DENSITY_MIXTURE_REACTION_1/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_2_NORMALIZED  =  DENSITY_MIXTURE_REACTION_2/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_3_NORMALIZED  =  DENSITY_MIXTURE_REACTION_3/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_4_NORMALIZED  =  DENSITY_MIXTURE_REACTION_4/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_5_NORMALIZED  =  DENSITY_MIXTURE_REACTION_5/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_6_NORMALIZED  =  DENSITY_MIXTURE_REACTION_6/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_7_NORMALIZED  =  DENSITY_MIXTURE_REACTION_7/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_8_NORMALIZED  =  DENSITY_MIXTURE_REACTION_8/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_9_NORMALIZED = DENSITY_MIXTURE_REACTION_9/SUM_DENSITY_MIXTURE;



!FLAMABILITY CALCULATIONS;
!Equation (28);

UPPER_FLAMABILITY_1 = I1*1/(0.001 +((2*x1/(TOTAL_MOLES_REACTION_1*75)) + (x1/
(TOTAL_MOLES_REACTION_1*74))));
LOWER_FLAMABILITY_1 = I1*1/(0.001 +((2*x1/(TOTAL_MOLES_REACTION_1*4))   + (x1/
(TOTAL_MOLES_REACTION_1*12.5))));
DELTA_FLAMABILITY_1 = UPPER_FLAMABILITY_1 - LOWER_FLAMABILITY_1 ;

UPPER_FLAMABILITY_2 = I2*1/(0.001 +((3*x2/(TOTAL_MOLES_REACTION_2*75)) + (x2/
(TOTAL_MOLES_REACTION_2*36 )))) ;
LOWER_FLAMABILITY_2 = I2*1/(0.001 +((3*x2/(TOTAL_MOLES_REACTION_2*4)) + (x2/
(TOTAL_MOLES_REACTION_2*6.7)))) ;
DELTA_FLAMABILITY_2 = UPPER_FLAMABILITY_2 - LOWER_FLAMABILITY_2;

UPPER_FLAMABILITY_3 = I3*1/(0.001 +((x3/(TOTAL_MOLES_REACTION_3*15))+ (3*x3/
(TOTAL_MOLES_REACTION_3*75))+ (x3/(TOTAL_MOLES_REACTION_3*74)))) ;
LOWER_FLAMABILITY_3 = I3*1/(0.001 +((x3/(TOTAL_MOLES_REACTION_3*5)) + (3*x3/
(TOTAL_MOLES_REACTION_3*4)) + (x3/(TOTAL_MOLES_REACTION_3*12.5)))) ;
DELTA_FLAMABILITY_3 = UPPER_FLAMABILITY_3 - LOWER_FLAMABILITY_3;

UPPER_FLAMABILITY_4 = I4*1/(0.001 +((x4/(TOTAL_MOLES_REACTION_4*15))+ (x4*4/
(TOTAL_MOLES_REACTION_4*75))));
LOWER_FLAMABILITY_4 = I4*1/(0.001 +((x4/(TOTAL_MOLES_REACTION_4*5)) + (x4*4/
(TOTAL_MOLES_REACTION_4*4))));
DELTA_FLAMABILITY_4 = UPPER_FLAMABILITY_4 - LOWER_FLAMABILITY_4;

UPPER_FLAMABILITY_5 = I5*1/(0.001 +((x5*7/(TOTAL_MOLES_REACTION_5*75))));
LOWER_FLAMABILITY_5 = I5*1/(0.001 +((x5*7/(TOTAL_MOLES_REACTION_5*4))));
DELTA_FLAMABILITY_5 = UPPER_FLAMABILITY_5 - LOWER_FLAMABILITY_5;

UPPER_FLAMABILITY_6 = I6*1/(0.001 +((x6/(TOTAL_MOLES_REACTION_6*74))   + (x6/
(TOTAL_MOLES_REACTION_6*75))));
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LOWER_FLAMABILITY_6 = I6*1/(0.001 +((x6/(TOTAL_MOLES_REACTION_6*12.5))+ (x6/
(TOTAL_MOLES_REACTION_6*4))));
DELTA_FLAMABILITY_6 = UPPER_FLAMABILITY_6 - LOWER_FLAMABILITY_6;

UPPER_FLAMABILITY_7 = I7*1/(0.001 +((x7/(TOTAL_MOLES_REACTION_7*74))   + (x7/
(TOTAL_MOLES_REACTION_7*75))));
LOWER_FLAMABILITY_7 = I7*1/(0.001 +((x7/(TOTAL_MOLES_REACTION_7*12.5))+ (x7/
(TOTAL_MOLES_REACTION_7*4))));
DELTA_FLAMABILITY_7 = UPPER_FLAMABILITY_7 - LOWER_FLAMABILITY_7;


UPPER_FLAMABILITY_8 = I8*1/(0.001 +((x8/(TOTAL_MOLES_REACTION_8*75))+ (x8/
(TOTAL_MOLES_REACTION_8*17.4))));
LOWER_FLAMABILITY_8 = I8*1/(0.001 +((x8/(TOTAL_MOLES_REACTION_8*4)) + (x8/
(TOTAL_MOLES_REACTION_8*2.4))));
DELTA_FLAMABILITY_8 = UPPER_FLAMABILITY_8 - LOWER_FLAMABILITY_8;

UPPER_FLAMABILITY_9 = I9*1/(0.001 +((x9/(TOTAL_MOLES_REACTION_9*31))));
LOWER_FLAMABILITY_9 = I9*1/(0.001 +((x9/(TOTAL_MOLES_REACTION_9*2.8))));
DELTA_FLAMABILITY_9 = UPPER_FLAMABILITY_9 - LOWER_FLAMABILITY_9;

SUM_DELAT-FLAMABILITY = DELTA_FLAMABILITY_1 + DELTA_FLAMABILITY_2 + DELTA_FLAMABILITY_3 +
DELTA_FLAMABILITY_4 + DELTA_FLAMABILITY_5 + DELTA_FLAMABILITY_6 +DELTA_FLAMABILITY_7 +
DELTA_FLAMABILITY_8 + DELTA_FLAMABILITY_9 ;
DELTA_FLAMABILITY_NORM_1 = DELTA_FLAMABILITY_1 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_2 = DELTA_FLAMABILITY_2 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_3 = DELTA_FLAMABILITY_3 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_4 = DELTA_FLAMABILITY_4 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_5 = DELTA_FLAMABILITY_5 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_6 = DELTA_FLAMABILITY_6 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_7 = DELTA_FLAMABILITY_7 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_8 = DELTA_FLAMABILITY_8 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_9 = DELTA_FLAMABILITY_9 / SUM_DELAT-FLAMABILITY ;

!chemical species properties;
TOTAL_MOLES_REACTION_1 = (2*x1) + x1 +x1;
TOTAL_MOLES_REACTION_2 = (3*x2) + x2 + x2 + x2 ;
TOTAL_MOLES_REACTION_3 = x3 + x3 + (3*x3) + x3 ;
TOTAL_MOLES_REACTION_4 = x4 + (x4*2) + (x4*4) + x4;
TOTAL_MOLES_REACTION_5 = x5 + (x5*3) + (x5*3) + (x5*7);
TOTAL_MOLES_REACTION_6 = x6 + x6 + x6 + x6;
TOTAL_MOLES_REACTION_7 = x7 + x7 + x7 + x7;
TOTAL_MOLES_REACTION_8 = x8 + x8 + x8 + x8;
TOTAL_MOLES_REACTION_9 = x9 + x9 + (2*x9);

TOTAL_MASS_REACTION_1 = (2*x1)  + (x1*28) + (x1*32);
TOTAL_MASS_REACTION_2 = (3*x2)  + (x2*44) + (x2*32) + (x2*18);
TOTAL_MASS_REACTION_3 = (16*x3) + (x3*28) + (x3*3)  + (x3*18);
TOTAL_MASS_REACTION_4 = (16*x4) + (x4*44) + (x4*4)  + (x4*36);
TOTAL_MASS_REACTION_5 = (7*x5) + (x5*132)+ (x5*92) + (x5*54);
TOTAL_MASS_REACTION_6 = (x6)    + (x6*44) + (x6*28) + (x6*18);
TOTAL_MASS_REACTION_7 = (x7)    + (x7*44) + (x7*28) + (x7*18);
TOTAL_MASS_REACTION_8 = (x8)    + (x8*76) + (x8*92) + (x8*18);
TOTAL_MASS_REACTION_9 = (56*x9) + (x9*92) + (x9*36);


H2_DENSITY = 0.08988;
CO_DENSITY = 1.14;
CO2_DENSITY = 1.98;
C3H8O3_DENSITY = 1.26;
CH3OH_DENSITY = 792;
H2O_DENSITY = 997;
CH4_DENSITY= 0.656;
C3H8O2_DENSITY = 1.04;
C3H4O_DENSITY = 839;

H2_MOLECULAR_WEIGHT = 1;
```

```
CO_MOLECULAR_WEIGHT= 28;
CO2_MOLECULAR_WEIGHT = 44;
C3H8O3_MOLECULAR_WEIGHT = 92;
CH3OH_MOLECULAR_WEIGHT = 32;
H2O_MOLECULAR_WEIGHT = 18;
CH4_MOLECULAR_WEIGHT = 16;
C3H8O2_MOLECULAR_WEIGHT = 76;
C3H4O_MOLECULAR_WEIGHT = 56;

!PROCESS SAFETY INDEX;
!Equation (33);

PSI_1 = DELTA_FLAMABILITY_NORM_1 * HEATING_VALUE_1_NORMALIZED * DENSITY_MIXTURE_REACTION_1
_NORMALIZED * T1_new_normalized * P1_new_normalized *10000  ;
PSI_2 = DELTA_FLAMABILITY_NORM_2 * HEATING_VALUE_2_NORMALIZED * DENSITY_MIXTURE_REACTION_2
_NORMALIZED * T2_new_normalized * P2_new_normalized *10000  ;
PSI_3 = DELTA_FLAMABILITY_NORM_3 * HEATING_VALUE_3_NORMALIZED * DENSITY_MIXTURE_REACTION_3
_NORMALIZED * T3_new_normalized * P3_new_normalized *10000   ;
PSI_4 = DELTA_FLAMABILITY_NORM_4 * HEATING_VALUE_4_NORMALIZED * DENSITY_MIXTURE_REACTION_4
_NORMALIZED * T4_new_normalized * P4_new_normalized *10000   ;
PSI_5 = DELTA_FLAMABILITY_NORM_5 * HEATING_VALUE_5_NORMALIZED * DENSITY_MIXTURE_REACTION_5
_NORMALIZED * T5_new_normalized * P5_new_normalized *10000   ;
PSI_6 = DELTA_FLAMABILITY_NORM_6 * HEATING_VALUE_6_NORMALIZED * DENSITY_MIXTURE_REACTION_6
_NORMALIZED * T6_new_normalized * P6_new_normalized *10000  ;
PSI_7 = DELTA_FLAMABILITY_NORM_7 * HEATING_VALUE_7_NORMALIZED * DENSITY_MIXTURE_REACTION_7
_NORMALIZED * T7_new_normalized * P7_new_normalized *10000   ;
PSI_8 = DELTA_FLAMABILITY_NORM_8 * HEATING_VALUE_8_NORMALIZED * DENSITY_MIXTURE_REACTION_8
_NORMALIZED * T8_new_normalized * P8_new_normalized *10000  ;
PSI_9 = DELTA_FLAMABILITY_NORM_9 * HEATING_VALUE_9_NORMALIZED * DENSITY_MIXTURE_REACTION_9
_NORMALIZED * T9_new_normalized * P9_new_normalized *10000  ;
TOTAL_PSI = (PSI_1 + PSI_2 + PSI_3 + PSI_4 + PSI_5 + PSI_6 +PSI_7+ PSI_8 + PSI_9);

!metrics calculation;
!Equations (27, 34-35);
ROI          = ( Annual_sales_final/ Total_Capital_cost_final) * 100 ;
SASWROIM = Annual_sales_final *100* (1 + ((0.2*((13000- D_CO2)/(13000-0))) + (0.3*((5000 -
DI_H2O)/(5000-0))) + (0.2*((15 - Total_PSI)/(15-1)))))/Total_Capital_cost_final;
```

Appendix 1(d): LINGO mathematical modeling codes for case 2 – Scenario 2

```
!objective function   ;
!Minimum external sources;

min = EX_C3H8O3+ EX_CH4  + EX_H2 + EX_CO;

!Atomic Targeting
!IS STANDS FOR INTERNAL SOURCES INSIDE EIP (kmole/hr);
! Calculation of number of CHO atoms in internal streams;

IS_CO       = 930;
IS_CO2      = 3990;
IS_H2       = 9965;
IS_CH4      = 39;
IS_C3H8O3   = 1000;

AC_SRC  = IS_CO * 1 + IS_CO2 * 1 + IS_CH4 * 1 + IS_C3H8O3 * 3;
AH_SRC      =              IS_H2 * 2 + IS_CH4 * 4 + IS_C3H8O3 * 8;
AO_SRC      = IS_CO * 1 + IS_CO2 * 2              + IS_C3H8O3 * 3;

!Atomic Targeting
!DMD STANDS FOR DEMAND BY FACTORIES (kmole/hr);
! Calculation of number of CHO atoms in demand streams;

CH3OH_DEMAND      = 7500;
H2_Demand         = 5000;
C3H8O2_DEMAND     = 1000;
C3H4O_DEMAND      = 1000;


AC_DMD      = CH3OH_DEMAND * 1                  + 3 * C3H8O2_DEMAND  + 3 * C3H4O_DEMAND ;
AH_DMD  = CH3OH_DEMAND * 4 + 2 * H2_DEMAND + 8 * C3H8O2_DEMAND  + 4 * C3H4O_DEMAND ;
AO_DMD      = CH3OH_DEMAND * 1                  + 2 * C3H8O2_DEMAND  + 1 * C3H4O_DEMAND ;

!Atomic Targeting
!NET STANDS FOR NET RESULT BETWEEN INTERNAL AND DEMAND streams (kmole/hr);

AC_NET      = AC_SRC - AC_DMD;
AH_NET      = AH_SRC - AH_DMD;
AO_NET      = AO_SRC - AO_DMD;

!Atomic Targeting - overall atomic balanced equation;
!calculation of external, recycled, discharged species in the CHOSYN (kmole/hr);
!Equations (10-12);


AC_NET + 3 * EX_C3H8O3 + 3 * RE_C3H8O3 - 3 * Di_C3H8O3  + 1 * EX_CH4 + 1 * RE_CH4  - 1 *
Di_CH4 + 0 * EX_H2 + 0 * RE_H2  - 0 * Di_H2 + 1 * EX_CO + 1 * RE_CO  - 1 * Di_CO + 0 *
EX_H2O - 0 * DI_H2O - 1 * D_CO2 = 0;
AH_NET + 8 * EX_C3H8O3 + 3 * RE_C3H8O3 - 8 * Di_C3H8O3  + 4 * EX_CH4 + 1 * RE_CH4  - 4 *
Di_CH4 + 2 * EX_H2 + 0 * RE_H2  - 2 * Di_H2 + 0 * EX_CO + 0 * RE_CO  - 0 * Di_CO + 2 *
EX_H2O - 2 * DI_H2O - 0 * D_CO2 = 0;
AO_NET + 3 * EX_C3H8O3 + 3 * RE_C3H8O3 - 3 * Di_C3H8O3  + 0 * EX_CH4 + 1 * RE_CH4  - 0 *
Di_CH4 + 0 * EX_H2 + 0 * RE_H2  - 0 * Di_H2 + 1 * EX_CO + 1 * RE_CO  - 1 * Di_CO + 1 *
EX_H2O - 1 * DI_H2O - 2 * D_CO2 = 0;

!maximum allowable purchased and discharged chemical species if need;
!Equations (13-14);

!DI_H2O < 5000 ;
!D_CO2 < 13000;
!EX_C3H8O3 < 15000;
!EX_CH4 < 15000;
!EX_H2 < 15000;
!EX_CO < 15000;

@FREE(AC_NET);
```

```
@FREE(AH_NET);
@FREE(AO_NET);
@FREE(EX_C3H8O3);
@FREE(EX_CH4);
@FREE(EX_H2O);
@FREE(D_CO2);
@FREE(EX_H2);
@FREE(EX_CO);

!total discharged species can be divided to recycled species and final discharged species;

Discharge_C3H8O3 = RE_C3H8O3 + DI_C3H8O3 ;
Discharge_Ch4 = RE_Ch4 + DI_Ch4 ;
Discharge_Co = RE_Co + DI_Co ;
Discharge_h2 = RE_h2 + DI_h2 ;

!Overall mass balanced equation (kmole/hr);
!Equation (15);

IN_C3H8O3  = (IS_C3H8O3 + EX_C3H8O3 + RE_C3H8O3) ;
Out_C3H8O3 = (Discharge_C3H8O3) ;

IN_CH4     = (IS_CH4 + EX_CH4 + RE_CH4);
Out_CH4    = (Discharge_Ch4);

IN_H2      = (IS_H2 + EX_H2 + RE_H2);
Out_H2     = (Discharge_h2);

IN_CO      = (IS_CO + EX_CO + RE_CO) ;
Out_CO     = (Discharge_Co);

D_CO2 >  0;
EX_H2O > 0;
DI_H2O > 0;

RE_C3H8O3 > 0;
EX_C3H8O3 > 0;
DI_C3H8O3 > 0;

RE_CO > 0;
EX_CO > 0;
DI_CO > 0;

RE_H2 > 0;
EX_H2 > 0;
DI_H2 > 0;

RE_CH4 > 0;
EX_CH4 > 0;
DI_CH4 > 0;


(IN_C3H8O3 - Out_C3H8O3 ) + (IN_CH4 - Out_CH4) + (IS_CO2 - D_CO2) + (IN_H2 - Out_H2 - H2
_DEMAND) + (IN_CO - Out_CO) + (EX_H2O - DI_H2O) = CH3OH_DEMAND + C3H8O2_DEMAND +
C3H4O_DEMAND;

OVR_C3H8O3        = (IN_C3H8O3 - Out_C3H8O3)     ;
OVR_CO            = (IN_CO - Out_CO)             ;
OVR_CO2           = (IS_CO2    - D_CO2)          ;
OVR_H2            = (IN_H2 - Out_H2 - H2_DEMAND);
OVR_CH4           = (IN_CH4 - Out_CH4)           ;
OVR_H2O           = (EX_H2O - DI_H2O)            ;
!OVR_C3H8O2   = (C3H8O2_DEMAND)                                    ;
!OVR_C3H4O    = C3H4O_DEMAND                                       ;


@FREE(OVR_C3H8O3);
```

```
@FREE(OVR_CO);
@FREE(OVR_CO2);
@FREE(OVR_H2);
@FREE(OVR_CH4);
@FREE(OVR_H2O);
@FREE(CH3OH_DEMAND);
@FREE(H2_DEMAND);
@FREE(OVR_C3H8O2);
@FREE(C3H8O2_DEMAND);

! Calculation of reaction flowrates
! X_old STANDS FOR theoretical STOICHMETRIC COFFICIENT FOR A SET OF EQUATIONS DETERMINED
BY THE CHOSYN AND the PARTICIPATING plants;
!Equations (16-17);

(x5_old   + x8_old   + x9_old  )                                                    =
OVR_C3H8O3 ;
(x1_old   - x3_old   + x6_old   - x7_old  )                                         =
OVR_CO ;
(x2_old   - x4_old   - 3*x5_old - x6_old   + x7_old  )                              =
OVR_CO2;
(2*x1_old + 3*x2_old - 3*x3_old - 4*x4_old - 7*x5_old - x6_old   + x7_old + x8_old ) =
OVR_H2;
(-1*x2_old+ x3_old   + 2*x4_old + 3*x5_old + x6_old   - x7_old  - x8_old - 2*x9_old) =
OVR_H2O;
(x3_old   + x4_old          )                                                       =
OVR_CH4;
(x1_old   + x2_old        )                                                         =
CH3OH_DEMAND;
(x8_old             )                                                               =
C3H8O2_DEMAND;
(x9_old           )                                                                 =
C3H4O_DEMAND;

!reaction conversion calculations, all reactions are assumed having 80% conversion rate;
!Equations (18);

X1 = 1.2*X1_old;
X2 = 1.2*X2_old;
X3 = 1.2*X3_old;
X4 = 1.2*X4_old;
X5 = 1.2*X5_old;
X6 = 1.2*X6_old;
X7 = 1.2*X7_old;
X8 = 1.2*X8_old;
X9 = 1.2*X9_old;

H2_x1 = 2* X1 ;
H2_X2 = 3* X2 ;
H2_x7 =    X7 ;
H2_x8 =    X8 ;
CO_x1 =    X1 ;
CO_x6  =   X6  ;
CH4_x3 =   X3  ;
CH4_x4 =   X4  ;
C3H8O3_x5 =X5 ;
C3H8O3_x8 =X8 ;
C3H8O3_x9 =X9 ;

!Recycling mass balance equations;
!Total recycled chemical species ( Unreacted raw materials + By-products) ;
!Equation (19);

REE_H2     =  H2_x1     + H2_X2     + H2_x7     + H2_x8 - 2*x1_old - 3*x2_old - x7_old -
x8 old ;
REE CO     =  CO x1     + CO x6     - x1 old    - x6 old
;
```

```
REE_CH4    =  CH4_x3    + CH4_x4    - x3_old    - x4_old
;
REE_C3H8O3 =  C3H8O3_x5 + C3H8O3_x8 + C3H8O3_x9 - x5_old - x8_old    - x9_old
;
Reycled_H2      = REE_H2 + RE_H2 ;
Reycled_CO      = REE_CO + RE_CO ;
Reycled_CH4     = REE_Ch4 + RE_Ch4 ;
Reycled_C3H8O3 = REE_C3H8O3 + RE_C3H8O3 ;

x1>0;
x2>0;
x3>0;
x4>0;
x5>0;
x6>0;
x7 > 0;
x6 + x7 < 1;
x8>0;
x9>0;

x1_old>0;
x2_old>0;
x3_old>0;
x4_old>0;
x5_old>0;
x6_old>0;
x7_old > 0;
x6_old + x7_old < 1;
x8_old>0;
x9_old>0;

!Economics calculations ;
!raw materials and sales calculations ($/hr) ;
!each species flowrate is multiplied first by molecular weight to convert to KG/hr, then
multiplied by the price in $/kg;
!part of Equation (26);
COST_C3H8O3       = EX_C3H8O3 * 92 * 1.09 ;
COST_CH4          = EX_CH4    * 16 * 7.25 ;
COST_H2           = EX_H2     * 1  * 3      ;
COST_CO           = EX_CO     * 28 * 0.18    ;

PROFIT_CH3OH      = CH3OH_DEMAND  * 32 * 1.5 ;
PROFIT_C3H8O2     = C3H8O2_DEMAND * 76  * 5 ;
PROFIT_C3H4O      = C3H4O_DEMAND  * 56  * 3 ;

!production costs ($/hr);
!the number of moles of each species is multiplied by flowrate and then multiplied by
moleular weight to convert to KG/hr, then multiplied by the price in $/kg;
! production costs 6/7 are assumed small numbers because they are water-gas shift
reactions, which occur as side reactions;
!Equation (21);

Production_cost_1 = 1 * 32 * 0.61 * x1  ;
Production_cost_2 = 1 * 32 * 1.01 * x2  ;
Production_cost_3 = 3 * 1  * 0.66 * x3  ;
Production_cost_4 = 4 * 1  * 0.66 * x4  ;
Production_cost_5 = 7 * 1  * 2.6  * x5  ;
Production_cost_6 = 0.1           * x6  ;
Production_cost_7 = 0.1           * x7  ;
Production_cost_8 = 1 * 76 * 0.85 * x8  ;
Production_cost_9 = 1 * 56 * 0.42 * x9  ;
Total_production_cost = Production_cost_1 + Production_cost_2 + Production_cost_3 +
Production_cost_4 + Production_cost_5 + Production_cost_6 + Production_cost_7 +
Production_cost_8+Production_cost_9;

!Capital costs ;
!the number of moles of each species is multiplied by flowrate and then multiplied by
```

```
molecular weight to convert to KG/hr, then multiplied by the price in $/kg;
!Equation (22) and (24) + factorial method;

EQUIP_cost_1 = (0.31 * (x1)  * 1 * 32) ;
EQUIP_cost_2 = (0.49  * (x2) * 1 * 32) ;
EQUIP_cost_3 = (0.29 * (x3)  * 3 * 1)  ;
EQUIP_cost_4 = (0.29 * (x4)  * 4 * 1)  ;
EQUIP_cost_5 = (0.66 * (x5)  * 7 * 1)  ;
EQUIP_cost_6 = (0.1  * (x6))           ;
EQUIP_cost_7  =  (0.1   *  (x7)  )     ;
EQUIP_cost_8 = (0.28 * (x8) * 1 * 76)  ;
EQUIP_cost_9 = (0.21 * (x9) * 1 * 56)  ;

PPC_1 = 3.47*EQUIP_cost_1;
IPC_1 = 0.45* PPC_1;
Fixed_cost_1 = PPC_1+IPC_1;
Capital_cost_1 = Fixed_cost_1*1.18;

PPC_2 = 3.47*EQUIP_cost_2;
IPC_2 = 0.45* PPC_2;
Fixed_cost_2 = PPC_2+IPC_2;
Capital_cost_2 = Fixed_cost_2*1.18;

PPC_3          = 3.47*       EQUIP_cost_3;
IPC 3          = 0.45*              PPC 3;
Fixed cost 3   =        PPC 3+      IPC 3;
Capital_cost_3 = Fixed_cost_3*1.18;

PPC_4          = 3.47*       EQUIP_cost_4;
IPC_4          = 0.45*              PPC_4;
Fixed cost 4   =        PPC 4+      IPC 4;
Capital_cost_4 = Fixed_cost_4*1.18;

PPC_5          = 3.47*       EQUIP_cost_5;
IPC 5          = 0.45*              PPC 5;
Fixed cost 5   =        PPC 5+      IPC 5;
Capital_cost_5 = Fixed_cost_5*1.18;

PPC_6          = 3.47*       EQUIP_cost_6;
IPC 6          = 0.45*              PPC 6;
Fixed cost 6   =        PPC 6+      IPC 6;
Capital_cost_6 = Fixed_cost_6*1.18;

PPC_7          = 3.47*       EQUIP_cost_7;
IPC_7          = 0.45*              PPC_7;
Fixed cost 7   =        PPC 7+      IPC 7;
Capital_cost_7 = Fixed_cost_7*1.18;


PPC_8          = 3.47*       EQUIP_cost_8;
IPC 8          = 0.45*              PPC 8;
Fixed cost 8   =        PPC 8+      IPC 8;
Capital_cost_8 = Fixed_cost_8*1.18;

PPC_9          = 3.47*       EQUIP_cost_9;
IPC_9          = 0.45*              PPC_9;
Fixed cost 9   =        PPC 9+      IPC 9;
Capital_cost_9 = Fixed_cost_9*1.18;

capital_cost = Capital_cost_1 + Capital_cost_2 + Capital_cost_3 + Capital_cost_4 +
Capital_cost_5 + Capital_cost_6 + Capital_cost_7 + Capital_cost_8 + Capital_cost_9 ;


!annualized fixed costs and annual sales calculations;
!Equations (25-26);

AFC          = 0.1 * capital_cost  ;
```

```
sales = ((PROFIT_CH3OH + PROFIT_C3H8O2 + PROFIT_C3H40 - COST_C3H8O3 - COST_CH4 - COST_H2 -
COST_CO -(Total_production_cost+AFC))*(1-0.25)) + AFC ;
Annual_sales_final = sales * 300 * 24 ;
Total_Capital_cost_final = Capital_cost * 24 * 300;
ROI > 10;
SASWROIM > 10;

!binary equations;
!Equation (22-23);
(x1) >= 1*I1;
(x1) <= 100000*(I1);
(x2) >= 1*I2;
(x2) <= 100000*(I2);
(x3) >= 1*I3;
(x3) <= 100000*(I3);
(x4)>= 1*I4;
(x4)<= 100000*(I4);
(x5)>= 1*I5;
(x5)<= 100000*(I5);
(x6)>= 1*I6;
(x6)<= 100000*(I6);
(x7)>= 1*I7;
(x7)<= 100000*(I7);
(x8)>= 1*I8;
(x8)<= 100000*(I8);
(x9)>= 1*I9;
(x9)<= 100000*(I9);
!I1+I2+I3+I4+I5+I6+I7+I8+I9 = 5;


@BIN(I1);
@BIN(I2);
@BIN(I3);
@BIN(I4);
@BIN(I5);
@BIN(I6);
@BIN(I7);
@BIN(I8);
@BIN(I9);

! SAFETY pressure calculations;
!Equation (31);

P1 = 98.5*I1;
P2 = 75*I2;
P3 = 30*I3;
P4 = 30*I4;
P5 = 2*I5;
P6 = 1*I6;
P7 = 1 * I7;
P8 = 19.7*I8;
P9 = 0.98*I9;
Sum_pressure = (P1)+(P2)+(P3)+(P4)+(P5)+ P6 +(P7)+(P8)+(P9);
P1_new_normalized = P1/Sum_pressure;
P2_new_normalized = P2/Sum_pressure;
P3_new_normalized = P3/Sum_pressure;
P4_new_normalized = P4/Sum_pressure;
P5_new_normalized = P5/Sum_pressure;
P6_new_normalized = P6/Sum_pressure;
P7_new_normalized = P7/Sum_pressure;
P8_new_normalized = P8/Sum_pressure;
P9_new_normalized = P9/Sum_pressure;

! SAFETY Temperature calculations;
!Equation (32);

T1 = 573*I1;
```

```
T2 = 483*I2;
T3 = 1152*I3;
T4 = 1152*I4;
T5 = 900*I5;
T6 = 100*I6;
T7 = 100*I7;
T8 = 478*I8;
T9 = 683.15*I9;
Sum_tempruture = (T1)+(T2)+(T3)+(T4)+(T5)+(T6) + T7 +(T8)+(T9);
T1_new_normalized = T1/Sum_tempruture;
T2_new_normalized = T2/Sum_tempruture;
T3_new_normalized = T3/Sum_tempruture;
T4_new_normalized = T4/Sum_tempruture;
T5_new_normalized = T5/Sum_tempruture;
T6_new_normalized = T6/Sum_tempruture;
T7_new_normalized = T7/Sum_tempruture;
T8_new_normalized = T8/Sum_tempruture;
T9_new_normalized = T9/Sum_tempruture;

! Heating value calculations;
!Equation (30);

AVERAGE_HEATING_VALUE_REACTION_1 = I1*((283   *x1)       + (x1*282.8)   + (x1*723.2))/3;
AVERAGE_HEATING_VALUE_REACTION_2 = I2*((424.5*x2)       + (x2*723.2))/4;
AVERAGE_HEATING_VALUE_REACTION_3 = I3*((880   *x3)       + (x3*282.8)   + (x3*424.5))/4;
AVERAGE_HEATING_VALUE_REACTION_4 = I4*((880   *x4)       + (x4*566))/4;
AVERAGE_HEATING_VALUE_REACTION_5 = I5*((990.5*x5)       + (x5*1652.32))/4;
AVERAGE_HEATING_VALUE_REACTION_6 = I6*((141.5*x6)       + (x6*282.8))/4;
AVERAGE_HEATING_VALUE_REACTION_7 = I7*((141.5*x7)       + (x7*282.8))/4;
AVERAGE_HEATING_VALUE_REACTION_8 = I8*((141.5*x8) + (x8*1824)         + (x8*1652.32))/4;
AVERAGE_HEATING_VALUE_REACTION_9 = I9*((1624   *x9) + (x9*1652.32))/3;
SUM_AVERAGE_HEATING_VALUE = AVERAGE_HEATING_VALUE_REACTION_1 +
AVERAGE_HEATING_VALUE_REACTION_2 + AVERAGE_HEATING_VALUE_REACTION_3 +
AVERAGE_HEATING_VALUE_REACTION_4 + AVERAGE_HEATING_VALUE_REACTION_5 +
AVERAGE_HEATING_VALUE_REACTION_6 + AVERAGE_HEATING_VALUE_REACTION_7 +
AVERAGE_HEATING_VALUE_REACTION_8 + AVERAGE_HEATING_VALUE_REACTION_9 ;
HEATING_VALUE_1_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_1/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_2_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_2/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_3_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_3/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_4_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_4/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_5_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_5/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_6_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_6/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_7_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_7/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_8_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_8/SUM_AVERAGE_HEATING_VALUE;
HEATING_VALUE_9_NORMALIZED = AVERAGE_HEATING_VALUE_REACTION_9/SUM_AVERAGE_HEATING_VALUE;


!DENSITY OF MIXTURE Calculations;
!Equation (29);

DENSITY_MIXTURE_REACTION_1 = I1*1/(0.001 + ((2*x1*H2_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_1*H2_DENSITY))+ (x1*CO_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_1
*CO_DENSITY))+(x1*CH3OH_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_1*CH3OH_DENSITY))));
DENSITY_MIXTURE_REACTION_2 = I2*1/(0.001 +((3*x2*H2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_
2*H2_DENSITY)) + (x2*CO2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_2*CO2_DENSITY)) + (x2
*CH3OH_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_2*CH3OH_DENSITY)) + (x2*H2O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_2*H2O_DENSITY))));
DENSITY_MIXTURE_REACTION_3 = I3*1/(0.001 +((x3*CH4_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_3
*CH4_DENSITY)) + (x3*CO_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_3*CO_DENSITY) ) + (3*x3*H2
_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_3*H2_DENSITY)) + (x3*H2O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_3*H2O_DENSITY))));
DENSITY_MIXTURE_REACTION_4 = I4*1/(0.001 +((x4*CH4_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_4
*CH4_DENSITY)) + (x4*CO2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_4*CO2_DENSITY) ) + (4*x4*H2
_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_4*H2_DENSITY)) + (2*x4*H2O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_4*H2O_DENSITY))));
DENSITY_MIXTURE_REACTION_5 = I5*1/(0.001 +((7*x5*H2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_
5*H2_DENSITY)) + (3*x5*CO2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_5*CO2_DENSITY) ) + (x5
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*C3H8O3_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_5*C3H8O3_DENSITY)) + (3*x5
*H2O_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_5*H2O_DENSITY))));
DENSITY_MIXTURE_REACTION_6 = I6*1/(0.001 +((x6*H2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_6
*H2_DENSITY)) + (x6*CO2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_6*CO2_DENSITY) ) + (x6
*CO_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_6*CO_DENSITY)) + (x6*H2O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_6*H20_DENSITY))));
DENSITY_MIXTURE_REACTION_7 = I7*1/(0.001 +((x7*H2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_7
*H2_DENSITY)) + (x7*CO2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_7*CO2_DENSITY) ) + (x7
*CO_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_7*CO_DENSITY)) + (x7*H2O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_7*H20_DENSITY))));
DENSITY_MIXTURE_REACTION_8 = I8*1/(0.001 +((x8*H2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_8
*H2_DENSITY)) + (x8*C3H8O2_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_8*C3H8O2_DENSITY) ) + (x8
*C3H8O3_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_8*C3H8O3_DENSITY)) + (x8
*H2O_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_8*H2O_DENSITY))));
DENSITY_MIXTURE_REACTION_9 = I9*1/(0.001 +((x9*C3H4O_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_9*C3H4O_DENSITY) ) + (x9*C3H8O3_MOLECULAR_WEIGHT/
(TOTAL_MASS_REACTION_9*C3H8O3_DENSITY)) + (2*x9*H2O_MOLECULAR_WEIGHT/(TOTAL_MASS_REACTION_
9*H2O_DENSITY))));
SUM_DENSITY_MIXTURE = DENSITY_MIXTURE_REACTION_1 + DENSITY_MIXTURE_REACTION_2 +
DENSITY_MIXTURE_REACTION_3 + DENSITY_MIXTURE_REACTION_4 + DENSITY_MIXTURE_REACTION_5 +
DENSITY_MIXTURE_REACTION_6 +DENSITY_MIXTURE_REACTION_7+ DENSITY_MIXTURE_REACTION_8 +
DENSITY_MIXTURE_REACTION_9;
DENSITY_MIXTURE_REACTION_1_NORMALIZED  =  DENSITY_MIXTURE_REACTION_1/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_2_NORMALIZED  =  DENSITY_MIXTURE_REACTION_2/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_3_NORMALIZED  =  DENSITY_MIXTURE_REACTION_3/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_4_NORMALIZED  =  DENSITY_MIXTURE_REACTION_4/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_5_NORMALIZED  =  DENSITY_MIXTURE_REACTION_5/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_6_NORMALIZED  =  DENSITY_MIXTURE_REACTION_6/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_7_NORMALIZED  =  DENSITY_MIXTURE_REACTION_7/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_8_NORMALIZED  =  DENSITY_MIXTURE_REACTION_8/SUM_DENSITY_MIXTURE;
DENSITY_MIXTURE_REACTION_9_NORMALIZED = DENSITY_MIXTURE_REACTION_9/SUM_DENSITY_MIXTURE;



!FLAMABILITY CALCULATIONS;
!Equation (28);

UPPER_FLAMABILITY_1 = I1*1/(0.001 +((2*x1/(TOTAL_MOLES_REACTION_1*75)) + (x1/
(TOTAL_MOLES_REACTION_1*74))));
LOWER_FLAMABILITY_1 = I1*1/(0.001 +((2*x1/(TOTAL_MOLES_REACTION_1*4))   + (x1/
(TOTAL_MOLES_REACTION_1*12.5))));
DELTA_FLAMABILITY_1 = UPPER_FLAMABILITY_1 - LOWER_FLAMABILITY_1 ;

UPPER_FLAMABILITY_2 = I2*1/(0.001 +((3*x2/(TOTAL_MOLES_REACTION_2*75)) + (x2/
(TOTAL_MOLES_REACTION_2*36 )))) ;
LOWER_FLAMABILITY_2 = I2*1/(0.001 +((3*x2/(TOTAL_MOLES_REACTION_2*4)) + (x2/
(TOTAL_MOLES_REACTION_2*6.7)))) ;
DELTA_FLAMABILITY_2 = UPPER_FLAMABILITY_2 - LOWER_FLAMABILITY_2;

UPPER_FLAMABILITY_3 = I3*1/(0.001 +((x3/(TOTAL_MOLES_REACTION_3*15))+ (3*x3/
(TOTAL_MOLES_REACTION_3*75))+ (x3/(TOTAL_MOLES_REACTION_3*74)))) ;
LOWER_FLAMABILITY_3 = I3*1/(0.001 +((x3/(TOTAL_MOLES_REACTION_3*5)) + (3*x3/
(TOTAL_MOLES_REACTION_3*4)) + (x3/(TOTAL_MOLES_REACTION_3*12.5)))) ;
DELTA_FLAMABILITY_3 = UPPER_FLAMABILITY_3 - LOWER_FLAMABILITY_3;

UPPER_FLAMABILITY_4 = I4*1/(0.001 +((x4/(TOTAL_MOLES_REACTION_4*15))+ (x4*4/
(TOTAL_MOLES_REACTION_4*75))));
LOWER_FLAMABILITY_4 = I4*1/(0.001 +((x4/(TOTAL_MOLES_REACTION_4*5)) + (x4*4/
(TOTAL_MOLES_REACTION_4*4))));
DELTA_FLAMABILITY_4 = UPPER_FLAMABILITY_4 - LOWER_FLAMABILITY_4;

UPPER_FLAMABILITY_5 = I5*1/(0.001 +((x5*7/(TOTAL_MOLES_REACTION_5*75))));
LOWER_FLAMABILITY_5 = I5*1/(0.001 +((x5*7/(TOTAL_MOLES_REACTION_5*4))));
DELTA_FLAMABILITY_5 = UPPER_FLAMABILITY_5 - LOWER_FLAMABILITY_5;

UPPER_FLAMABILITY_6 = I6*1/(0.001 +((x6/(TOTAL_MOLES_REACTION_6*74))   + (x6/
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(TOTAL_MOLES_REACTION_6*75))));
LOWER_FLAMABILITY_6 = I6*1/(0.001 +((x6/(TOTAL_MOLES_REACTION_6*12.5))+ (x6/
(TOTAL_MOLES_REACTION_6*4))));
DELTA_FLAMABILITY_6 = UPPER_FLAMABILITY_6 - LOWER_FLAMABILITY_6;

UPPER_FLAMABILITY_7 = I7*1/(0.001 +((x7/(TOTAL_MOLES_REACTION_7*74))   + (x7/
(TOTAL_MOLES_REACTION_7*75))));
LOWER_FLAMABILITY_7 = I7*1/(0.001 +((x7/(TOTAL_MOLES_REACTION_7*12.5))+ (x7/
(TOTAL_MOLES_REACTION_7*4))));
DELTA_FLAMABILITY_7 = UPPER_FLAMABILITY_7 - LOWER_FLAMABILITY_7;


UPPER_FLAMABILITY_8 = I8*1/(0.001 +((x8/(TOTAL_MOLES_REACTION_8*75))+ (x8/
(TOTAL_MOLES_REACTION_8*17.4))));
LOWER_FLAMABILITY_8 = I8*1/(0.001 +((x8/(TOTAL_MOLES_REACTION_8*4)) + (x8/
(TOTAL_MOLES_REACTION_8*2.4))));
DELTA_FLAMABILITY_8 = UPPER_FLAMABILITY_8 - LOWER_FLAMABILITY_8;

UPPER_FLAMABILITY_9 = I9*1/(0.001 +((x9/(TOTAL_MOLES_REACTION_9*31))));
LOWER_FLAMABILITY_9 = I9*1/(0.001 +((x9/(TOTAL_MOLES_REACTION_9*2.8))));
DELTA_FLAMABILITY_9 = UPPER_FLAMABILITY_9 - LOWER_FLAMABILITY_9;

SUM_DELAT-FLAMABILITY = DELTA_FLAMABILITY_1 + DELTA_FLAMABILITY_2 + DELTA_FLAMABILITY_3 +
DELTA_FLAMABILITY_4 + DELTA_FLAMABILITY_5 + DELTA_FLAMABILITY_6 +DELTA_FLAMABILITY_7 +
DELTA_FLAMABILITY_8 + DELTA_FLAMABILITY_9 ;
DELTA_FLAMABILITY_NORM_1 = DELTA_FLAMABILITY_1 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_2 = DELTA_FLAMABILITY_2 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_3 = DELTA_FLAMABILITY_3 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_4 = DELTA_FLAMABILITY_4 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_5 = DELTA_FLAMABILITY_5 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_6 = DELTA_FLAMABILITY_6 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_7 = DELTA_FLAMABILITY_7 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_8 = DELTA_FLAMABILITY_8 / SUM_DELAT-FLAMABILITY ;
DELTA_FLAMABILITY_NORM_9 = DELTA_FLAMABILITY_9 / SUM_DELAT-FLAMABILITY ;

!chemical species properties;
TOTAL_MOLES_REACTION_1 = (2*x1) + x1 +x1;
TOTAL_MOLES_REACTION_2 = (3*x2) + x2 + x2 + x2 ;
TOTAL_MOLES_REACTION_3 = x3 + x3 + (3*x3) + x3 ;
TOTAL_MOLES_REACTION_4 = x4 + (x4*2) + (x4*4) + x4;
TOTAL_MOLES_REACTION_5 = x5 + (x5*3) + (x5*3) + (x5*7);
TOTAL_MOLES_REACTION_6 = x6 + x6 + x6 + x6;
TOTAL_MOLES_REACTION_7 = x7 + x7 + x7 + x7;
TOTAL_MOLES_REACTION_8 = x8 + x8 + x8 + x8;
TOTAL_MOLES_REACTION_9 = x9 + x9 + (2*x9);

TOTAL_MASS_REACTION_1 = (2*x1)  + (x1*28) + (x1*32);
TOTAL_MASS_REACTION_2 = (3*x2)  + (x2*44) + (x2*32) + (x2*18);
TOTAL_MASS_REACTION_3 = (16*x3) + (x3*28) + (x3*3)  + (x3*18);
TOTAL_MASS_REACTION_4 = (16*x4) + (x4*44) + (x4*4)  + (x4*36);
TOTAL_MASS_REACTION_5 = (7*x5) + (x5*132)+ (x5*92) + (x5*54);
TOTAL_MASS_REACTION_6 = (x6)    + (x6*44) + (x6*28) + (x6*18);
TOTAL_MASS_REACTION_7 = (x7)    + (x7*44) + (x7*28) + (x7*18);
TOTAL_MASS_REACTION_8 = (x8)    + (x8*76) + (x8*92) + (x8*18);
TOTAL_MASS_REACTION_9 = (56*x9) + (x9*92) + (x9*36);


H2_DENSITY = 0.08988;
CO_DENSITY = 1.14;
CO2_DENSITY = 1.98;
C3H8O3_DENSITY = 1.26;
CH3OH_DENSITY = 792;
H2O_DENSITY = 997;
CH4_DENSITY= 0.656;
C3H8O2_DENSITY = 1.04;
C3H4O_DENSITY = 839;
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H2_MOLECULAR_WEIGHT = 1;
CO_MOLECULAR_WEIGHT= 28;
CO2_MOLECULAR_WEIGHT = 44;
C3H8O3_MOLECULAR_WEIGHT = 92;
CH3OH_MOLECULAR_WEIGHT = 32;
H2O_MOLECULAR_WEIGHT = 18;
CH4_MOLECULAR_WEIGHT = 16;
C3H8O2_MOLECULAR_WEIGHT = 76;
C3H4O_MOLECULAR_WEIGHT = 56;

!PROCESS SAFETY INDEX;
!Equation (33);

PSI_1 = DELTA_FLAMABILITY_NORM_1 * HEATING_VALUE_1_NORMALIZED * DENSITY_MIXTURE_REACTION_1
_NORMALIZED * T1_new_normalized * P1_new_normalized *10000  ;
PSI_2 = DELTA_FLAMABILITY_NORM_2 * HEATING_VALUE_2_NORMALIZED * DENSITY_MIXTURE_REACTION_2
_NORMALIZED * T2_new_normalized * P2_new_normalized *10000  ;
PSI_3 = DELTA_FLAMABILITY_NORM_3 * HEATING_VALUE_3_NORMALIZED * DENSITY_MIXTURE_REACTION_3
_NORMALIZED * T3_new_normalized * P3_new_normalized *10000   ;
PSI_4 = DELTA_FLAMABILITY_NORM_4 * HEATING_VALUE_4_NORMALIZED * DENSITY_MIXTURE_REACTION_4
_NORMALIZED * T4_new_normalized * P4_new_normalized *10000   ;
PSI_5 = DELTA_FLAMABILITY_NORM_5 * HEATING_VALUE_5_NORMALIZED * DENSITY_MIXTURE_REACTION_5
_NORMALIZED * T5_new_normalized * P5_new_normalized *10000   ;
PSI_6 = DELTA_FLAMABILITY_NORM_6 * HEATING_VALUE_6_NORMALIZED * DENSITY_MIXTURE_REACTION_6
_NORMALIZED * T6_new_normalized * P6_new_normalized *10000  ;
PSI_7 = DELTA_FLAMABILITY_NORM_7 * HEATING_VALUE_7_NORMALIZED * DENSITY_MIXTURE_REACTION_7
_NORMALIZED * T7_new_normalized * P7_new_normalized *10000   ;
PSI_8 = DELTA_FLAMABILITY_NORM_8 * HEATING_VALUE_8_NORMALIZED * DENSITY_MIXTURE_REACTION_8
_NORMALIZED * T8_new_normalized * P8_new_normalized *10000  ;
PSI_9 = DELTA_FLAMABILITY_NORM_9 * HEATING_VALUE_9_NORMALIZED * DENSITY_MIXTURE_REACTION_9
_NORMALIZED * T9_new_normalized * P9_new_normalized *10000  ;
TOTAL_PSI = (PSI_1 + PSI_2 + PSI_3 + PSI_4 + PSI_5 + PSI_6 +PSI_7+ PSI_8 + PSI_9);

!metrics calculation;
!Equations (27, 34-35);
ROI          = ( Annual_sales_final/ Total_Capital_cost_final) * 100 ;
SASWROIM = Annual_sales_final *100* (1 + ((0.2*((13000- D_CO2)/(13000-0))) + (0.3*((5000 -
DI_H2O)/(5000-0))) + (0.2*((15 - Total_PSI)/(15-1)))))/Total_Capital_cost_final;
```

Appendix 2: LINGO model formulation for chapter 4

Appendix 2(a1): LINGO mathematical modeling codes for Scenario 1 – mass network

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!objective function;
!Minimum external source;

!atomic targeting ;
!IS STANDS FOR INTERNAL SOURCES INSIDE EIP;
 ! Calculation of number of CHO atoms in internal streams;
IS_CO       = 930;
IS_CO2      = 3990;
IS_H2       = 9965;
IS_CH4      = 39;
IS_C3H8O3   = 1000;
AC_SRC  = IS_CO * 1 + IS_CO2 * 1 + IS_CH4 * 1 + IS_C3H8O3 * 3;
AH_SRC      =              IS_H2 * 2 + IS_CH4 * 4 + IS_C3H8O3 * 8;
AO_SRC      = IS_CO * 1 + IS_CO2 * 2              + IS_C3H8O3 * 3;
!DMD STANDS FOR DEMAND BY the participating plants;
 ! Calculation of number of CHO atoms in demand streams;
CH3OH_DEMAND      = 7500;
C3H8O2_DEMAND     = 1000;
C3H4O_DEMAND      = 1000;
AC_DMD  = CH3OH_DEMAND * 1  + 3 * C3H8O2_DEMAND  + 3 * C3H4O_DEMAND ;
AH_DMD  = CH3OH_DEMAND * 4  + 8 * C3H8O2_DEMAND  + 4 * C3H4O_DEMAND ;
AO_DMD      = CH3OH_DEMAND * 1  + 2 * C3H8O2_DEMAND  + 1 * C3H4O_DEMAND ;
!NET STANDS FOR NET RESULT BETWEEN INTERNAL AND DEMAND streams;
AC_NET      = AC_SRC - AC_DMD;
AH_NET      = AH_SRC - AH_DMD;
AO_NET      = AO_SRC - AO_DMD;
!EX STANDS FOR EXTERNAL SOURCES REQUIRED BY EIP TO ACHIEVE DEMAND REQUESTED BY THE
participating plants while DI is the discharged chemical species in the process;
AC_NET + 3 * EX_C3H8O3  - 3 * DI_C3H8O3  + 1 * EX_CH4  - 1 * DI_CH4 + 0 * EX_H2  - 0 *
DI_H2 + 1 * EX_CO - 1 * DI_CO + 0 * EX_H2O - 0 * D_H2O - 1 * D_CO2 = 0;
AH_NET + 8 * EX_C3H8O3  - 8 * DI_C3H8O3  + 4 * EX_CH4  - 4 * DI_CH4 + 2 * EX_H2  - 2 *
DI_H2 + 0 * EX_CO - 0 * DI_CO + 2 * EX_H2O - 2 * D_H2O - 0 * D_CO2 = 0;
AO_NET + 3 * EX_C3H8O3  - 3 * DI_C3H8O3  + 0 * EX_CH4  - 0 * DI_CH4 + 0 * EX_H2  - 0 *
DI_H2 + 1 * EX_CO - 1 * DI_CO + 1 * EX_H2O - 1 * D_H2O - 2 * D_CO2 = 0;

@FREE(AC_NET);
@FREE(AH_NET);
@FREE(AO_NET);
@FREE(EX_C3H8O3);
@FREE(EX_CH4);
@FREE(EX_H2O);
@FREE(D_CO2);
@FREE(EX_H2);
@FREE(EX_CO);
!overall mass balanced equations for the MWCHOSYN);
IN_C3H8O3  = (IS_C3H8O3 + EX_C3H8O3 ) ;
Out_C3H8O3 = ( DI_C3H8O3) ;

IN_CH4     = (IS_CH4 + EX_CH4 );
Out_CH4    = (DI_CH4);

IN_H2      = (IS_H2 + EX_H2 );
Out_H2     = ( DI_H2);

IN_CO      = (IS_CO + EX_CO ) ;
Out_CO     = (DI_CO);

D_CO2 >  0;
EX_H2O > 0;
DI_H2O > 0;
EX_C3H8O3 > 0;
DI_C3H8O3 > 0;
```

```
EX_CO > 0;
DI_CO > 0;

EX_H2 > 0;
DI_H2 > 0;

EX_CH4 > 0;
DI_CH4 > 0;

(IN_C3H8O3 - Out_C3H8O3 ) + (IN_CH4 - Out_CH4) + (IS_CO2 - D_CO2) + (IN_H2 - Out_H2 ) +
(IN_CO - Out_CO) + (EX_H2O - D_H2O) = CH3OH_DEMAND + C3H8O2_DEMAND + C3H4O_DEMAND;

OVR_C3H8O3        = (IN_C3H8O3 - Out_C3H8O3)    ;
OVR_CO            = (IN_CO - Out_CO)            ;
OVR_CO2           = (IS_CO2    - D_CO2)         ;
OVR_H2            = (IN_H2 - Out_H2 );
OVR_CH4           = (IN_CH4 - Out_CH4)          ;
OVR_H2O           = (EX_H2O - D_H2O)           ;



@FREE(OVR_C3H8O3);
@FREE(OVR_CO);
@FREE(OVR_CO2);
@FREE(OVR_H2);
@FREE(OVR_CH4);
@FREE(OVR_H2O);


! X STANDS FOR STOICHMETRIC COEFFICIENT FOR A SET OF EQUATIONS DETERMINED BY THE

MWCHOSYN; The set of equations represents the interceptors needed to transfer the

incoming chemical species to participating plant demands;

(x5    + x8   + x9  )                                                    = OVR_C3H8O3
;
 (x1   - x3   + x6   - x7  )                                             = OVR_CO ;
 (x2   - x4   - 3*x5 - x6   + x7  )                                      = OVR_CO2;
 (2*x1 + 3*x2 - 3*x3 - 4*x4 - 7*x5 - x6  + x7 + x8 )                     = OVR_H2;
 (-1*x2+ x3   + 2*x4 + 3*x5 + x6_  - x7  - x8 - 2*x9)                    = OVR_H2O;
 (x3   + x4          )                                                   = OVR_CH4;
 (x1   + x2        )                                                     =
 CH3OH_DEMAND;
 (x8            )                                                        = C3H8O2
 _DEMAND;
 (x9           )                                                         =
 C3H4O_DEMAND;

 x1>0;
 x2>0;
 x3 >0;
 x4>0;
 x5>0;
 x6>0;
 x7 > 0;
 x6 + x7 < 1;
 x8>0;
 x9>0;
 !purchased chemical species costs;
 COST_C3H8O3       = (EX_C3H8O3)  * 1.2    * 24 * 300 ;
 COST_CH4          = (EX_CH4)     * 1      * 24 * 300  ;
 COST_H2           = (EX_H2 )     * 2      * 24 * 300       ;
 COST_CO           = (EX_CO )     * 1      * 24 * 300     ;

 !sold chemical species profits;
 PROFIT_CH3OH      = CH3OH_DEMAND  * 53   * 24 * 300  ;
```

```
PROFIT_C3H8O2     = C3H8O2_DEMAND * 80    * 24 * 300  ;
PROFIT C3H40      = C3H4O DEMAND  * 72    * 24 * 300  ;
!mass network operating costs;
Production_cost_1 = 19.52 * x1 * 24 * 300    ;
Production_cost_2 = 32.32 * x2 * 24 * 300    ;
Production_cost_3 = 1.98  * x3 * 24 * 300    ;
Production_cost_4 = 2.64  * x4 * 24 * 300    ;
Production_cost_5 = 18.2  * x5 * 24 * 300    ;
Production_cost_6 = 0.1   * x6 * 24 * 300    ;
Production_cost_7 = 2.8   * x7 * 24 * 300    ;
Production_cost_8 = 64.6  * x8 * 24 * 300    ;
Production_cost_9 = 23.52 * x9 * 24 * 300    ;
Total_production_cost = Production_cost_1 + Production_cost_2 + Production_cost_3 +
Production_cost_4 + Production_cost_5 + Production_cost_6 + Production_cost_7 +
Production_cost_8+Production_cost_9;

!mass network equipment costs;
EQUIP_cost_1 = (0.31 * (x1) * 32) * 24 * 300   ;
EQUIP_cost_2 = (0.49  * (x2) * 32)* 24 * 300   ;
EQUIP_cost_3 = (0.29 * (x3)  * 3) * 24 * 300  ;
EQUIP_cost_4 = (0.29 * (x4)  * 4) * 24 * 300    ;
EQUIP_cost_5 = (0.66 * (x5)  * 7) * 24 * 300    ;
EQUIP_cost_6 = (0.1  * (x6))      * 24 * 300        ;
EQUIP_cost_7 = (0.1  * (x7) * 28) * 24 * 300        ;
EQUIP_cost_8 = (0.18 * (x8) * 76) * 24 * 300 ;
EQUIP_cost_9 = (0.21 * (x9) * 56) * 24 * 300    ;

! mass network capital costs
using factorial method;
PPC_1 = 3.47*EQUIP_cost_1;
IPC_1 = 0.45* PPC_1;
Fixed_cost_1 = PPC_1+IPC_1;
Capital_cost_1 = Fixed_cost_1*1.18;

PPC_2 = 3.47*EQUIP_cost_2;
IPC_2 = 0.45* PPC_2;
Fixed_cost_2 = PPC_2+IPC_2;
Capital_cost_2 = Fixed_cost_2*1.18;

PPC_3          = 3.47*       EQUIP_cost_3;
IPC 3          = 0.45*              PPC 3;
Fixed cost 3   =        PPC 3+      IPC 3;
Capital_cost_3 = Fixed_cost_3*1.18;

PPC_4          = 3.47*       EQUIP_cost_4;
IPC 4          = 0.45*              PPC 4;
Fixed cost 4   =        PPC 4+      IPC 4;
Capital_cost_4 = Fixed_cost_4*1.18;

PPC_5          = 3.47*       EQUIP_cost_5;
IPC 5          = 0.45*              PPC 5;
Fixed cost 5   =        PPC 5+      IPC 5;
Capital_cost_5 = Fixed_cost_5*1.18;

PPC_6          = 3.47*       EQUIP_cost_6;
IPC 6          = 0.45*              PPC 6;
Fixed cost 6   =        PPC 6+      IPC 6;
Capital_cost_6 = Fixed_cost_6*1.18;

PPC_7          = 3.47*       EQUIP_cost_7;
IPC_7          = 0.45*              PPC_7;
Fixed cost 7   =        PPC 7+      IPC 7;
Capital_cost_7 = Fixed_cost_7*1.18;


PPC_8          = 3.47*       EQUIP_cost_8;
IPC_8          = 0.45*              PPC_8;
Fixed_cost_8   =        PPC_8+      IPC_8;
```

```
Capital_cost_8 = Fixed_cost_8*1.18;

PPC_9          = 3.47*       EQUIP_cost_9;
IPC 9          = 0.45*              PPC 9;
Fixed cost 9   =        PPC 9+      IPC 9;
Capital_cost_9 = Fixed_cost_9*1.18;

Cost_piping      = 5 * ( 300 + 50 + 150 + 150 + 200 + 200 + 200 + 200) ;
Total_capital_cost = Cost_piping + Capital_cost_1 + Capital_cost_2 + Capital_cost_3 +
Capital_cost_4 + Capital_cost_5 + Capital_cost_6 + Capital_cost_7 + Capital_cost_8 +
Capital_cost_9 ;

!annual sales;
Annual_sales = PROFIT_CH3OH + PROFIT_C3H8O2 + PROFIT_C3H40 - (EX_H2O*1.2) -   COST_C3H8O3 -
COST_CH4 - COST_H2 - COST_CO   -Total_production_cost;

!Annual_sales = ((PROFIT_CH3OH + PROFIT_C3H8O2 + PROFIT_C3H40 - COST_C3H8O3 - COST_CH4 -
COST_H2 - COST_CO   -(Total_production_cost+AFC))*(1-0.25)) + AFC ;
!ROI          = ( Annual_sales/ Total_Capital_cost) * 100 ;
!SWROIM = (Annual_sales *100* ( 1 + (0.1*((15000-D_CO2)/10000)) + (0.1*((10000-
D_H2O)/10000))) )/Total_capital_cost ;
!SASWROIM = Annual_sales * (1 + ((0.1*((15000- D_CO2)/(15000-1000))) + (0.1*((15000 -
F_discharge)/(1000-0))))))/Total_Capital_cost;


!CO2_base             = 15000 ;
!Actual emissions     =  D_CO2 ;
!CO2_target_reduction =
!CO2_actual_reduction = ;
!max = Annual_sales   ;
!min = F_fresh_1 + EX_H2O - ROI   ;
!min = EX_H2O   ;
!D_CO2 > 1;
!ROI > 15;
!objective function;
min =    EX_c3h8o3 + EX_CO + EX_h2 +EX_ch4    ;
!min = F_discharge + D_CO2   ;
!Max = Annual_sales ;
!EX_C3H8O3 < 1000;
```

Appendix 2(a2): LINGO mathematical modeling codes for Scenario 1 – water network

```
!objective function;
Minimum freshwater;

!Water network sinks Demands;
!flowrate(ton/day);
F_demand_1 = 100 ;
F_demand_2 = 20 ;
F_demand_3 = 80 ;
F_demand_4 = 60 ;
F_demand_5_EIP = EX_H2O * 0.432 ;
!water quality (mg/liter);
C_demand_1 = 10 ;
C_demand_2 = 100 ;
C_demand_3 = 20 ;
C_demand_4 = 50 ;
C_demand_5 = 70 ;
!available water sources;
!flowrate(ton/day);
F_available_1 = 100 ;
F_available_2 = 20 ;
F_available_3 = 50 ;
F_available_4 = 100 ;
F_available_5_EIP = D_H2O * 0.432 ;
!available water quality
(mg/liter);
C_available_1 = 100 ;
C_available_2 = 250 ;
C_available_3 = 80 ;
C_available_4 = 200 ;
C_available_5 = 80 ;

!Freshwater quality ;
C_fresh_1 = 10 ;

!regeneration facilities output water quality ;
C_treated_1 = 25  ;
C_treated_2 = 65 ;
! Mixer's water balances;
F_demand_1       =  X_untreated_11 + X_untreated_21 + X_untreated_31 + X_untreated_41 +
X_untreated_51 + X_fresh_11   + X_treated_11 + X_treated_21    ;
F_demand_2       =  X_untreated_12 + X_untreated_22 + X_untreated_32 + X_untreated_42 +
X_untreated_52 + X_fresh_12   + X_treated_12 + X_treated_22    ;
F_demand_3       =  X_untreated_13 + X_untreated_23 + X_untreated_33 + X_untreated_43 +
X_untreated_53 + X_fresh_13   + X_treated_13 + X_treated_23    ;
F_demand_4       =  X_untreated_14 + X_untreated_24 + X_untreated_34 + X_untreated_44 +
X_untreated_54 + X_fresh_14   + X_treated_14 + X_treated_24    ;
F_demand_5_EIP   =  X_untreated_15 + X_untreated_25 + X_untreated_35 + X_untreated_45 +
X_untreated_55 + X_fresh_15   + X_treated_15 + X_treated_25 ;
!Participating plants/mass network Water sources ;
F_available_1   =  F_untreated_1  +  F_going_1  +  F_waste_1  ;
F_available_2   =  F_untreated_2  +  F_going_2  +  F_waste_2  ;
F_available_3   =  F_untreated_3  +  F_going_3  +  F_waste_3  ;
F_available_4   =  F_untreated_4  +  F_going_4  +  F_waste_4  ;
F_available_5_EIP = F_untreated_5 + F_going_5 + F_waste_5 ;
! water from Participating plants/mass network Water sources to the mixers water balance;
F_untreated_1 = X_untreated_11 + X_untreated_12 + X_untreated_13 + X_untreated_14 +
X_untreated_15 ;
F_untreated_2 = X_untreated_21 + X_untreated_22 + X_untreated_23 + X_untreated_24 +
X_untreated_25 ;
F_untreated_3 = X_untreated_31 + X_untreated_32 + X_untreated_33 + X_untreated_34 +
X_untreated_35 ;
F_untreated_4 = X_untreated_41 + X_untreated_42 + X_untreated_43 + X_untreated_44 +
X_untreated_45 ;
```

```
F_untreated_5 = X_untreated_51 + X_untreated_52 + X_untreated_53 +
X_untreated_54 + X_untreated_55 ;

 !regeneration facilities
 water balance;
 F_going_1 = X_going_11 +
 X_going_12                          ;
 F_going_2 = X_going_21 +
 X_going_22                          ;
 F_going_3 = X_going_31 +
 X_going_32                          ;
 F_going_4 = X_going_41 +
 X_going_42                          ;
 F_going_5 = X_going_51 +
 X_going_52                          ;

 F_treated_1 = X_treated_11 + X_treated_12 + X_treated_13 + X_treated_14 +
 X_treated_15;
 F_treated_2 = X_treated_21 + X_treated_22 + X_treated_23 + X_treated_24 +
 X_treated_25;

 F_treated_1 = X_going_11 + X_going_21 + X_going_31 + X_going_41 +
 X_going_51; F_treated_2 = X_going_12 + X_going_22 + X_going_32 +
 X_going_42 + X_going_52 ;

 !freshwater mass balance;
 F_fresh_1   = X_fresh_11 + X_fresh_12 + X_fresh_13 + X_fresh_14     ;
 !F_fresh_1 < F_fresh_max_1;
 !F_fresh_max_1 = 225;


 ! component mass balance;
 !equality constraints for each mixer (participating plants sinks);
 Mixers have to fulfill the participating plant water sinks constraints;
 F_demand_1 * C_demand_1 > (X_untreated_11 * C_available_1) + (X_untreated_21 *
 C_available_2) + (X_untreated_31 * C_available_3) + (X_untreated_41 *
 C_available_4)    + (X_fresh_11 * C_fresh_1)    + (X_treated_11 * C_treated_1) +
 (X_treated_21 * C_treated_2)
 ;
 F_demand_2     * C_demand_2 > (X_untreated_12 * C_available_1) +
 (X_untreated_22 * C_available_2) + (X_untreated_32 * C_available_3) +
 (X_untreated_42 * C_available_4)+ (X_fresh_12 * C_fresh_1)+ (X_treated_12 *
 C_treated_1) + (X_treated_22 * C_treated_2)
 ;
 F_demand_3     * C_demand_3 > (X_untreated_13 * C_available_1) +
 (X_untreated_23 * C_available_2) + (X_untreated_33 * C_available_3) +
 (X_untreated_43 * C_available_4)+ (X_fresh_13 * C_fresh_1)+ (X_treated_13 *
 C_treated_1) + (X_treated_23 * C_treated_2)
 ;
 F_demand_4     * C_demand_4 > (X_untreated_14 * C_available_1) +
 (X_untreated_24 * C_available_2) + (X_untreated_34 * C_available_3) +
 (X_untreated_44 * C_available_4)+ (X_fresh_14 * C_fresh_1)+ (X_treated_14 *
 C_treated_1) + (X_treated_24 * C_treated_2)
 ;

 !discharge water to treatment facility water balance;
 F_discharge = F_waste_1 + F_waste_2 + F_waste_3 +

 F_waste_4                                                    ;

 !F_discharge < F_discharge_max;

 !F_discharge_max = 1000 ;

 !objective function;
 min =  F_fresh_1 ;
```

```
!water network operating costs;
Cost_regeneration_1 = F_treated_1 *
1.5 * 300 ; Cost_regeneration_2 =
F_treated_2 * 0.7 * 300                          ; Cost_fresh= F_fresh_1 * 1 * 300 ;
Cost_treatment       = (F_discharge )     * 2 * 300  ;
Cost_operating_costs          = (F_available_1 + F_available_2 +
F_available_3 + F_available_4 + F_fresh_1) * 1.5     ;
Total_water_costs = (Cost_regeneration_1 + Cost_regeneration_2 + Cost_fresh +
Cost_treatment + Cost_operating_costs )       ;
```

Appendix 2(b): LINGO mathematical modeling codes for Scenario 2

```
!objective function;  maximum
SWROIM (sustainability
weighted return on investment
metric);

!Water network sinks Demands;
!flowrate(ton/day);
F_demand_1 = 100 ;
F_demand_2 = 20 ;
F_demand_3 = 80 ;
F_demand_4 = 60 ;
F_demand_5_EIP = EX_H2O * 0.432 ;
!water quality (mg/liter);
C_demand_1 = 10 ;
C_demand_2 = 100 ;
C_demand_3 = 20 ;
C_demand_4 = 50 ;
C_demand_5 = 70 ;
!available water sources;
!flowrate(ton/day);
F_available_1 = 100 ;
F_available_2 = 20 ;
F_available_3 = 50 ;
F_available_4 = 100 ;
F_available_5_EIP = D_H2O * 0.432 ;
!available water quality
(mg/liter);
C_available_1 = 100 ;
C_available_2 = 250 ;
C_available_3 = 80 ;
C_available_4 = 200 ;
C_available_5 = 80 ;
!Freshwater quality ;
C_fresh_1 = 10 ;
!regeneration facilities output water quality ;
C_treated_1 = 25  ;
C_treated_2 = 65 ;
! Mixer's water balances;
F_demand_1       =  X_untreated_11 + X_untreated_21 + X_untreated_31 + X_untreated_41 +
X_untreated_51 + X_fresh_11   + X_treated_11 + X_treated_21    ;
F_demand_2       =  X_untreated_12 + X_untreated_22 + X_untreated_32 + X_untreated_42 +
X_untreated_52 + X_fresh_12   + X_treated_12 + X_treated_22    ;
F_demand_3       =  X_untreated_13 + X_untreated_23 + X_untreated_33 + X_untreated_43 +
X_untreated_53 + X_fresh_13   + X_treated_13 + X_treated_23    ;
F_demand_4       =  X_untreated_14 + X_untreated_24 + X_untreated_34 + X_untreated_44 +
X_untreated_54 + X_fresh_14   + X_treated_14 + X_treated_24    ;
F_demand_5_EIP   =  X_untreated_15 + X_untreated_25 + X_untreated_35 + X_untreated_45 +
X_untreated_55 + X_fresh_15   + X_treated_15 + X_treated_25 ;
!Participating plants/mass network Water sources ;
F_available_1   =  F_untreated_1  +  F_going_1  +  F_waste_1  ;
F_available_2   =  F_untreated_2  +  F_going_2  +  F_waste_2  ;
F_available_3   =  F_untreated_3  +  F_going_3  +  F_waste_3  ;
F_available_4   =  F_untreated_4  +  F_going_4  +  F_waste_4  ;
F_available_5_EIP = F_untreated_5 + F_going_5 + F_waste_5 ;
! water from Participating plants/mass network Water sources to the mixers water balance;
F_untreated_1 = X_untreated_11 + X_untreated_12 + X_untreated_13 + X_untreated_14 +
X_untreated_15 ;
F_untreated_2 = X_untreated_21 + X_untreated_22 + X_untreated_23 + X_untreated_24 +
X_untreated_25 ;
F_untreated_3 = X_untreated_31 + X_untreated_32 + X_untreated_33 + X_untreated_34 +
X_untreated_35 ;
F_untreated_4 = X_untreated_41 + X_untreated_42 + X_untreated_43 + X_untreated_44 +
X_untreated_45 ;
```

```
F_untreated_5 = X_untreated_51 + X_untreated_52 + X_untreated_53 + X_untreated_54 +
X_untreated_55 ;

 !regeneration facilities water balance;
 F_going_1 = X_going_11 + X_going_12  ;
 F_going_2 = X_going_21 + X_going_22  ;
 F_going_3 = X_going_31 + X_going_32  ;
 F_going_4 = X_going_41 + X_going_42  ;
 F_going_5 = X_going_51 + X_going_52  ;

 F_treated_1 = X_treated_11 + X_treated_12 + X_treated_13 + X_treated_14 + X_treated_15   ;
 F_treated_2 = X_treated_21 + X_treated_22 + X_treated_23 + X_treated_24 + X_treated_25   ;

 F_treated_1 = X_going_11 + X_going_21 + X_going_31 + X_going_41 + X_going_51;
 F_treated_2 = X_going_12 + X_going_22 + X_going_32 + X_going_42 + X_going_52 ;

 !freshwater mass balance;
 F_fresh_1   = X_fresh_11 + X_fresh_12 + X_fresh_13 + X_fresh_14 + X_fresh_15    ;
 F_fresh_1 < F_fresh_max_1;
 F_fresh_max_1 = 225;

 !component mass balance;

 !equality constraints for each mixer (participating plants sinks);
 Mixers have to fulfill the participating plant water sinks constraints;
 F_demand_1     * C_demand_1 > (X_untreated_11 * C_available_1) + (X_untreated_21 *
 C_available_2) + (X_untreated_31 * C_available_3) + (X_untreated_41 * C_available_4)   +
 (X_untreated_51 * C_available_5) + (X_fresh_11 * C_fresh_1)    + (X_treated_11 * C_treated_
 1) + (X_treated_21 * C_treated_2)    ;
 F_demand_2     * C_demand_2 > (X_untreated_12 * C_available_1) + (X_untreated_22 *
 C_available_2) + (X_untreated_32 * C_available_3) + (X_untreated_42 * C_available_4)   +
 (X_untreated_52 * C_available_5) + (X_fresh_12 * C_fresh_1)    + (X_treated_12 * C_treated_
 1) + (X_treated_22 * C_treated_2)    ;
 F_demand_3     * C_demand_3 > (X_untreated_13 * C_available_1) + (X_untreated_23 *
 C_available_2) + (X_untreated_33 * C_available_3) + (X_untreated_43 * C_available_4)   +
 (X_untreated_53 * C_available_5) + (X_fresh_13 * C_fresh_1)    + (X_treated_13 * C_treated_
 1) + (X_treated_23 * C_treated_2)    ;
 F_demand_4     * C_demand_4 > (X_untreated_14 * C_available_1) + (X_untreated_24 *
 C_available_2) + (X_untreated_34 * C_available_3) + (X_untreated_44 * C_available_4)   +
 (X_untreated_54 * C_available_5) + (X_fresh_14 * C_fresh_1)    + (X_treated_14 * C_treated_
 1) + (X_treated_24 * C_treated_2)    ;
 F_demand_5_EIP * C_demand_5 > (X_untreated_15 * C_available_1) + (X_untreated_25 *
 C_available_2) + (X_untreated_35 * C_available_3) + (X_untreated_45 * C_available_4)   +
 (X_untreated_55 * C_available_5) + (X_fresh_15 * C_fresh_1)    + (X_treated_15 * C_treated_
 1) + (X_treated_25 * C_treated_2)    ;


 !discharge water to treatment facility water balance;

 F_discharge = F_waste_1 + F_waste_2 + F_waste_3 + F_waste_4 + F_waste_5 ;

 !F_discharge < F_discharge_max;

 !F_discharge_max = 1000 ;


 !F_discharge*C_discharge = (F_waste_1*C_available_1) + (F_waste_2*C_available_2) +
 (F_waste_3*C_available_3) + (F_waste_4*C_available_4) + (F_waste_5*C_EIP_avalaible_H2O) ;
 !Environmental_impact     = (F_discharge*C_discharge) - (F_fresh_1 *C_fresh_1);

 !atomic targeting ;
 !C_DEMAND;
 !IS STANDS FOR INTERNAL SOURCES INSIDE EIP;
 ! Calculation of number of CHO atoms in internal streams;


 IS_CO       = 930;
 IS_CO2      = 3990;
```

```
IS_H2       = 9965;
IS_CH4      = 39;
IS_C3H8O3   = 1000;

AC_SRC  = IS_CO * 1 + IS_CO2 * 1 + IS_CH4 * 1 + IS_C3H8O3 * 3;
AH_SRC      =              IS_H2 * 2 + IS_CH4 * 4 + IS_C3H8O3 * 8;
AO_SRC      = IS_CO * 1 + IS_CO2 * 2              + IS_C3H8O3 * 3;

!DMD STANDS FOR DEMAND BY the participating plants;
! Calculation of number of CHO atoms in demand streams;
CH3OH_DEMAND      = 7500;
C3H8O2_DEMAND     = 1000;
C3H4O_DEMAND      = 1000;

AC_DMD  = CH3OH_DEMAND * 1  + 3 * C3H8O2_DEMAND  + 3 * C3H4O_DEMAND ;
AH_DMD  = CH3OH_DEMAND * 4  + 8 * C3H8O2_DEMAND  + 4 * C3H4O_DEMAND ;
AO_DMD      = CH3OH_DEMAND * 1  + 2 * C3H8O2_DEMAND  + 1 * C3H4O_DEMAND ;

!NET STANDS FOR NET RESULT BETWEEN INTERNAL AND DEMAND streams;
AC_NET      = AC_SRC - AC_DMD;
AH_NET      = AH_SRC - AH_DMD;
AO_NET      = AO_SRC - AO_DMD;

!EX STANDS FOR EXTERNAL SOURCES REQUIRED BY EIP TO ACHIEVE DEMAND REQUESTED BY THE
participating plants while DI is the chemical species discharged in the process;
AC_NET + 3 * EX_C3H8O3  - 3 * DI_C3H8O3  + 1 * EX_CH4  - 1 * DI_CH4 + 0 * EX_H2  - 0 *
DI_H2 + 1 * EX_CO - 1 * DI_CO + 0 * EX_H2O - 0 * D_H2O - 1 * D_CO2 = 0;
AH_NET + 8 * EX_C3H8O3  - 8 * DI_C3H8O3  + 4 * EX_CH4  - 4 * DI_CH4 + 2 * EX_H2  - 2 *
DI_H2 + 0 * EX_CO - 0 * DI_CO + 2 * EX_H2O - 2 * D_H2O - 0 * D_CO2 = 0;
AO_NET + 3 * EX_C3H8O3  - 3 * DI_C3H8O3  + 0 * EX_CH4  - 0 * DI_CH4 + 0 * EX_H2  - 0 *
DI_H2 + 1 * EX_CO - 1 * DI_CO + 1 * EX_H2O - 1 * D_H2O - 2 * D_CO2 = 0;

@FREE(AC_NET);
@FREE(AH_NET);
@FREE(AO_NET);
@FREE(EX_C3H8O3);
@FREE(EX_CH4);
@FREE(EX_H2O);
@FREE(D_CO2);
@FREE(EX_H2);
@FREE(EX_CO);


!overall mass balanced equations for the MWCHOSYN);
IN_C3H8O3   = (IS_C3H8O3 + EX_C3H8O3 ) ;
Out_C3H8O3 = ( DI_C3H8O3) ;

IN_CH4      = (IS_CH4 + EX_CH4 );
Out_CH4     = (DI_CH4);

IN_H2       = (IS_H2 + EX_H2 );
Out_H2      = ( DI_H2);

IN_CO       = (IS_CO + EX_CO ) ;
Out_CO      = (DI_CO);

D_CO2 >  0;
EX_H2O > 0;
DI_H2O > 0;

EX_C3H8O3 > 0;
DI_C3H8O3 > 0;

EX_CO > 0;
DI_CO > 0;

EX_H2 > 0;
DI_H2 > 0;
```

```
EX_CH4 > 0;
DI_CH4 > 0;

(IN_C3H8O3 - Out_C3H8O3 ) + (IN_CH4 - Out_CH4) + (IS_CO2 - D_CO2) + (IN_H2 - Out_H2 ) +
(IN_CO - Out_CO) + (EX_H2O - D_H2O) = CH3OH_DEMAND + C3H8O2_DEMAND + C3H4O_DEMAND;

OVR_C3H8O3        = (IN_C3H8O3 - Out_C3H8O3)    ;
OVR_CO            = (IN_CO - Out_CO)            ;
OVR_CO2           = (IS_CO2    - D_CO2)         ;
OVR_H2            = (IN_H2 - Out_H2 );
OVR_CH4           = (IN_CH4 - Out_CH4)          ;
OVR_H2O           = (EX_H2O - D_H2O)           ;



@FREE(OVR_C3H8O3);
@FREE(OVR_CO);
@FREE(OVR_CO2);
@FREE(OVR_H2);
@FREE(OVR_CH4);
@FREE(OVR_H2O);



! X STANDS FOR STOICHMETRIC COFFICIENT FOR A SET OF EQUATIONS DETERMINED BY THE MWCHOSYN;

(x5   + x8   + x9  )                                                    = OVR_C3H8O3
;
(x1   - x3   + x6   - x7  )                                             = OVR_CO ;
(x2   - x4   - 3*x5 - x6   + x7  )                                      = OVR_CO2;
(2*x1 + 3*x2 - 3*x3 - 4*x4 - 7*x5 - x6  + x7 + x8 )                     = OVR_H2;
(-1*x2+ x3   + 2*x4 + 3*x5 + x6_  - x7  - x8 - 2*x9)                    = OVR_H2O;
(x3   + x4          )                                                   = OVR_CH4;
(x1   + x2        )                                                     =
CH3OH_DEMAND;
(x8            )                                                        = C3H8O2
_DEMAND;
(x9           )                                                         =
C3H4O_DEMAND;

x1>0;
x2>0;
x3 >0;
x4>0;
x5>0;
x6>0;
x7 > 0;
x6 + x7 < 1;
x8>0;
x9>0;


!purchased chemical species costs;
COST_C3H8O3       = (EX_C3H8O3)  * 1.2    * 24 * 300 ;
COST_CH4          = (EX_CH4)     * 1      * 24 * 300  ;
COST_H2           = (EX_H2 )     * 2      * 24 * 300       ;
COST_CO           = (EX_CO )     * 1      * 24 * 300     ;

!sold chemical species profit;
PROFIT_CH3OH      = CH3OH_DEMAND  * 54   * 24 * 300  ;
PROFIT_C3H8O2     = C3H8O2_DEMAND * 85   * 24 * 300  ;
PROFIT_C3H4O      = C3H4O_DEMAND  * 75   * 24 * 300  ;

!mass network operating costs;
Production_cost_1 = 19.52 * x1 * 24 * 300    ;
Production_cost_2 = 32.32 * x2 * 24 * 300    ;
```

```
Production_cost_3 = 1.98  * x3 * 24 * 300  ;
Production_cost_4 = 2.64  * x4 * 24 * 300  ;
Production_cost_5 = 18.2  * x5 * 24 * 300  ;
Production_cost_6 = 0.1   * x6 * 24 * 300  ;
Production_cost_7 = 2.8   * x7 * 24 * 300  ;
Production_cost_8 = 64.6  * x8 * 24 * 300  ;
Production_cost_9 = 23.52 * x9 * 24 * 300   ;
Total_production_cost = Production_cost_1 + Production_cost_2 + Production_cost_3 +
Production_cost_4 + Production_cost_5 + Production_cost_6 + Production_cost_7 +
Production_cost_8+Production_cost_9;

!mass network equipment costs;
EQUIP_cost_1 = (0.31 * (x1) * 32) * 24 * 300  ;
EQUIP_cost_2 = (0.49  * (x2) * 32)* 24 * 300  ;
EQUIP_cost_3 = (0.29 * (x3)  * 3) * 24 * 300  ;
EQUIP_cost_4 = (0.29 * (x4)  * 4) * 24 * 300   ;
EQUIP_cost_5 = (0.66 * (x5)  * 7) * 24 * 300   ;
EQUIP_cost_6 = (0.1  * (x6))      * 24 * 300       ;
EQUIP_cost_7 = (0.1  * (x7) * 28) * 24 * 300       ;
EQUIP_cost_8 = (0.28 * (x8) * 76) * 24 * 300 ;
EQUIP_cost_9 = (0.21 * (x9) * 56) * 24 * 300   ;

! mass network capital costs;
PPC_1 = 3.47*EQUIP_cost_1;
IPC_1 = 0.45* PPC_1;
Fixed_cost_1 = PPC_1+IPC_1;
Capital_cost_1 = Fixed_cost_1*1.18;

PPC_2 = 3.47*EQUIP_cost_2;
IPC_2 = 0.45* PPC_2;
Fixed_cost_2 = PPC_2+IPC_2;
Capital_cost_2 = Fixed_cost_2*1.18;

PPC_3          = 3.47*       EQUIP_cost_3;
IPC 3          = 0.45*              PPC 3;
Fixed cost 3   =        PPC 3+      IPC 3;
Capital_cost_3 = Fixed_cost_3*1.18;

PPC_4          = 3.47*       EQUIP_cost_4;
IPC 4          = 0.45*              PPC 4;
Fixed cost 4   =        PPC 4+      IPC 4;
Capital_cost_4 = Fixed_cost_4*1.18;

PPC_5          = 3.47*       EQUIP_cost_5;
IPC_5          = 0.45*              PPC_5;
Fixed cost 5   =        PPC 5+      IPC 5;
Capital_cost_5 = Fixed_cost_5*1.18;

PPC_6          = 3.47*       EQUIP_cost_6;
IPC 6          = 0.45*              PPC 6;
Fixed cost 6   =        PPC 6+      IPC 6;
Capital_cost_6 = Fixed_cost_6*1.18;

PPC_7          = 3.47*       EQUIP_cost_7;
IPC 7          = 0.45*              PPC 7;
Fixed cost 7   =        PPC 7+      IPC 7;
Capital_cost_7 = Fixed_cost_7*1.18;


PPC_8          = 3.47*       EQUIP_cost_8;
IPC 8          = 0.45*              PPC 8;
Fixed cost 8   =        PPC 8+      IPC 8;
Capital_cost_8 = Fixed_cost_8*1.18;

PPC_9          = 3.47*       EQUIP_cost_9;
IPC 9          = 0.45*              PPC 9;
Fixed_cost_9   =        PPC_9+      IPC_9;
```

```
Capital_cost_9 = Fixed_cost_9*1.18;

Cost_piping      = 5 * ( 300 + 50 + 150 + 150 + 200 + 200 + 200 + 200) ;
Total_capital_cost = Cost_piping + Capital_cost_1 + Capital_cost_2 + Capital_cost_3 +
Capital_cost_4 + Capital_cost_5 + Capital_cost_6 + Capital_cost_7 + Capital_cost_8 +
Capital_cost_9 ;

!annualized fixed costs, sales, return on investment, sustainability weighted return on
investment calculations;
AFC          = 0.1 * Total_capital_cost  ;
Annual_sales = ((PROFIT_CH3OH + PROFIT_C3H8O2 + PROFIT_C3H4O - COST_C3H8O3 - COST_CH4 -
COST_H2 - COST_CO   -(Total_water_costs+Total_production_cost+AFC))*(1-0.25)) + AFC ;
ROI          = ( Annual_sales/ Total_Capital_cost) * 100 ;
SWROIM = (Annual_sales *100* ( 1 + (0.1*((15000-D_CO2)/10000)) + (0.1*((10000-
F_discharge)/10000))) )/Total_capital_cost ;
!SASWROIM = Annual_sales * (1 + ((0.1*((15000- D_CO2)/(15000-1000))) + (0.1*((15000 -
F_discharge)/(1000-0))))))/Total_Capital_cost;


!CO2_base             = 15000 ;
!Actual emissions     =  D_CO2 ;
!CO2_target_reduction =
!CO2_actual_reduction = ;
!max = Annual_sales   ;
!min = F_fresh_1 + EX_H2O - ROI  ;
!min = EX_H2O   ;
!D_CO2 > 1;
!ROI > 15;
!min =  F_fresh_1 +  EX_c3h8o3 + EX_CO + EX_h2 +EX_ch4    ;
!min = F_discharge + D_CO2   ;
Max = SWROIM ;
!EX_C3H8O3 < 1000;


!water network operating costs;
Cost_regeneration_1 = F_treated_1 * 1.5 * 300 ;
Cost_regeneration_2 = F_treated_2 * 0.7 * 300  ;
Cost fresh       = F fresh 1 * 1 * 300 ;
Cost treatment       = (F discharge )     * 2 * 300  ;
Cost_operating_costs          = (F_available_1 + F_available_2 + F_available_3 +
F_available_4 + F_fresh_1) * 1.5   ;
Total_water_costs = (Cost_regeneration_1 + Cost_regeneration_2 + Cost_fresh +
Cost_treatment + Cost_operating_costs  )   ;
!min = F_waste_1 + F_waste_2 + F_waste_3 + F_waste_4;

!max = F_waste_1 + F_waste_2 + F_waste_3 + F_waste_4;
```

Appendix 2(c): LINGO mathematical modeling codes for Scenario 3

```
!objective function;
 Minimum external sources and
freshwater;
!Water network sinks Demands;
!flowrate(ton/day);
F_demand_1 = 100 ;
F_demand_2 = 20 ;
F_demand_3 = 80 ;
F_demand_4 = 60 ;
F_demand_5_EIP = EX_H2O * 0.432 ;
!water quality (mg/liter);
C_demand_1 = 10 ;
C_demand_2 = 100 ;
C_demand_3 = 20 ;
C_demand_4 = 50 ;
C_demand_5 = 70 ;
!available water sources;
!flowrate(ton/day);
F_available_1 = 100 ;
F_available_2 = 20 ;
F_available_3 = 50 ;
F_available_4 = 100 ;
F_available_5_EIP = D_H2O * 0.432 ;
!available water sources
quality (mg/liter);
C_available_1 = 100 ;
C_available_2 = 250 ;
C_available_3 = 80 ;
C_available_4 = 200 ;
C_available_5 = 80 ;

!Freshwater quality ;
C_fresh_1 = 10 ;
!regeneration facilities output water quality ;
C_treated_1 = 25  ;
C_treated_2 = 65 ;
! Mixer's water balances;
F_demand_1       =  X_untreated_11 + X_untreated_21 + X_untreated_31 + X_untreated_41 +
X_untreated_51 + X_fresh_11   + X_treated_11 + X_treated_21    ;
F_demand_2       =  X_untreated_12 + X_untreated_22 + X_untreated_32 + X_untreated_42 +
X_untreated_52 + X_fresh_12   + X_treated_12 + X_treated_22    ;
F_demand_3       =  X_untreated_13 + X_untreated_23 + X_untreated_33 + X_untreated_43 +
X_untreated_53 + X_fresh_13   + X_treated_13 + X_treated_23    ;
F_demand_4       =  X_untreated_14 + X_untreated_24 + X_untreated_34 + X_untreated_44 +
X_untreated_54 + X_fresh_14   + X_treated_14 + X_treated_24    ;
F_demand_5_EIP   =  X_untreated_15 + X_untreated_25 + X_untreated_35 + X_untreated_45 +
X_untreated_55 + X_fresh_15   + X_treated_15 + X_treated_25 ;
!Participating plants/mass network Water sources ;
F_available_1   =  F_untreated_1  +  F_going_1  +  F_waste_1  ;
F_available_2   =  F_untreated_2  +  F_going_2  +  F_waste_2  ;
F_available_3   =  F_untreated_3  +  F_going_3  +  F_waste_3  ;
F_available_4   =  F_untreated_4  +  F_going_4  +  F_waste_4  ;
F_available_5_EIP = F_untreated_5 + F_going_5 + F_waste_5 ;
! water from Participating plants/mass network Water sources to the mixers water balance;
F_untreated_1 = X_untreated_11 + X_untreated_12 + X_untreated_13 + X_untreated_14 +
X_untreated_15 ;
F_untreated_2 = X_untreated_21 + X_untreated_22 + X_untreated_23 + X_untreated_24 +
X_untreated_25 ;
F_untreated_3 = X_untreated_31 + X_untreated_32 + X_untreated_33 + X_untreated_34 +
X_untreated_35 ;
F_untreated_4 = X_untreated_41 + X_untreated_42 + X_untreated_43 + X_untreated_44 +
X_untreated_45 ;
```

```
F_untreated_5 = X_untreated_51 + X_untreated_52 + X_untreated_53 + X_untreated_54 +
X_untreated_55 ;

 !regeneration facilities water balance;
 F_going_1 = X_going_11 + X_going_12  ;
 F_going_2 = X_going_21 + X_going_22  ;
 F_going_3 = X_going_31 + X_going_32  ;
 F_going_4 = X_going_41 + X_going_42  ;
 F_going_5 = X_going_51 + X_going_52  ;

 F_treated_1 = X_treated_11 + X_treated_12 + X_treated_13 + X_treated_14 + X_treated_15   ;
 F_treated_2 = X_treated_21 + X_treated_22 + X_treated_23 + X_treated_24 + X_treated_25   ;

 F_treated_1 = X_going_11 + X_going_21 + X_going_31 + X_going_41 + X_going_51;
 F_treated_2 = X_going_12 + X_going_22 + X_going_32 + X_going_42 + X_going_52 ;

 !freshwater balance;
 F_fresh_1   = X_fresh_11 + X_fresh_12 + X_fresh_13 + X_fresh_14 + X_fresh_15    ;
 !F_fresh_1 < F_fresh_max_1;
 !F_fresh_max_1 = 130;


 !component mass balance;

 !equality constraints for each mixer (participating plants sinks);
 Mixers have to fulfill the participating plant water sinks constraints;
 F_demand_1     * C_demand_1 > (X_untreated_11 * C_available_1) + (X_untreated_21 *
 C_available_2) + (X_untreated_31 * C_available_3) + (X_untreated_41 * C_available_4)   +
 (X_untreated_51 * C_available_5) + (X_fresh_11 * C_fresh_1)    + (X_treated_11 * C_treated_
 1) + (X_treated_21 * C_treated_2)    ;
 F_demand_2     * C_demand_2 > (X_untreated_12 * C_available_1) + (X_untreated_22 *
 C_available_2) + (X_untreated_32 * C_available_3) + (X_untreated_42 * C_available_4)   +
 (X_untreated_52 * C_available_5) + (X_fresh_12 * C_fresh_1)    + (X_treated_12 * C_treated_
 1) + (X_treated_22 * C_treated_2)    ;
 F_demand_3     * C_demand_3 > (X_untreated_13 * C_available_1) + (X_untreated_23 *
 C_available_2) + (X_untreated_33 * C_available_3) + (X_untreated_43 * C_available_4)   +
 (X_untreated_53 * C_available_5) + (X_fresh_13 * C_fresh_1)    + (X_treated_13 * C_treated_
 1) + (X_treated_23 * C_treated_2)    ;
 F_demand_4     * C_demand_4 > (X_untreated_14 * C_available_1) + (X_untreated_24 *
 C_available_2) + (X_untreated_34 * C_available_3) + (X_untreated_44 * C_available_4)   +
 (X_untreated_54 * C_available_5) + (X_fresh_14 * C_fresh_1)    + (X_treated_14 * C_treated_
 1) + (X_treated_24 * C_treated_2)    ;
 F_demand_5_EIP * C_demand_5 > (X_untreated_15 * C_available_1) + (X_untreated_25 *
 C_available_2) + (X_untreated_35 * C_available_3) + (X_untreated_45 * C_available_4)   +
 (X_untreated_55 * C_available_5) + (X_fresh_15 * C_fresh_1)    + (X_treated_15 * C_treated_
 1) + (X_treated_25 * C_treated_2)    ;


 !discharge water to treatment facility water balance;

 F_discharge = F_waste_1 + F_waste_2 + F_waste_3 + F_waste_4 + F_waste_5 ;

 !F_discharge < F_discharge_max;

 !F_discharge_max = 1000 ;
 !F_discharge*C_discharge = (F_waste_1*C_available_1) + (F_waste_2*C_available_2) +
 (F_waste_3*C_available_3) + (F_waste_4*C_available_4) + (F_waste_5*C_EIP_avalaible_H2O) ;
 !Environmental_impact     = (F_discharge*C_discharge) - (F_fresh_1 *C_fresh_1);

 !atomic targeting ;
 !C_DEMAND;
 !IS STANDS FOR INTERNAL SOURCES INSIDE EIP;
 ! Calculation of number of CHO atoms in internal streams;


 IS_CO       = 930;
 IS_CO2      = 3990;
```

```
IS_H2       = 9965;
IS_CH4      = 39;
IS_C3H8O3   = 1000;

AC_SRC  = IS_CO * 1 + IS_CO2 * 1 + IS_CH4 * 1 + IS_C3H8O3 * 3;
AH_SRC      =              IS_H2 * 2 + IS_CH4 * 4 + IS_C3H8O3 * 8;
AO_SRC      = IS_CO * 1 + IS_CO2 * 2              + IS_C3H8O3 * 3;

!DMD STANDS FOR DEMAND BY the participating plants;
! Calculation of number of CHO atoms in demand streams;
CH3OH_DEMAND      = 7500;
C3H8O2_DEMAND     = 1000;
C3H4O_DEMAND      = 1000;

AC_DMD  = CH3OH_DEMAND * 1  + 3 * C3H8O2_DEMAND  + 3 * C3H4O_DEMAND ;
AH_DMD  = CH3OH_DEMAND * 4  + 8 * C3H8O2_DEMAND  + 4 * C3H4O_DEMAND ;
AO_DMD      = CH3OH_DEMAND * 1  + 2 * C3H8O2_DEMAND  + 1 * C3H4O_DEMAND ;

!NET STANDS FOR NET RESULT BETWEEN INTERNAL AND DEMAND streams;
AC_NET      = AC_SRC - AC_DMD;
AH_NET      = AH_SRC - AH_DMD;
AO_NET      = AO_SRC - AO_DMD;

!EX STANDS FOR EXTERNAL SOURCES REQUIRED BY EIP TO ACHIEVE DEMAND REQUESTED BY THE
participating plants while DI is the chemical species discharged in the process;
AC_NET + 3 * EX_C3H8O3  - 3 * DI_C3H8O3  + 1 * EX_CH4  - 1 * DI_CH4 + 0 * EX_H2  - 0 *
DI_H2 + 1 * EX_CO - 1 * DI_CO + 0 * EX_H2O - 0 * D_H2O - 1 * D_CO2 = 0;
AH_NET + 8 * EX_C3H8O3  - 8 * DI_C3H8O3  + 4 * EX_CH4  - 4 * DI_CH4 + 2 * EX_H2  - 2 *
DI_H2 + 0 * EX_CO - 0 * DI_CO + 2 * EX_H2O - 2 * D_H2O - 0 * D_CO2 = 0;
AO_NET + 3 * EX_C3H8O3  - 3 * DI_C3H8O3  + 0 * EX_CH4  - 0 * DI_CH4 + 0 * EX_H2  - 0 *
DI_H2 + 1 * EX_CO - 1 * DI_CO + 1 * EX_H2O - 1 * D_H2O - 2 * D_CO2 = 0;

@FREE(AC_NET);
@FREE(AH_NET);
@FREE(AO_NET);
@FREE(EX_C3H8O3);
@FREE(EX_CH4);
@FREE(EX_H2O);
@FREE(D_CO2);
@FREE(EX_H2);
@FREE(EX_CO);

!overall mass balanced equations for the MWCHOSYN);
IN_C3H8O3  = (IS_C3H8O3 + EX_C3H8O3 ) ;
Out_C3H8O3 = ( DI_C3H8O3) ;

IN_CH4      = (IS_CH4 + EX_CH4 );
Out_CH4     = (DI_CH4);

IN_H2       = (IS_H2 + EX_H2 );
Out_H2      = ( DI_H2);

IN_CO       = (IS_CO + EX_CO ) ;
Out_CO      = (DI_CO);

D_CO2 >  0;
EX_H2O > 0;
DI_H2O > 0;
!D_H2O < D_H2O_Max ;
D_H2O= 1998;
EX_C3H8O3 > 0;
DI_C3H8O3 > 0;

EX_CO > 0;
DI_CO > 0;

EX_H2 > 0;
```

```
DI_H2 > 0;

EX_CH4 > 0;
DI_CH4 > 0;

(IN_C3H8O3 - Out_C3H8O3 ) + (IN_CH4 - Out_CH4) + (IS_CO2 - D_CO2) + (IN_H2 - Out_H2 ) +
(IN_CO - Out_CO) + (EX_H2O - D_H2O) = CH3OH_DEMAND + C3H8O2_DEMAND + C3H4O_DEMAND;

OVR_C3H8O3        = (IN_C3H8O3 - Out_C3H8O3)    ;
OVR_CO            = (IN_CO - Out_CO)            ;
OVR_CO2           = (IS_CO2    - D_CO2)         ;
OVR_H2            = (IN_H2 - Out_H2 );
OVR_CH4           = (IN_CH4 - Out_CH4)          ;
OVR_H2O           = (EX_H2O - D_H2O)           ;



@FREE(OVR_C3H8O3);
@FREE(OVR_CO);
@FREE(OVR_CO2);
@FREE(OVR_H2);
@FREE(OVR_CH4);
@FREE(OVR_H2O);



! X STANDS FOR STOICHMETRIC COFFICIENT FOR A SET OF EQUATIONS DETERMINED BY THE MWCHOSYN;

(x5   + x8   + x9  )                                                    = OVR_C3H8O3
;
(x1   - x3   + x6   - x7  )                                             = OVR_CO ;
(x2   - x4   - 3*x5 - x6   + x7  )                                      = OVR_CO2;
(2*x1 + 3*x2 - 3*x3 - 4*x4 - 7*x5 - x6  + x7 + x8 )                     = OVR_H2;
(-1*x2+ x3   + 2*x4 + 3*x5 + x6_  - x7  - x8 - 2*x9)                    = OVR_H2O;
(x3   + x4          )                                                   = OVR_CH4;
(x1   + x2        )                                                     =
CH3OH_DEMAND;
(x8           )                                                         = C3H8O2
_DEMAND;
(x9           )                                                         =
C3H4O_DEMAND;

x1>0;
x2>0;
x3 >0;
x4>0;
x5>0;
x6>0;
x7 > 0;
x6 + x7 < 1;
x8>0;
x9>0;


!purchased chemical species costs;
COST_C3H8O3       = (EX_C3H8O3)  * 1.2  * 24 * 300 ;
COST_CH4          = (EX_CH4)     * 1      * 24 * 300  ;
COST_H2           = (EX_H2 )     * 2      * 24 * 300       ;
COST_CO           = (EX_CO )     * 1      * 24 * 300     ;

!sold chemical species profit;
PROFIT_CH3OH      = CH3OH_DEMAND  * 52  * 24 * 300 ;
PROFIT_C3H8O2     = C3H8O2_DEMAND * 78 * 24 * 300  ;
PROFIT_C3H40      = C3H4O_DEMAND  * 75 * 24 * 300  ;

!mass network operating costs;
Production_cost_1 = 19.52 * x1 * 24 * 300    ;
```

```
Production_cost_2 = 32.32 * x2 * 24 * 300  ;
Production_cost_3 = 1.98  * x3 * 24 * 300  ;
Production_cost_4 = 2.64  * x4 * 24 * 300  ;
Production_cost_5 = 18.2  * x5 * 24 * 300  ;
Production_cost_6 = 0.1   * x6 * 24 * 300  ;
Production_cost_7 = 2.8   * x7 * 24 * 300  ;
Production_cost_8 = 64.6  * x8 * 24 * 300  ;
Production_cost_9 = 23.52 * x9 * 24 * 300   ;
Total_production_cost = Production_cost_1 + Production_cost_2 + Production_cost_3 +
Production_cost_4 + Production_cost_5 + Production_cost_6 + Production_cost_7 +
Production_cost_8+Production_cost_9;

!mass network equipment costs;
EQUIP_cost_1 = (0.31 * (x1) * 32) * 24 * 300  ;
EQUIP_cost_2 = (0.49  * (x2) * 32)* 24 * 300  ;
EQUIP_cost_3 = (0.29 * (x3)  * 3) * 24 * 300  ;
EQUIP_cost_4 = (0.29 * (x4)  * 4) * 24 * 300   ;
EQUIP_cost_5 = (0.66 * (x5)  * 7) * 24 * 300   ;
EQUIP_cost_6 = (0.1  * (x6))      * 24 * 300       ;
EQUIP_cost_7 = (0.1  * (x7) * 28) * 24 * 300       ;
EQUIP_cost_8 = (0.28 * (x8) * 76) * 24 * 300 ;
EQUIP_cost_9 = (0.21 * (x9) * 56) * 24 * 300   ;

! mass network capital costs;
PPC_1 = 3.47*EQUIP_cost_1;
IPC_1 = 0.45* PPC_1;
Fixed_cost_1 = PPC_1+IPC_1;
Capital_cost_1 = Fixed_cost_1*1.18;

PPC_2 = 3.47*EQUIP_cost_2;
IPC_2 = 0.45* PPC_2;
Fixed_cost_2 = PPC_2+IPC_2;
Capital_cost_2 = Fixed_cost_2*1.18;

PPC_3          = 3.47*       EQUIP_cost_3;
IPC_3          = 0.45*              PPC_3;
Fixed cost 3   =        PPC 3+      IPC 3;
Capital_cost_3 = Fixed_cost_3*1.18;

PPC_4          = 3.47*       EQUIP_cost_4;
IPC 4          = 0.45*              PPC 4;
Fixed cost 4   =        PPC 4+      IPC 4;
Capital_cost_4 = Fixed_cost_4*1.18;

PPC_5          = 3.47*       EQUIP_cost_5;
IPC 5          = 0.45*              PPC 5;
Fixed cost 5   =        PPC 5+      IPC 5;
Capital_cost_5 = Fixed_cost_5*1.18;

PPC_6          = 3.47*       EQUIP_cost_6;
IPC 6          = 0.45*              PPC 6;
Fixed cost 6   =        PPC 6+      IPC 6;
Capital_cost_6 = Fixed_cost_6*1.18;

PPC_7          = 3.47*       EQUIP_cost_7;
IPC_7          = 0.45*              PPC_7;
Fixed cost 7   =        PPC 7+      IPC 7;
Capital_cost_7 = Fixed_cost_7*1.18;


PPC_8          = 3.47*       EQUIP_cost_8;
IPC_8          = 0.45*              PPC_8;
Fixed cost 8   =        PPC 8+      IPC 8;
Capital_cost_8 = Fixed_cost_8*1.18;

PPC_9          = 3.47*       EQUIP_cost_9;
IPC_9          = 0.45*              PPC_9;
```

```
Fixed_cost_9    =         PPC_9+       IPC_9;
Capital_cost_9 = Fixed_cost_9*1.18;

Cost_piping      = 5 * ( 300 + 50 + 150 + 150 + 200 + 200 + 200 + 200) ;
Total_capital_cost = Cost_piping + Capital_cost_1 + Capital_cost_2 + Capital_cost_3 +
Capital_cost_4 + Capital_cost_5 + Capital_cost_6 + Capital_cost_7 + Capital_cost_8 +
Capital_cost_9 ;

!annualized fixed costs, sales, return on investment, sustainability weighted return on
investment calculations;
AFC          = 0.1 * Total_capital_cost  ;
Annual_sales = ((PROFIT_CH3OH + PROFIT_C3H8O2 + PROFIT_C3H4O - COST_C3H8O3 - COST_CH4 -
COST_H2 - COST_CO   -(Total_water_costs+Total_production_cost+AFC))*(1-0.25)) + AFC ;
ROI          = ( Annual_sales/ Total_Capital_cost) * 100 ;
SWROIM = (Annual_sales *100* ( 1 + (0.2*((15000-D_CO2)/10000)) + (0.2*((10000-
F_discharge)/10000))) )/Total_capital_cost ;
!SASWROIM = Annual_sales * (1 + ((0.1*((15000- D_CO2)/(15000-1000))) + (0.1*((15000 -
F_discharge)/(1000-0))))))/Total_Capital_cost;


!CO2_base             = 15000 ;
!Actual emissions     =  D_CO2 ;
!CO2_target_reduction =
!CO2_actual_reduction = ;
!max = Annual_sales   ;
!min = F_fresh_1 + EX_H2O - ROI  ;
!min = EX_H2O   ;
!D_CO2 > 1;
!ROI > 15;
min =  F_fresh_1 +  EX_c3h8o3 + EX_CO + EX_h2 +EX_ch4    ;
!min = F_discharge + D_CO2   ;
!Max = Annual_sales ;
!EX_C3H8O3 < 1000;


!water network operating costs;
Cost_regeneration_1 = F_treated_1 * 1.5 * 300 ;
Cost_regeneration_2 = F_treated_2 * 0.7 * 300  ;
Cost_fresh       = F_fresh_1 * 1 * 300 ;
Cost_treatment       = (F_discharge )     * 2 * 300  ;
Cost_operating_costs          = (F_available_1 + F_available_2 + F_available_3 +
F_available_4 + F_fresh_1) * 1.5   ;
Total_water_costs = (Cost_regeneration_1 + Cost_regeneration_2 + Cost_fresh +
Cost_treatment + Cost_operating_costs  )   ;
!min = F_waste_1 + F_waste_2 + F_waste_3 + F_waste_4;

!max = F_waste_1 + F_waste_2 + F_waste_3 + F_waste_4;
```

Appendix 3: LINGO model formulation for chapter 5

Appendix 3(a): LINGO mathematical modeling codes for scenario 1 – base case

```
!objective function maximum annual sales;
!Available internal sources for each operation period;
!IS STANDS FOR INTERNAL SOURCES INSIDE EIP;
! Calculation of number of CHO atoms in internal streams;
IS_CO_t1          = 930;
IS_CO2_t1         = 3990;
IS_H2_t1          = 10000;
IS_CH4_t1         = 500 ;
IS_C3H8O3_t1      = 1500;
AC_SRC_t1  = IS_CO_t1 * 1 + IS_CO2_t1 * 1 + IS_CH4_t1 * 1 + IS_C3H8O3_t1 * 3;
AH_SRC_t1   =               IS_H2_t1  * 2 + IS_CH4_t1 * 4 + IS_C3H8O3_t1 * 8;
AO_SRC_t1   = IS_CO_t1 * 1 + IS_CO2_t1 * 2                + IS_C3H8O3_t1 * 3;

IS_CO_t2          = 530;
IS_CO2_t2         = 2000;
IS_H2_t2          = 15000;
IS_CH4_t2         = 2000;
IS_C3H8O3_t2      = 4000;
AC_SRC_t2  = IS_CO_t2 * 1 + IS_CO2_t2 * 1 + IS_CH4_t2 * 1 + IS_C3H8O3_t2 * 3;
AH_SRC_t2   =               IS_H2_t2  * 2 + IS_CH4_t2 * 4 + IS_C3H8O3_t2 * 8;
AO_SRC_t2   = IS_CO_t2 * 1 + IS_CO2_t2 * 2                + IS_C3H8O3_t2 * 3;
!Required demand by each participating plant for each operation period;
!DMD STANDS FOR DEMAND BY FACTORIES;
! Calculation of number of CHO atoms in demand streams;
CH3OH_DEMAND_t1      = 10000;
H2_Demand_t1         = 5000;
C3H8O2_DEMAND_t1     = 2000;
C3H4O_DEMAND_t1      = 2000;
AC_DMD_t1   = CH3OH_DEMAND_t1 * 1                    + 3 * C3H8O2_DEMAND_t1  + 3 *
C3H4O_DEMAND_t1 ;
AH_DMD_t1   = CH3OH_DEMAND_t1 * 4 + 2 * H2_DEMAND_t1 + 8 * C3H8O2_DEMAND_t1  + 4 *
C3H4O_DEMAND_t1 ;
AO_DMD_t1   = CH3OH_DEMAND_t1 * 1                    + 2 * C3H8O2_DEMAND_t1  + 1 *
C3H4O_DEMAND_t1 ;

CH3OH_DEMAND_t2      = 7500;
H2_Demand_t2         = 11000;
C3H8O2_DEMAND_t2     = 1000;
C3H4O_DEMAND_t2      = 1000;
AC_DMD_t2   = CH3OH_DEMAND_t2 * 1                    + 3 * C3H8O2_DEMAND_t2  + 3 *
C3H4O_DEMAND_t2 ;
AH_DMD_t2   = CH3OH_DEMAND_t2 * 4 + 2 * H2_DEMAND_t2 + 8 * C3H8O2_DEMAND_t2  + 4 *
C3H4O_DEMAND_t2 ;
AO_DMD_t2   = CH3OH_DEMAND_t2 * 1                    + 2 * C3H8O2_DEMAND_t2  + 1 *
C3H4O_DEMAND_t2 ;
!Atomic balanced equations to determine a minimum benchmark for required and discharged
chemical species;
!NET STANDS FOR NET RESULT BETWEEN INTERNAL SOURCES AND DEMAND;
!calculated for each operation period;
AC_NET_t1  = AC_SRC_t1 - AC_DMD_t1;
AH_NET_t1  = AH_SRC_t1 - AH_DMD_t1;
AO_NET_t1   = AO_SRC_t1 - AO_DMD_t1;

AC_NET_t2  = AC_SRC_t2 - AC_DMD_t2;
AH_NET_t2  = AH_SRC_t2 - AH_DMD_t2;
AO_NET_t2   = AO_SRC_t2 - AO_DMD_t2;
!Molecular balanced equations for each operation period to determine required flowrates of
external sources and discharged chemical species;
AC_NET_t1 + 3 * EX_C3H8O3_t1    - 3 * DI_C3H8O3_t1  + 1 * EX_CH4_t1  - 1 * DI_CH4_t1 + 0 *
EX_H2_t1   - 0 * DI_H2_t1 + 1 * EX_CO_t1   - 1 * DI_CO_t1 + 0 * EX_H2O_t1 - 0 * DI_H2O_t1 -
1 * D_CO2_t1 = 0;
AH_NET_t1 + 8 * EX_C3H8O3_t1   - 8 * DI_C3H8O3_t1  + 4 * EX_CH4_t1  - 4 * DI_CH4_t1 + 2 *
EX_H2_t1  - 2 * DI_H2_t1 + 0 * EX_CO_t1   - 0 * DI_CO_t1 + 2 * EX_H2O_t1 - 2 * DI_H2O_t1 -
```

```
0 * D_CO2_t1 = 0;
AO_NET_t1 + 3 * EX_C3H8O3_t1   - 3 * DI_C3H8O3_t1  + 0 * EX_CH4_t1  - 0 * DI_CH4_t1 + 0 *
EX_H2_t1  - 0 * DI_H2_t1 + 1 * EX_CO_t1   - 1 * DI_CO_t1 + 1 * EX_H2O_t1 - 1 * DI_H2O_t1 -
2 * D_CO2_t1 = 0;

AC_NET_t2 + 3 * EX_C3H8O3_t2   - 3 * DI_C3H8O3_t2  + 1 * EX_CH4_t2  - 1 * DI_CH4_t2 + 0 *
EX_H2_t2  - 0 * DI_H2_t2 + 1 * EX_CO_t2   - 1 * DI_CO_t2 + 0 * EX_H2O_t2 - 0 * DI_H2O_t2 -
1 * D_CO2_t2 = 0;
AH_NET_t2 + 8 * EX_C3H8O3_t2   - 8 * DI_C3H8O3_t2  + 4 * EX_CH4_t2  - 4 * DI_CH4_t2 + 2 *
EX_H2_t2  - 2 * DI_H2_t2 + 0 * EX_CO_t2   - 0 * DI_CO_t2 + 2 * EX_H2O_t2 - 2 * DI_H2O_t2 -
0 * D_CO2_t2 = 0;
AO_NET_t2 + 3 * EX_C3H8O3_t2   - 3 * DI_C3H8O3_t2  + 0 * EX_CH4_t2  - 0 * DI_CH4_t2 + 0 *
EX_H2_t2  - 0 * DI_H2_t2 + 1 * EX_CO_t2   - 1 * DI_CO_t2 + 1 * EX_H2O_t2 - 1 * DI_H2O_t2 -
2 * D_CO2_t2 = 0;

@free(AC_NET_t1);
@free(AH_NET_t1);
@free(AO_NET_t1);
@free(AC_NET_t2);
@free(AH_NET_t2);
@free(AO_NET_t2);
D_CO2_t1  > 0;
EX_H2O_t1 > 0;
DI_H2O_t1 > 0;
D_CO2_t2  > 0;
EX_H2O_t2 > 0;
DI_H2O_t2 > 0;

EX_C3H8O3_t1    > 0;
DI_C3H8O3_t1    > 0;
EX_C3H8O3_t2    > 0;
DI_C3H8O3_t2    > 0;


EX_CO_t1    > 0;
DI_CO_t1    > 0;
EX_CO_t2    > 0;
DI_CO_t2    > 0;


EX_H2_t1    > 0;
DI_H2_t1    > 0;
EX_H2_t2    > 0;
DI_H2_t2    > 0;

EX_CH4_t1    > 0;
DI_CH4_t1    > 0;
EX_CH4_t2    > 0;
DI_CH4_t2    > 0;

!overall mass balanced equation;
!OVR STANDS FOR THE OVERALL EQUATION FOR THE WHOLE EIP for each operation period;

(EX_C3H8O3_t1 + IS_C3H8O3_t1 - DI_C3H8O3_t1) + (IS_CO_t1 + EX_CO_t1   -DI_CO_t1) + (IS_CO2
_t1 - D_CO2_t1) + (IS_H2_t1 + EX_H2_t1 - H2_DEMAND_t1-DI_H2_t1) + (IS_CH4_t1 + EX_CH4_t1 -
DI_CH4_t1) + (EX_H2O_t1-DI_H2O_t1) = CH3OH_DEMAND_t1 + C3H8O2_DEMAND_t1 + C3H4O_DEMAND_t1;
OVR_C3H8O3_t1  = (EX_C3H8O3_t1 + IS_C3H8O3_t1   - DI_C3H8O3_t1);
OVR_CO_t1      = (IS_CO_t1     + EX_CO_t1       - DI_CO_t1);
OVR_CO2_t1     = (IS_CO2_t1    - D_CO2_t1);
OVR_H2_t1      = (IS_H2_t1     + EX_H2_t1     - H2_DEMAND_t1 -DI_H2_t1);
OVR_CH4_t1     = (IS_CH4_t1    + EX_CH4_t1    -DI_CH4_t1);
OVR_H2O_t1     = (EX_H2O_t1                   -DI_H2O_t1);
OVR_C3H8O2_t1  = (C3H8O2_DEMAND_t1);
OVR_C3H4O_t1   = C3H4O_DEMAND_t1;

(EX_C3H8O3_t2 + IS_C3H8O3_t2 -DI_C3H8O3_t2) + (IS_CO_t2 + EX_CO_t2 -DI_CO_t2) + (IS_CO2_t2
- D_CO2_t2) + (IS_H2_t2 + EX_H2_t2 - H2_DEMAND_t2-DI_H2_t2) + (IS_CH4_t2 + EX_CH4_t2 -
```

```
DI_CH4_t2) + (EX_H2O_t2-DI_H2O_t2) = CH3OH_DEMAND_t2 + C3H8O2_DEMAND_t2 + C3H4O_DEMAND_t2;
OVR_C3H8O3_t2  = (EX_C3H8O3_t2 + IS_C3H8O3_t2 -DI_C3H8O3_t2);
OVR_CO_t2      = (IS_CO_t2     + EX_CO_t2  -DI_CO_t2);
OVR_CO2_t2     = (IS_CO2_t2    - D_CO2_t2);
OVR_H2_t2      = (IS_H2_t2     + EX_H2_t2  - H2_DEMAND_t2-DI_H2_t2);
OVR_CH4_t2     = (IS_CH4_t2    + EX_CH4_t2 - DI_CH4_t2);
OVR_H2O_t2     = (EX_H2O_t2-DI_H2O_t2);
OVR_C3H8O2_t2  = (C3H8O2_DEMAND_t2);
OVR_C3H4O_t2   = C3H4O_DEMAND_t2;

@FREE(OVR_C3H8O3_t1);
@FREE(OVR_CO_t1);
@FREE(OVR_CO2_t1);
@FREE(OVR_H2_t1);
@FREE(OVR_CH4_t1);
@FREE(OVR_H2O_t1);
@FREE(CH3OH_DEMAND_t1);
@FREE(H2_DEMAND_t1);
@FREE(OVR_C3H8O2_t1);
@FREE(C3H8O2_DEMAND_t1);

@FREE(OVR_C3H8O3_t2);
@FREE(OVR_CO_t2);
@FREE(OVR_CO2_t2);
@FREE(OVR_H2_t2);
@FREE(OVR_CH4_t2);
@FREE(OVR_H2O_t2);
@FREE(CH3OH_DEMAND_t2);
@FREE(H2_DEMAND_t2);
@FREE(OVR_C3H8O2_t2);
@FREE(C3H8O2_DEMAND_t2);

! determine the required reactions to achieve the participating plant demands
! X STANDS FOR STOICHIOMETRIC COEFFICIENT FOR A SET OF EQUATIONS DETERMINED BY THE EIP AND
NUMBER OF COMPONENTS PARTICIPATING;

x5_t1   + x8_t1   + x9_t1                                                    = OVR_C3H8O3
_t1;
x1_t1   - x3_t1   + x6_t1   - x7_t1                                          = OVR_CO_t1;
x2_t1   - x4_t1   - 3*x5_t1 - x6_t1   + x7_t1                                = OVR_CO2_t1;
2*x1_t1 + 3*x2_t1 - 3*x3_t1 - 4*x4_t1 - 7*x5_t1 - x6_t1   + x7_t1 + x8_t1    = OVR_H2_t1;
-1*x2_t1+ x3_t1   + 2*x4_t1 + 3*x5_t1 + x6_t1   - x7_t1   - x8_t1 - 2*x9_t1 = OVR_H2O_t1;
x3_t1   + x4_t1                                                              = OVR_CH4_t1;
x1_t1   + x2_t1                                                              =
CH3OH_DEMAND_t1;
x8_t1                                                                        = C3H8O2
_DEMAND_t1;
x9_t1                                                                        =
C3H4O_DEMAND_t1;

x5_t2   + x8_t2   + x9_t2                                                    = OVR_C3H8O3
_t2;
x1_t2   - x3_t2   + x6_t2   - x7_t2                                          = OVR_CO_t2;
x2_t2   - x4_t2   - 3*x5_t2 - x6_t2   + x7_t2                                = OVR_CO2_t2;
2*x1_t2 + 3*x2_t2 - 3*x3_t2 - 4*x4_t2 - 7*x5_t2 - x6_t2   + x7_t2 + x8_t2    = OVR_H2_t2;
-1*x2_t2+ x3_t2   + 2*x4_t2 + 3*x5_t2 + x6_t2   - x7_t2   - x8_t2 - 2*x9_t2 = OVR_H2O_t2;
x3_t2   + x4_t2                                                              = OVR_CH4_t2;
x1_t2   + x2_t2                                                              =
CH3OH_DEMAND_t2;
x8_t2                                                                        = C3H8O2
_DEMAND_t2;
x9_t2                                                                        =
C3H4O_DEMAND_t2;


x1_t1>0;
x2_t1>0;
```

```
x3_t1>0;
x4_t1>0;
x5_t1>0;
x6_t1>0;
x7_t1> 0;
x6_t1 + x7_t1 < 1;
x8_t1>0;
x9_t1>0;

x1_t2>0;
x2_t2>0;
x3_t2>0;
x4_t2>0;
x5_t2>0;
x6_t2>0;
x7_t2> 0;
x6_t2 + x7_t2 < 1;
x8_t2>0;
x9_t2>0;

!CHOSYN Reactions;
!chemical species flowrates per each reaction;
!during t1 operation;


F_H2_x1_P1    = 2*x1_t1;
F_CO_x1_P1    = x1_t1;
F_CH3OH_x1_P1 = x1_t1 ;

F_H2_x2_P1    = 3*x2_t1;
F_CO2_x2_P1   = x2_t1;
F_CH3OH_x2_P1 = x2_t1;
F_H2O_x2_P1   = x2_t1;

F_CH4_x3_P1    = x3_t1;
F_H2O_x3_P1    = x3_t1;
F_H2_x3_P1     = 3*x3_t1;
F_CO_x3_P1     = x3_t1;

F_CH4_x4_P1    = x4_t1;
F_H2O_x4_P1    = 2*x4_t1;
F_H2_x4_P1     = 4*x4_t1;
F_CO2_x4_P1    = x4_t1;

F_C3H8O3_x5_P1 = x5_t1;
F_H2O_x5_P1    = 3*x5_t1;
F_H2_x5_P1     = 7*x5_t1;
F_CO2_x5_P1    = 3*x5_t1;

F_H2O_x6_P1    = x6_t1;
F_CO_x6_P1     = x6_t1;
F_H2_x6_P1     = x6_t1;
F_CO2_x6_P1    = x6_t1;

F_H2_x7_P1    =   x7_t1;
F_CO2_x7_P1   =  x7_t1;
F_H2O_x7_P1   =  x7_t1;
F_CO_x7_P1     = x7_t1;

F_C3H8O3_x8_P1 = x8_t1;
F_H2_x8_P1    =   x8_t1;
F_C3H8O2_x8_P1 = x8_t1;
F_H2O_x8_P1    = x8_t1;

F_C3H8O3_x9_P1 = x9_t1;
F_H2O_x9_P1    = 2*x9_t1;
F_C3H4O_x9_P1  = x9_t1;
```

```
!During t2 operation;

F_H2_x1_P2     = 2*x1_t2;
F_CO_x1_P2     = x1_t2;
F_CH3OH_x1_P2 = x1_t2 ;

F_H2_x2_P2     = 3*x2_t2;
F_CO2_x2_P2    = x2_t2;
F_CH3OH_x2_P2 = x2_t2;
F_H2O_x2_P2    = x2_t2;

F_CH4_x3_P2     = x3_t2;
F_H2O_x3_P2     = x3_t2;
F_H2_x3_P2     = 3*x3_t2;
F_CO_x3_P2     = x3_t2;

F_CH4_x4_P2     = x4_t2;
F_H2O_x4_P2     = 2*x4_t2;
F_H2_x4_P2      = 4*x4_t2;
F_CO2_x4_P2     = x4_t2;

F_C3H8O3_x5_P2 = x5_t2;
F_H2O_x5_P2     = 3*x5_t2;
F_H2_x5_P2      = 7*x5_t2;
F_CO2_x5_P2     = 3*x5_t2;

F_H2O_x6_P2     = x6_t2;
F_CO_x6_P2      = x6_t2;
F_H2_x6_P2      = x6_t2;
F_CO2_x6_P2     = x6_t2;

F_H2_x7_P2    =   x7_t2;
F_CO2_x7_P2    =  x7_t2;
F_H2O_x7_P2    =  x7_t2;
F_CO_x7_P2      = x7_t2;

F_C3H8O3_x8_P2 = x8_t2;
F_H2_x8_P2    =   x8_t2;
F_C3H8O2_x8_P2 = x8_t2;
F_H2O_x8_P2     = x8_t2;

F_C3H8O3_x9_P2 = x9_t2;
F_H2O_x9_P2     = 2*x9_t2;
F_C3H4O_x9_P2  = x9_t2;

!Component Material Balance;
!during t1 operation;
 F_CO_x1_P1      - F_CO_x3_P1      + F_CO_x6_P1      - F_CO_x7_P1 - IS_CO_t1      - EX_CO_t1
+ DI_CO_t1 =0;
 F_H2_x1_P1      + F_H2_x2_P1      - F_H2_x3_P1      - F_H2_x4_P1 - F_H2_x5_P1 - F_H2_x6_P1 +
F_H2_x7_P1 + F_H2_x8_P1 - IS_H2_t1      - EX_H2_t1      + H2_DEMAND_t1 +DI_H2_t1 =0;
 F_CH4_x3_P1     + F_CH4_x4_P1     - IS_CH4_t1     - EX_CH4_t1       +DI_CH4_t1 =0;
 F_C3H8O3_x5_P1 + F_C3H8O3_x8_P1 + F_C3H8O3_x9_P1 - EX_C3H8O3_t1 - IS_C3H8O3_t1    +
DI_C3H8O3_t1 =0;

 F_CH3OH_x1_P1  + F_CH3OH_x2_P1 - CH3OH_DEMAND_t1 =0;
F_C3H8O2_x8_P1 - C3H8O2_DEMAND_t1 =0;
F_C3H4O_x9_P1  - C3H4O_DEMAND_t1 =0;

 -F_H2O_x2_P1 + F_H2O_x3_P1 + F_H2O_x4_P1 + F_H2O_x5_P1 + F_H2O_x6_P1 - F_H2O_x7_P1 -
F_H2O_x8_P1 - F_H2O_x9_P1 - EX_H2O_t1     +DI_H2O_t1 =0;
F_CO2_x2_P1 - F_CO2_x4_P1 - F_CO2_x5_P1 - F_CO2_x6_P1 + F_CO2_x7_P1 - IS_CO2_t1     + D_CO2
_t1  =0;


!during t2 operation;
```

```
F_CO_x1_P2     - F_CO_x3_P2     + F_CO_x6_P2     - F_CO_x7_P2 - IS_CO_t2     - EX_CO_t2
+DI_CO_t2 =0;
F_H2_x1_P2     + F_H2_x2_P2     - F_H2_x3_P2     - F_H2_x4_P2 - F_H2_x5_P2 - F_H2_x6_P2 +
F_H2_x7_P2 + F_H2_x8_P2 - IS_H2_t2     - EX_H2_t2 + H2_DEMAND_t2+DI_H2_t2 =0;
F_CH4_x3_P2    + F_CH4_x4_P2    - IS_CH4_t2    - EX_CH4_t2  + DI_CH4_t2 =0;
F_C3H8O3_x5_P2 + F_C3H8O3_x8_P2 + F_C3H8O3_x9_P2 - EX_C3H8O3_t2 - IS_C3H8O3_t2   +DI_C3H8O3
_t2 =0;

F_CH3OH_x1_P2  + F_CH3OH_x2_P2 - CH3OH_DEMAND_t2 =0;
F_C3H8O2_x8_P2 - C3H8O2_DEMAND_t2 =0;
F_C3H4O_x9_P2  - C3H4O_DEMAND_t2 =0;

 -F_H2O_x2_P2 + F_H2O_x3_P2 + F_H2O_x4_P2 + F_H2O_x5_P2 + F_H2O_x6_P2 - F_H2O_x7_P2 -
F_H2O_x8_P2 - F_H2O_x9_P2 - EX_H2O_t2+DI_H2O_t2 =0;
F_CO2_x2_P2 - F_CO2_x4_P2 - F_CO2_x5_P2 - F_CO2_x6_P2 + F_CO2_x7_P2 - IS_CO2_t2     + D_CO2
_t2 =0;


!Cost analysis;

!COST CALCULATIONS in $/kg for purchased and sold chemical species;

COST_C3H8O3_t1    = EX_C3H8O3_t1 * 115  ;
COST_CH4_t1       = EX_CH4_t1    * 116 ;
COST_H2_t1        = EX_H2_t1     * 50    ;
COST_CO_t1        = EX_CO_t1     * 120   ;
PROFIT_CH3OH_t1   = CH3OH_DEMAND_t1  * 35;
PROFIT_C3H8O2_t1  = C3H8O2_DEMAND_t1 * 380 ;
PROFIT_C3H4O_t1   = C3H4O_DEMAND_t1  * 168 ;

COST_C3H8O3_t2    = EX_C3H8O3_t2 * 115  ;
COST_CH4_t2       = EX_CH4_t2    * 116 ;
COST_H2_t2        = EX_H2_t2     * 3      ;
COST_CO_t2        = EX_CO_t2     * 120    ;
PROFIT_CH3OH_t2   = CH3OH_DEMAND_t2  * 35  ;
PROFIT_C3H8O2_t2  = C3H8O2_DEMAND_t2 * 380 ;
PROFIT_C3H4O_t2   = C3H4O_DEMAND_t2  * 168 ;


!Capital cost calculations using factorial method;
EQUIP_cost_1 = (0.31 * (x1_t1*I1) * 32) + (2.31 * x1_t2*(1-I1) * 32)  ;
EQUIP_cost_2 = (0.49 * (x2_t1*I2) * 32) + (3.4  * x2_t2*(1-I2) * 32)  ;
EQUIP_cost_3 = (0.29 * (x3_t1*I3)  * 3)+ (2.33 * x3_t2*(1-I3)  * 3)  ;
EQUIP_cost_4 = (0.29 * (x4_t1*I4)  * 4)+ (2.33 * x4_t2*(1-I4)  * 4)  ;
EQUIP_cost_5 = (0.66 * (x5_t1*I5)  * 7)+ (4.64 * x5_t2*(1-I5)  * 7)  ;
EQUIP_cost_6 = (0.1  * (x6_t1*I6))    + (0.1  * x6_t2*(1-I6) )      ;
EQUIP_cost_7 = (0.1  * (x7_t1*I7) * 28)    + (0.1  * x7_t2*(1-I7) * 28);
EQUIP_cost_8 = (0.28 * (x8_t1*I8) * 76)+ (2.13 * x8_t2*(1-I8) * 76)  ;
EQUIP_cost_9 = (0.21 * (x9_t1*I9) * 56) + (1.52 * x9_t2*(1-I9) * 56)  ;


PPC_1 = 3.32*EQUIP_cost_1;
IPC_1 = 0.45* PPC_1;
Fixed_cost_1 = PPC_1+IPC_1;
Capital_cost_1 = Fixed_cost_1*1.18;

PPC_2 = 3.32*EQUIP_cost_2;
IPC_2 = 0.45* PPC_2;
Fixed_cost_2 = PPC_2+IPC_2;
Capital_cost_2 = Fixed_cost_2*1.18;

PPC_3          = 3.32*       EQUIP_cost_3;
IPC 3          = 0.45*              PPC 3;
Fixed cost 3   =        PPC 3+      IPC 3;
Capital_cost_3 = Fixed_cost_3*1.18;

PPC_4          = 3.32*       EQUIP_cost_4;
```

```
IPC_4          = 0.45*              PPC_4;
Fixed cost 4   =        PPC 4+      IPC 4;
Capital_cost_4 = Fixed_cost_4*1.18;

PPC_5          = 3.32*       EQUIP_cost_5;
IPC 5          = 0.45*              PPC 5;
Fixed cost 5   =        PPC 5+      IPC 5;
Capital_cost_5 = Fixed_cost_5*1.18;

PPC_6          = 3.32*       EQUIP_cost_6;
IPC 6          = 0.45*              PPC 6;
Fixed cost 6   =        PPC 6+      IPC 6;
Capital_cost_6 = Fixed_cost_6*1.18;

PPC_7          = 3.32*       EQUIP_cost_7;
IPC_7          = 0.45*              PPC_7;
Fixed cost 7   =        PPC 7+      IPC 7;
Capital_cost_7 = Fixed_cost_7*1.18;


PPC_8          = 3.32*       EQUIP_cost_8;
IPC_8          = 0.45*              PPC_8;
Fixed cost 8   =        PPC 8+      IPC 8;
Capital_cost_8 = Fixed_cost_8*1.18;

PPC_9          = 3.32*       EQUIP_cost_9;
IPC_9          = 0.45*              PPC_9;
Fixed cost 9   =        PPC 9+      IPC 9;
Capital_cost_9 = Fixed_cost_9*1.18;



Total_capital_cost = Capital_cost_1 + Capital_cost_2 + Capital_cost_3 + Capital_cost_4 +
Capital_cost_5 + Capital_cost_6 + Capital_cost_7 + Capital_cost_8 + Capital_cost_9 ;

x1_t1        > x1_t2*I1;
x1_t1*(1-I1) < x1_t2;
x2_t1        > x2_t2*I2;
x2_t1*(1-I2) < x2_t2;
x3_t1        > x3_t2*I3;
x3_t1*(1-I3) < x3_t2;
x4_t1        > x4_t2*I4;
x4_t1*(1-I4) < x4_t2;
x5_t1        > x5_t2*I5;
x5_t1*(1-I5) < x5_t2;
x6_t1        > x6_t2*I6;
x6_t1*(1-I6) < x6_t2;
x7_t1        > x7_t2*I7;
x7_t1*(1-I7) < x7_t2;
x8_t1        > x8_t2*I8;
x8_t1*(1-I8) < x8_t2;
x9_t1        > x9_t2*I9;
x9_t1*(1-I9) < x9_t2;
@bin (I1);
@bin (I2);
@bin (I3);
@bin (I4);
@bin (I5);
@bin (I6);
@bin (I7);
@bin (I8);
@bin (I9);

!production cost calculations for each operation period;
Production_cost_1_t1 = 19.52 * x1_t1  ;
Production_cost_2_t1 = 32.32 * x2_t1  ;
Production_cost_3_t1 = 1.98  * x3_t1  ;
```

```
Production_cost_4_t1 = 2.64  * x4_t1  ;
Production_cost_5_t1 = 18.2  * x5_t1  ;
Production_cost_6_t1 =  0.1  * x6_t1  ;
Production_cost_7_t1 =  2.8  * x7_t1  ;
Production_cost_8_t1 = 64.6  * x8_t1  ;
Production_cost_9_t1 = 23.52 * x9_t1  ;
production_cost_t1 = 0.7*( Production_cost_1_t1 + Production_cost_2_t1 + Production_cost_3
_t1 + Production_cost_4_t1 + Production_cost_5_t1 + Production_cost_6_t1 +
Production_cost_7_t1 + Production_cost_8_t1 +Production_cost_9_t1);

Production_cost_1_t2 = 19.52 * x1_t2  ;
Production_cost_2_t2 = 32.32 * x2_t2  ;
Production_cost_3_t2 = 1.98  * x3_t2  ;
Production_cost_4_t2 = 2.64  * x4_t2  ;
Production_cost_5_t2 = 18.2  * x5_t2  ;
Production_cost_6_t2 =  0.1  * x6_t2  ;
Production_cost_7_t2 =  2.8  * x7_t2  ;
Production_cost_8_t2 = 64.6  * x8_t2  ;
Production_cost_9_t2 = 23.52 * x9_t2  ;
production_cost_t2 = 0.3*( Production_cost_1_t2 + Production_cost_2_t2 + Production_cost_3
_t2 + Production_cost_4_t2 + Production_cost_5_t2 + Production_cost_6_t2 +
Production_cost_7_t2 + Production_cost_8_t2 +Production_cost_9_t2);


!sales, ROI calculations;
AFC = 0.1* Total_capital_cost;
sales_t1 = (PROFIT_CH3OH_t1 + PROFIT_C3H8O2_t1 + PROFIT_C3H40_t1 - COST_C3H8O3_t1 -
COST_CH4_t1 - COST_H2_t1 - (COST_CO_t1))*0.5;
sales_t2 = (PROFIT_CH3OH_t2 + PROFIT_C3H8O2_t2 + PROFIT_C3H40_t2 - COST_C3H8O3_t2 -
COST_CH4_t2 - COST_H2_t2 - COST_CO_t2)*0.5;
sales = ((sales_t1 + sales_t2 -(production_cost_t1 + production_cost_t2 + AFC))*(1-0.25))
+ AFC ;
ROI = ( sales/ Total_Capital_cost) * 100 ;
!Min = D_CO2_t1 + D_CO2_t2;
!Min = DI_H2O_t1 + DI_H2O_t2;
ROI > 18;
!Max = ROI;
Total_production_cost_t1 = production_cost_t1  * 24 * 300 ;
Total_production_cost_t2 = production_cost_t2  * 24 * 300 ;
Annual_sales = sales  * 24 * 300;
Capital = Total_capital_cost * 24 * 300;

!SASWROIM = Annual_sales * (1 + ((0.1*((2990- D_CO2)/(2990-0))) + (0.1*((-4000 - EX_H2O)/
(-4000-0))) + (0.1*((35 - Total_PSI)/(35-2)))))/Total_Capital_cost;
!Max = Annual_sales;
!Min = Total_PSI;
!Min = EX_C3H8O3 + EX_CH4;
!min = Total_capital_cost;
!EX_H2 < -3000;

!Objective function;
Max = Annual_sales;


@FREE(COST_C3H8O3_t1);
@FREE(PROFIT_CH3OH_t1);
@FREE(COST_CH4_t1);
@FREE( COST_H2_t1) ;
@FREE( COST_CO_t1) ;
D_CO2_t1 > 0;
@FREE(COST_C3H8O3_t2);
@FREE(PROFIT_CH3OH_t2);
@FREE(COST_CH4_t2);
@FREE( COST_H2_t2) ;
@FREE( COST_CO_t2) ;
D_CO2_t2 > 0;
```

Appendix 3(b): LINGO mathematical modeling codes for scenario 2

```
!objective function maximum return on investment;
!Available internal sources for each operation period;
!IS STANDS FOR INTERNAL SOURCES INSIDE EIP;
! Calculation of number of CHO atoms in internal streams;
IS_CO_t1          = 930;
IS_CO2_t1         = 3990;
IS_H2_t1          = 10000;
IS_CH4_t1         = 500 ;
IS_C3H8O3_t1      = 1500;
AC_SRC_t1  = IS_CO_t1 * 1 + IS_CO2_t1 * 1 + IS_CH4_t1 * 1 + IS_C3H8O3_t1 * 3;
AH_SRC_t1   =                IS_H2_t1  * 2 + IS_CH4_t1 * 4 + IS_C3H8O3_t1 * 8;
AO_SRC_t1   = IS_CO_t1 * 1 + IS_CO2_t1 * 2                 + IS_C3H8O3_t1 * 3;

IS_CO_t2          = 530;
IS_CO2_t2         = 2000;
IS_H2_t2          = 15000;
IS_CH4_t2         = 2000;
IS_C3H8O3_t2      = 4000;
AC_SRC_t2  = IS_CO_t2 * 1 + IS_CO2_t2 * 1 + IS_CH4_t2 * 1 + IS_C3H8O3_t2 * 3;
AH_SRC_t2   =                IS_H2_t2  * 2 + IS_CH4_t2 * 4 + IS_C3H8O3_t2 * 8;
AO_SRC_t2   = IS_CO_t2 * 1 + IS_CO2_t2 * 2                 + IS_C3H8O3_t2 * 3;
!Required demand by each participating plant for each operation period;
!DMD STANDS FOR DEMAND BY FACTORIES;
! Calculation of number of CHO atoms in demand streams;
 CH3OH_DEMAND_t1     = 10000;
H2_Demand_t1         = 5000;
C3H8O2_DEMAND_t1     = 2000;
C3H4O_DEMAND_t1      = 2000;
AC_DMD_t1   = CH3OH_DEMAND_t1 * 1                    + 3 * C3H8O2_DEMAND_t1  + 3 *
C3H4O_DEMAND_t1 ;
AH_DMD_t1   = CH3OH_DEMAND_t1 * 4 + 2 * H2_DEMAND_t1 + 8 * C3H8O2_DEMAND_t1  + 4 *
C3H4O_DEMAND_t1 ;
AO_DMD_t1   = CH3OH_DEMAND_t1 * 1                    + 2 * C3H8O2_DEMAND_t1  + 1 *
C3H4O_DEMAND_t1 ;

CH3OH_DEMAND_t2      = 7500;
H2_Demand_t2         = 11000;
C3H8O2_DEMAND_t2     = 1000;
C3H4O_DEMAND_t2      = 1000;
AC_DMD_t2   = CH3OH_DEMAND_t2 * 1                    + 3 * C3H8O2_DEMAND_t2  + 3 *
C3H4O_DEMAND_t2 ;
AH_DMD_t2   = CH3OH_DEMAND_t2 * 4 + 2 * H2_DEMAND_t2 + 8 * C3H8O2_DEMAND_t2  + 4 *
C3H4O_DEMAND_t2 ;
AO_DMD_t2   = CH3OH_DEMAND_t2 * 1                    + 2 * C3H8O2_DEMAND_t2  + 1 *
C3H4O_DEMAND_t2 ;
!Atomic balanced equations to determine minimum benchmark for required and discharged
chemical species;
!NET STANDS FOR NET RESULT BETWEEN INTERNAL SOURCES AND DEMAND;
AC_NET_t1   = AC_SRC_t1 - AC_DMD_t1;
AH_NET_t1   = AH_SRC_t1 - AH_DMD_t1;
AO_NET_t1   = AO_SRC_t1 - AO_DMD_t1;

AC_NET_t2   = AC_SRC_t2 - AC_DMD_t2;
AH_NET_t2   = AH_SRC_t2 - AH_DMD_t2;
AO_NET_t2   = AO_SRC_t2 - AO_DMD_t2;
!Molecular balanced equations for each operation period to determine required flowrates of
external sources and discharged chemical species;
!EX STANDS FOR EXTERNAL SOURCES REQUIRED BY EIP TO ACHIEVE DEMAND REQUESTED BY THE
FACTORIES;
AC_NET_t1 + 3 * EX_C3H8O3_t1 + 3 * F_C3H8O3_IFS_t1 - 3 * F_C3H8O3_ITS_t1  - 3 * DI_C3H8O3
_t1  + 1 * EX_CH4_t1 + 1 * F_CH4_IFS_t1 - 1 * F_CH4_ITS_t1 - 1 * DI_CH4_t1 + 0 * EX_H2_t1
+ 0 * F_H2_IFS_t1 - 0 * F_H2_ITS_t1 - 0 * DI_H2_t1 + 1 * EX_CO_t1 + 1 * F_CO_IFS_t1 - 1 *
F_CO_ITS_t1  - 1 * DI_CO_t1 + 0 * EX_H2O_t1 - 0 * DI_H2O_t1 - 1 * D_CO2_t1 = 0;
AH_NET_t1 + 8 * EX_C3H8O3_t1 + 8 * F_C3H8O3_IFS_t1 - 8 * F_C3H8O3_ITS_t1  - 8 * DI_C3H8O3
```

```
_t1  + 4 * EX_CH4_t1 + 4 * F_CH4_IFS_t1 - 4 * F_CH4_ITS_t1 - 4 * DI_CH4_t1 + 2 * EX_H2_t1
+ 2 * F_H2_IFS_t1 - 2 * F_H2_ITS_t1 - 2 * DI_H2_t1 + 0 * EX_CO_t1 + 0 * F_CO_IFS_t1 - 0 *
F_CO_ITS_t1  - 0 * DI_CO_t1 + 2 * EX_H2O_t1 - 2 * DI_H2O_t1 - 0 * D_CO2_t1 = 0;
AO_NET_t1 + 3 * EX_C3H8O3_t1 + 3 * F_C3H8O3_IFS_t1 - 3 * F_C3H8O3_ITS_t1  - 3 * DI_C3H8O3
_t1  + 0 * EX_CH4_t1 + 0 * F_CH4_IFS_t1 - 0 * F_CH4_ITS_t1 - 0 * DI_CH4_t1 + 0 * EX_H2_t1
+ 0 * F_H2_IFS_t1 - 0 * F_H2_ITS_t1 - 0 * DI_H2_t1 + 1 * EX_CO_t1 + 1 * F_CO_IFS_t1 - 1 *
F_CO_ITS_t1  - 1 * DI_CO_t1 + 1 * EX_H2O_t1 - 1 * DI_H2O_t1 - 2 * D_CO2_t1 = 0;

AC_NET_t2 + 3 * EX_C3H8O3_t2 + 3 * F_C3H8O3_IFS_t2 - 3 * F_C3H8O3_ITS_t2  - 3 * DI_C3H8O3
_t2  + 1 * EX_CH4_t2 + 1 * F_CH4_IFS_t2 - 1 * F_CH4_ITS_t2 - 1 * DI_CH4_t2 + 0 * EX_H2_t2
+ 0 * F_H2_IFS_t2 - 0 * F_H2_ITS_t2 - 0 * DI_H2_t2 + 1 * EX_CO_t2 + 1 * F_CO_IFS_t2 - 1 *
F_CO_ITS_t2  - 1 * DI_CO_t2 + 0 * EX_H2O_t2 - 0 * DI_H2O_t2 - 1 * D_CO2_t2 = 0;
AH_NET_t2 + 8 * EX_C3H8O3_t2 + 8 * F_C3H8O3_IFS_t2 - 8 * F_C3H8O3_ITS_t2  - 8 * DI_C3H8O3
_t2  + 4 * EX_CH4_t2 + 4 * F_CH4_IFS_t2 - 4 * F_CH4_ITS_t2 - 4 * DI_CH4_t2 + 2 * EX_H2_t2
+ 2 * F_H2_IFS_t2 - 2 * F_H2_ITS_t2 - 2 * DI_H2_t2 + 0 * EX_CO_t2 + 0 * F_CO_IFS_t2 - 0 *
F_CO_ITS_t2  - 0 * DI_CO_t2 + 2 * EX_H2O_t2 - 2 * DI_H2O_t2 - 0 * D_CO2_t2 = 0;
AO_NET_t2 + 3 * EX_C3H8O3_t2 + 3 * F_C3H8O3_IFS_t2 - 3 * F_C3H8O3_ITS_t2  - 3 * DI_C3H8O3
_t2  + 0 * EX_CH4_t2 + 0 * F_CH4_IFS_t2 - 0 * F_CH4_ITS_t2 - 0 * DI_CH4_t2 + 0 * EX_H2_t2
+ 0 * F_H2_IFS_t2 - 0 * F_H2_ITS_t2 - 0 * DI_H2_t2 + 1 * EX_CO_t2 + 1 * F_CO_IFS_t2 - 1 *
F_CO_ITS_t2  - 1 * DI_CO_t2 + 1 * EX_H2O_t2 - 1 * DI_H2O_t2 - 2 * D_CO2_t2 = 0;

@free(AC_NET_t1);
@free(AH_NET_t1);
@free(AO_NET_t1);
@free(AC_NET_t2);
@free(AH_NET_t2);
@free(AO_NET_t2);
D_CO2_t1  > 0;
EX_H2O_t1 > 0;
DI_H2O_t1 > 0;
D_CO2_t2  > 0;
EX_H2O_t2 > 0;
DI_H2O_t2 > 0;

EX_C3H8O3_t1    > 0;
DI_C3H8O3_t1    > 0;
F_C3H8O3_IFS_t1 > 0;
F_C3H8O3_ITS_t1 > 0;
EX_C3H8O3_t2    > 0;
DI_C3H8O3_t2    > 0;
F_C3H8O3_IFS_t2 > 0;
F_C3H8O3_ITS_t2 > 0;

EX_CO_t1    > 0;
DI_CO_t1    > 0;
F_CO_IFS_t1 > 0;
F_CO_ITS_t1 > 0;
EX_CO_t2    > 0;
DI_CO_t2    > 0;
F_CO_IFS_t2 > 0;
F_CO_ITS_t2 > 0;

EX_H2_t1    > 0;
DI_H2_t1    > 0;
F_H2_IFS_t1 > 0;
F_H2_ITS_t1 > 0;
EX_H2_t2    > 0;
DI_H2_t2    > 0;
F_H2_IFS_t2 > 0;
F_H2_ITS_t2 > 0;

EX_CH4_t1    > 0;
DI_CH4_t1    > 0;
F_CH4_IFS_t1 > 0;
F_CH4_ITS_t1 > 0;
EX_CH4_t2    > 0;
DI_CH4_t2    > 0;
```

```
F_CH4_IFS_t2 > 0;
F_CH4_ITS_t2 > 0;

!overall mass balanced equation;
!OVR STANDS FOR THE OVERALL EQUATION FOR THE WHOLE EIP;
(EX_C3H8O3_t1 + IS_C3H8O3_t1 + F_C3H8O3_IFS_t1 - F_C3H8O3_ITS_t1 - DI_C3H8O3_t1) +
(IS_CO_t1 + EX_CO_t1+ F_CO_IFS_t1 - F_CO_ITS_t1  -DI_CO_t1) + (IS_CO2_t1 - D_CO2_t1) +
(IS_H2_t1 + EX_H2_t1+ F_H2_IFS_t1 - F_H2_ITS_t1 - H2_DEMAND_t1-DI_H2_t1) + (IS_CH4_t1 +
EX_CH4_t1+ F_CH4_IFS_t1 - F_CH4_ITS_t1 -DI_CH4_t1) + (EX_H2O_t1-DI_H2O_t1) =
CH3OH_DEMAND_t1 + C3H8O2_DEMAND_t1 + C3H4O_DEMAND_t1;
OVR_C3H8O3_t1  = (EX_C3H8O3_t1 + IS_C3H8O3_t1 + F_C3H8O3_IFS_t1 - F_C3H8O3_ITS_t1  -
DI_C3H8O3_t1);
OVR_CO_t1      = (IS_CO_t1     + EX_CO_t1 + F_CO_IFS_t1 - F_CO_ITS_t1       - DI_CO_t1);
OVR_CO2_t1     = (IS_CO2_t1    - D_CO2_t1);
OVR_H2_t1      = (IS_H2_t1     + EX_H2_t1     - H2_DEMAND_t1 + F_H2_IFS_t1 - F_H2_ITS_t1-
DI_H2_t1);
OVR_CH4_t1     = (IS_CH4_t1    + EX_CH4_t1 + F_CH4_IFS_t1 - F_CH4_ITS_t1     -DI_CH4_t1);
OVR_H2O_t1     = (EX_H2O_t1                    -DI_H2O_t1);
OVR_C3H8O2_t1  = (C3H8O2_DEMAND_t1);
OVR_C3H4O_t1   = C3H4O_DEMAND_t1;

(EX_C3H8O3_t2 + IS_C3H8O3_t2+ F_C3H8O3_IFS_t2 - F_C3H8O3_ITS_t2 -DI_C3H8O3_t2) + (IS_CO_t2
+ EX_CO_t2+ F_CO_IFS_t2 - F_CO_ITS_t2 -DI_CO_t2) + (IS_CO2_t2 - D_CO2_t2) + (IS_H2_t2 +
EX_H2_t2+ F_H2_IFS_t2 - F_H2_ITS_t2 - H2_DEMAND_t2-DI_H2_t2) + (IS_CH4_t2 + EX_CH4_t2+
F_CH4_IFS_t2 - F_CH4_ITS_t2 -DI_CH4_t2) + (EX_H2O_t2-DI_H2O_t2) = CH3OH_DEMAND_t2 + C3H8O2
_DEMAND_t2 + C3H4O_DEMAND_t2;
OVR_C3H8O3_t2  = (EX_C3H8O3_t2 + IS_C3H8O3_t2+ F_C3H8O3_IFS_t2 - F_C3H8O3_ITS_t2 -
DI_C3H8O3_t2);
OVR_CO_t2      = (IS_CO_t2     + EX_CO_t2+ F_CO_IFS_t2 - F_CO_ITS_t2  -DI_CO_t2);
OVR_CO2_t2     = (IS_CO2_t2    - D_CO2_t2);
OVR_H2_t2      = (IS_H2_t2     + EX_H2_t2 + F_H2_IFS_t2 - F_H2_ITS_t2 - H2_DEMAND_t2-DI_H2
_t2);
OVR_CH4_t2     = (IS_CH4_t2    + EX_CH4_t2 + F_CH4_IFS_t1 - F_CH4_ITS_t1 -DI_CH4_t2);
OVR_H2O_t2     = (EX_H2O_t2-DI_H2O_t2);
OVR_C3H8O2_t2  = (C3H8O2_DEMAND_t2);
OVR_C3H4O_t2   = C3H4O_DEMAND_t2;

@FREE(OVR_C3H8O3_t1);
@FREE(OVR_CO_t1);
@FREE(OVR_CO2_t1);
@FREE(OVR_H2_t1);
@FREE(OVR_CH4_t1);
@FREE(OVR_H2O_t1);
@FREE(CH3OH_DEMAND_t1);
@FREE(H2_DEMAND_t1);
@FREE(OVR_C3H8O2_t1);
@FREE(C3H8O2_DEMAND_t1);

@FREE(OVR_C3H8O3_t2);
@FREE(OVR_CO_t2);
@FREE(OVR_CO2_t2);
@FREE(OVR_H2_t2);
@FREE(OVR_CH4_t2);
@FREE(OVR_H2O_t2);
@FREE(CH3OH_DEMAND_t2);
@FREE(H2_DEMAND_t2);
@FREE(OVR_C3H8O2_t2);
@FREE(C3H8O2_DEMAND_t2);



! determine the required reactions to achieve the participating plant demands
! X STANDS FOR STOICHMETRIC COEFFICIENT FOR A SET OF EQUATIONS DETERMINED BY THE EIP
AND NUMBER OF COMPONENTS PARTICIPATING;
x5_t1   + x8_t1   + x9_t1                                                  = OVR_C3H8O3
 t1;
x1_t1   - x3_t1   + x6_t1   - x7_t1                                        = OVR_CO_t1;
```

```
x2_t1   - x4_t1   - 3*x5_t1 - x6_t1   + x7_t1                                  = OVR_CO2_t1;
2*x1_t1 + 3*x2_t1 - 3*x3_t1 - 4*x4_t1 - 7*x5_t1 - x6_t1   + x7_t1 + x8_t1    = OVR_H2_t1;
-1*x2_t1+ x3_t1   + 2*x4_t1 + 3*x5_t1 + x6_t1   - x7_t1   - x8_t1 - 2*x9_t1 = OVR_H2O_t1;
x3_t1   + x4_t1                                                               = OVR_CH4_t1;
x1_t1   + x2_t1                                                               =
CH3OH_DEMAND_t1;
x8_t1                                                                         = C3H8O2
_DEMAND_t1;
x9_t1                                                                         =
C3H4O_DEMAND_t1;

x5_t2   + x8_t2   + x9_t2                                                     = OVR_C3H8O3
_t2;
x1_t2   - x3_t2   + x6_t2   - x7_t2                                           = OVR_CO_t2;
x2_t2   - x4_t2   - 3*x5_t2 - x6_t2   + x7_t2                                 = OVR_CO2_t2;
2*x1_t2 + 3*x2_t2 - 3*x3_t2 - 4*x4_t2 - 7*x5_t2 - x6_t2   + x7_t2 + x8_t2    = OVR_H2_t2;
-1*x2_t2+ x3_t2   + 2*x4_t2 + 3*x5_t2 + x6_t2   - x7_t2   - x8_t2 - 2*x9_t2 = OVR_H2O_t2;
x3_t2   + x4_t2                                                               = OVR_CH4_t2;
x1_t2   + x2_t2                                                               =
CH3OH_DEMAND_t2;
x8_t2                                                                         = C3H8O2
_DEMAND_t2;
x9_t2                                                                         =
C3H4O_DEMAND_t2;


x1_t1>0;
x2_t1>0;
x3_t1>0;
x4_t1>0;
x5_t1>0;
x6_t1>0;
x7_t1> 0;
x6_t1 + x7_t1 < 1;
x8_t1>0;
x9_t1>0;

x1_t2>0;
x2_t2>0;
x3_t2>0;
x4_t2>0;
x5_t2>0;
x6_t2>0;
x7_t2> 0;
x6_t2 + x7_t2 < 1;
x8_t2>0;
x9_t2>0;

!CHOSYN Reactions;
!chemical species flowrate per each reaction;
!during t1 operation;


F_H2_x1_P1    = 2*x1_t1;
F_CO_x1_P1    = x1_t1;
F_CH3OH_x1_P1 = x1_t1 ;

F_H2_x2_P1    = 3*x2_t1;
F_CO2_x2_P1   = x2_t1;
F_CH3OH_x2_P1 = x2_t1;
F_H2O_x2_P1   = x2_t1;

F_CH4_x3_P1    = x3_t1;
F_H2O_x3_P1    = x3_t1;
F_H2_x3_P1     = 3*x3_t1;
F_CO_x3_P1     = x3_t1;
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```
F_CH4_x4_P1     = x4_t1;
F_H2O_x4_P1     = 2*x4_t1;
F_H2_x4_P1      = 4*x4_t1;
F_CO2_x4_P1     = x4_t1;

F_C3H8O3_x5_P1 = x5_t1;
F_H2O_x5_P1     = 3*x5_t1;
F_H2_x5_P1      = 7*x5_t1;
F_CO2_x5_P1     = 3*x5_t1;

F_H2O_x6_P1     = x6_t1;
F_CO_x6_P1      = x6_t1;
F_H2_x6_P1      = x6_t1;
F_CO2_x6_P1     = x6_t1;

F_H2_x7_P1    =   x7_t1;
F_CO2_x7_P1   =  x7_t1;
F_H2O_x7_P1   =  x7_t1;
F_CO_x7_P1     = x7_t1;

F_C3H8O3_x8_P1 = x8_t1;
F_H2_x8_P1    =   x8_t1;
F_C3H8O2_x8_P1 = x8_t1;
F_H2O_x8_P1     = x8_t1;

F_C3H8O3_x9_P1 = x9_t1;
F_H2O_x9_P1     = 2*x9_t1;
F_C3H4O_x9_P1  = x9_t1;

!During t2 operation;

F_H2_x1_P2     = 2*x1_t2;
F_CO_x1_P2     = x1_t2;
F_CH3OH_x1_P2 = x1_t2 ;

F_H2_x2_P2     = 3*x2_t2;
F_CO2_x2_P2    = x2_t2;
F_CH3OH_x2_P2 = x2_t2;
F_H2O_x2_P2    = x2_t2;

F_CH4_x3_P2     = x3_t2;
F_H2O_x3_P2     = x3_t2;
F_H2_x3_P2     = 3*x3_t2;
F_CO_x3_P2     = x3_t2;

F_CH4_x4_P2     = x4_t2;
F_H2O_x4_P2     = 2*x4_t2;
F_H2_x4_P2      = 4*x4_t2;
F_CO2_x4_P2     = x4_t2;

F_C3H8O3_x5_P2 = x5_t2;
F_H2O_x5_P2     = 3*x5_t2;
F_H2_x5_P2      = 7*x5_t2;
F_CO2_x5_P2     = 3*x5_t2;

F_H2O_x6_P2     = x6_t2;
F_CO_x6_P2      = x6_t2;
F_H2_x6_P2      = x6_t2;
F_CO2_x6_P2     = x6_t2;

F_H2_x7_P2    =   x7_t2;
F_CO2_x7_P2   =  x7_t2;
F_H2O_x7_P2   =  x7_t2;
F_CO_x7_P2     = x7_t2;

F_C3H8O3_x8_P2 = x8_t2;
F_H2_x8_P2      = x8_t2;
```

```
F_C3H8O2_x8_P2 = x8_t2;
F_H2O_x8_P2    = x8_t2;

F_C3H8O3_x9_P2 = x9_t2;
F_H2O_x9_P2    = 2*x9_t2;
F_C3H4O_x9_P2  = x9_t2;

!Component Material Balance;
!during t1 operation;
 F_CO_x1_P1     - F_CO_x3_P1     + F_CO_x6_P1     - F_CO_x7_P1 - IS_CO_t1     - EX_CO_t1 -
F_CO_IFS_t1 + F_CO_ITS_t1       + DI_CO_t1 =0;
 F_H2_x1_P1     + F_H2_x2_P1     - F_H2_x3_P1     - F_H2_x4_P1 - F_H2_x5_P1 - F_H2_x6_P1 +
F_H2_x7_P1 + F_H2_x8_P1 - IS_H2_t1     - EX_H2_t1     + H2_DEMAND_t1 - F_H2_IFS_t1 + F_H2
_ITS_t1+DI_H2_t1 =0;
 F_CH4_x3_P1    + F_CH4_x4_P1    - IS_CH4_t1    - EX_CH4_t1 - F_CH4_IFS_t1 + F_CH4_ITS_t1
+DI_CH4_t1 =0;
 F_C3H8O3_x5_P1 + F_C3H8O3_x8_P1 + F_C3H8O3_x9_P1 - EX_C3H8O3_t1 - IS_C3H8O3_t1 - F_C3H8O3
_IFS_t1 + F_C3H8O3_ITS_t1  + DI_C3H8O3_t1 =0;

 F_CH3OH_x1_P1  + F_CH3OH_x2_P1 - CH3OH_DEMAND_t1 =0;
F_C3H8O2_x8_P1 - C3H8O2_DEMAND_t1 =0;
F_C3H4O_x9_P1  - C3H4O_DEMAND_t1 =0;

 -F_H2O_x2_P1 + F_H2O_x3_P1 + F_H2O_x4_P1 + F_H2O_x5_P1 + F_H2O_x6_P1 - F_H2O_x7_P1 -
F_H2O_x8_P1 - F_H2O_x9_P1 - EX_H2O_t1    +DI_H2O_t1 =0;
F_CO2_x2_P1 - F_CO2_x4_P1 - F_CO2_x5_P1 - F_CO2_x6_P1 + F_CO2_x7_P1 - IS_CO2_t1    + D_CO2
_t1  =0;


!during t2 operation;
F_CO_x1_P2     - F_CO_x3_P2+ F_CO_x6_P2          - F_CO_x7_P2 - IS_CO_t2     - EX_CO_t2-
F_CO_IFS_t2 + F_CO_ITS_t2  +DI_CO_t2 =0;
F_H2_x1_P2     + F_H2_x2_P2     - F_H2_x3_P2     - F_H2_x4_P2 - F_H2_x5_P2 - F_H2_x6_P2 +
F_H2_x7_P2 + F_H2_x8_P2 - IS_H2_t2     - EX_H2_t2 - F_H2_IFS_t2 + F_H2_ITS_t2 + H2
_DEMAND_t2+DI_H2_t2 =0;
F_CH4_x3_P2    + F_CH4_x4_P2    - IS_CH4_t2    - EX_CH4_t2 - F_CH4_IFS_t1 + F_CH4_ITS_t1 +
DI_CH4_t2 =0;
F_C3H8O3_x5_P2 + F_C3H8O3_x8_P2 + F_C3H8O3_x9_P2 - EX_C3H8O3_t2 - IS_C3H8O3_t2 - F_C3H8O3
_IFS_t2 + F_C3H8O3_ITS_t2 +DI_C3H8O3_t2 =0;

F_CH3OH_x1_P2  + F_CH3OH_x2_P2 - CH3OH_DEMAND_t2 =0;
F_C3H8O2_x8_P2 - C3H8O2_DEMAND_t2 =0;
F_C3H4O_x9_P2  - C3H4O_DEMAND_t2 =0;

 -F_H2O_x2_P2 + F_H2O_x3_P2 + F_H2O_x4_P2 + F_H2O_x5_P2 + F_H2O_x6_P2 - F_H2O_x7_P2 -
F_H2O_x8_P2 - F_H2O_x9_P2 - EX_H2O_t2+DI_H2O_t2 =0;
F_CO2_x2_P2 - F_CO2_x4_P2 - F_CO2_x5_P2 - F_CO2_x6_P2 + F_CO2_x7_P2 - IS_CO2_t2    + D_CO2
_t2 =0;



!Storage and dispatch system mass balanced equation;
!CO;
F_CO_I_storege = F_CO_ITS_t1 + F_CO_ITS_t2  - F_CO_IFS_t1 - F_CO_IFS_t2  ;
!F_CO_ITS_t1 < 2000;
!F_CO_ITS_t2  < 2000;
F_CO_ITS_t1  = F_CO_IFS_t2 ;
F_CO_ITS_t2  =  F_CO_IFS_t1  ;

!F_CO_I_storege_t1 = F_CO_ITS_t1 ;
!F_CO_I_storege_t2 = F_CO_ITS_t1 + F_CO_ITS_t2 - F_CO_IFS_t2  ;
!F_CO_I_storege_t3 = F_CO_ITS_t1 + F_CO_ITS_t2 - F_CO_IFS_t2 - F_CO_IFS_t3  ;



!H2;
F_H2_I_storege = F_H2_ITS_t1 + F_H2_ITS_t2 - F_H2_IFS_t1 - F_H2_IFS_t2 ;
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!F_H2_ITS_t1 < 2000;
!F_H2_ITS_t2 < 2000;
F_H2_ITS_t1 = F_H2_IFS_t2 ;
F_H2_ITS_t2 = F_H2_IFS_t1;
!Ch4;
F_CH4_I_storege = F_CH4_ITS_t1 + F_CH4_ITS_t2  - F_CH4_IFS_t1 - F_CH4_IFS_t2  ;
!C3h8o3;
F_C3h8o3_I_storege = F_C3H8O3_ITS_t1 + F_C3H8O3_ITS_t2  - F_C3H8O3_IFS_t1 - F_C3H8O3
_IFS_t2  ;
!F_C3H8O3_ITS_t1  < 1000;
!F_C3H8O3_ITS_t2 < 1000;
F_C3H8O3_ITS_t1  = F_C3H8O3_IFS_t2;
F_C3H8O3_ITS_t2 =F_C3H8O3_IFS_t1 ;


!Cost analysis;

!COST CALCULATIONS in $/kg for purchased and sold chemical species;
COST_C3H8O3_t1    = EX_C3H8O3_t1 * 115  ;
COST_CH4_t1       = EX_CH4_t1    * 115.84 ;
COST_H2_t1        = EX_H2_t1     * 3      ;
COST_CO_t1        = EX_CO_t1     * 120    ;
PROFIT_CH3OH_t1   = CH3OH_DEMAND_t1  * 35;
PROFIT_C3H8O2_t1  = C3H8O2_DEMAND_t1 * 380 ;
PROFIT_C3H40_t1   = C3H4O_DEMAND_t1  * 168 ;

COST_C3H8O3_t2    = EX_C3H8O3_t2 * 115.2  ;
COST_CH4_t2       = EX_CH4_t2    * 115.84 ;
COST_H2_t2        = EX_H2_t2     * 3.1      ;
COST_CO_t2        = EX_CO_t2     * 120    ;
PROFIT_CH3OH_t2   = CH3OH_DEMAND_t2  * 35  ;
PROFIT_C3H8O2_t2  = C3H8O2_DEMAND_t2 * 380 ;
PROFIT_C3H40_t2   = C3H4O_DEMAND_t2  * 168 ;


!Capital cost calculations using factorial method;
EQUIP_cost_1 = (0.31 * (x1_t1*I1) * 32) + (2.31 * x1_t2*(1-I1) * 32)    ;
EQUIP_cost_2 = (0.49  * (x2_t1*I2) * 32) + (3.4  * x2_t2*(1-I2) * 32);
EQUIP_cost_3 = (0.29 * (x3_t1*I3)  * 3)+ (2.33 * x3_t2*(1-I3)  * 3)  ;
EQUIP_cost_4 = (0.29 * (x4_t1*I4)  * 4)+ (2.33 * x4_t2*(1-I4)  * 4)  ;
EQUIP_cost_5 = (0.66 * (x5_t1*I5)  * 7)+ (4.64 * x5_t2*(1-I5)  * 7)  ;
EQUIP_cost_6 = (0.1  * (x6_t1*I6))    + (0.1  * x6_t2*(1-I6) )      ;
EQUIP_cost_7 = (0.1  * (x7_t1*I7) * 28)    + (0.1  * x7_t2*(1-I7) * 28);
EQUIP_cost_8 = (0.28 * (x8_t1*I8) * 76)+ (2.13 * x8_t2*(1-I8) * 76)  ;
EQUIP_cost_9 = (0.21 * (x9_t1*I9) * 56) + (1.52 * x9_t2*(1-I9) * 56)  ;

PPC_1 = 3.47*EQUIP_cost_1;
IPC_1 = 0.45* PPC_1;
Fixed_cost_1 = PPC_1+IPC_1;
Capital_cost_1 = Fixed_cost_1*1.18;

PPC_2 = 3.47*EQUIP_cost_2;
IPC_2 = 0.45* PPC_2;
Fixed_cost_2 = PPC_2+IPC_2;
Capital_cost_2 = Fixed_cost_2*1.18;

PPC_3          = 3.47*       EQUIP_cost_3;
IPC_3          = 0.45*              PPC_3;
Fixed cost 3   =        PPC 3+      IPC 3;
Capital_cost_3 = Fixed_cost_3*1.18;

PPC_4          = 3.47*       EQUIP_cost_4;
IPC_4          = 0.45*              PPC_4;
Fixed cost 4   =        PPC 4+      IPC 4;
Capital_cost_4 = Fixed_cost_4*1.18;

PPC_5          = 3.47*       EQUIP_cost_5;
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```
IPC_5          = 0.45*              PPC_5;
Fixed cost 5   =        PPC 5+      IPC 5;
Capital_cost_5 = Fixed_cost_5*1.18;

PPC_6          = 3.47*       EQUIP_cost_6;
IPC 6          = 0.45*              PPC 6;
Fixed cost 6   =        PPC 6+      IPC 6;
Capital_cost_6 = Fixed_cost_6*1.18;

PPC_7          = 3.47*       EQUIP_cost_7;
IPC_7          = 0.45*              PPC_7;
Fixed cost 7   =        PPC 7+      IPC 7;
Capital_cost_7 = Fixed_cost_7*1.18;


PPC_8          = 3.47*       EQUIP_cost_8;
IPC 8          = 0.45*              PPC 8;
Fixed cost 8   =        PPC 8+      IPC 8;
Capital_cost_8 = Fixed_cost_8*1.18;

PPC_9          = 3.47*       EQUIP_cost_9;
IPC_9          = 0.45*              PPC_9;
Fixed cost 9   =        PPC 9+      IPC 9;
Capital_cost_9 = Fixed_cost_9*1.18;

capital_cost = Capital_cost_1 + Capital_cost_2 + Capital_cost_3 + Capital_cost_4 +
Capital_cost_5 + Capital_cost_6 + Capital_cost_7 + Capital_cost_8 + Capital_cost_9 ;

x1_t1        > x1_t2*I1;
x1_t1*(1-I1) < x1_t2;
x2_t1        > x2_t2*I2;
x2_t1*(1-I2) < x2_t2;
x3_t1        > x3_t2*I3;
x3_t1*(1-I3) < x3_t2;
x4_t1        > x4_t2*I4;
x4_t1*(1-I4) < x4_t2;
x5_t1        > x5_t2*I5;
x5_t1*(1-I5) < x5_t2;
x6_t1        > x6_t2*I6;
x6_t1*(1-I6) < x6_t2;
x7_t1        > x7_t2*I7;
x7_t1*(1-I7) < x7_t2;
x8_t1        > x8_t2*I8;
x8_t1*(1-I8) < x8_t2;
x9_t1        > x9_t2*I9;
x9_t1*(1-I9) < x9_t2;
@bin (I1);
@bin (I2);
@bin (I3);
@bin (I4);
@bin (I5);
@bin (I6);
@bin (I7);
@bin (I8);
@bin (I9);

!production cost calculations for each operation period;
Production_cost_1_t1 = 19.52 * x1_t1  ;
Production_cost_2_t1 = 32.32 * x2_t1  ;
Production_cost_3_t1 = 1.98  * x3_t1  ;
Production_cost_4_t1 = 2.64  * x4_t1  ;
Production_cost_5_t1 = 18.2  * x5_t1  ;
Production_cost_6_t1 = 0.1   * x6_t1  ;
Production_cost_7_t1 = 2.8   * x7_t1  ;
Production_cost_8_t1 = 64.6  * x8_t1  ;
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```
Production_cost_9_t1 = 23.52 * x9_t1  ;
production_cost_t1 = 0.5*( Production_cost_1_t1 + Production_cost_2_t1 + Production_cost_3
_t1 + Production_cost_4_t1 + Production_cost_5_t1 + Production_cost_6_t1 +
Production_cost_7_t1 + Production_cost_8_t1 +Production_cost_9_t1);

Production_cost_1_t2 = 19.52 * x1_t2  ;
Production_cost_2_t2 = 32.32 * x2_t2  ;
Production_cost_3_t2 = 1.98  * x3_t2  ;
Production_cost_4_t2 = 2.64  * x4_t2  ;
Production_cost_5_t2 = 18.2  * x5_t2  ;
Production_cost_6_t2 =  0.1  * x6_t2  ;
Production_cost_7_t2 =  2.8  * x7_t2  ;
Production_cost_8_t2 = 64.6  * x8_t2  ;
Production_cost_9_t2 = 23.52 * x9_t2  ;
production_cost_t2 = 0.5*( Production_cost_1_t2 + Production_cost_2_t2 + Production_cost_3
_t2 + Production_cost_4_t2 + Production_cost_5_t2 + Production_cost_6_t2 +
Production_cost_7_t2 + Production_cost_8_t2 +Production_cost_9_t2);

!sales, ROI calculations;
AFC = 0.1* capital_cost;
sales_t1 = (PROFIT_CH3OH_t1 + PROFIT_C3H8O2_t1 + PROFIT_C3H40_t1 - COST_C3H8O3_t1 -
COST_CH4_t1 - COST_H2_t1 - (COST_CO_t1))*0.5;
sales_t2 = (PROFIT_CH3OH_t2 + PROFIT_C3H8O2_t2 + PROFIT_C3H40_t2 - COST_C3H8O3_t2 -
COST_CH4_t2 - COST_H2_t2 - COST_CO_t2)*0.5;
sales = ((sales_t1 + sales_t2 -(production_cost_t1 + production_cost_t2 + AFC))*(1-0.25))
+ AFC ;
ROI = ( sales/ Capital_cost) * 100 ;
!Max = Annual_sales;
!Min = D_CO2_t1 + D_CO2_t2;
!Min = DI_H2O_t1 + DI_H2O_t2;
!ROI > 19;

Annual_sales = sales * 24*300;
!Annual_sales_t2 = sales_t2 * 24*300;
Total_production_cost_t1 = production_cost_t1 * 24*300;
Total_production_cost_t2 = production_cost_t2 * 24*300;
Total_capital_cost = capital_cost * 24 * 300;
!SASWROIM = Annual_sales * (1 + ((0.1*((2990- D_CO2)/(2990-0))) + (0.1*((-4000 - EX_H2O)/
(-4000-0))) + (0.1*((35 - Total_PSI)/(35-2)))))/Total_Capital_cost;
!Max = Annual_sales;
!Min = Total_PSI;
!Min = EX_C3H8O3 + EX_CH4;
!min = Total_capital_cost;
!EX_H2 < -3000;

!objective function;
Max = ROI;

@FREE(COST_C3H8O3_t1);
@FREE(PROFIT_CH3OH_t1);
@FREE(COST_CH4_t1);
@FREE( COST_H2_t1) ;
@FREE( COST_CO_t1) ;
D_CO2_t1 > 0;
@FREE(COST_C3H8O3_t2);
@FREE(PROFIT_CH3OH_t2);
@FREE(COST_CH4_t2);
@FREE( COST_H2_t2) ;
@FREE( COST_CO_t2) ;
D_CO2_t2 > 0;
```

Appendix 3(c): LINGO mathematical modeling codes for scenario 3

```
!objective function minimum external sources;
!Available internal sources for each operation period;
!IS STANDS FOR INTERNAL SOURCES INSIDE EIP;
! Calculation of number of CHO atoms in internal streams;
IS_CO_t1          = 930;
IS_CO2_t1         = 3990;
IS_H2_t1          = 10000;
IS_CH4_t1         = 500 ;
IS_C3H8O3_t1      = 1500;
AC_SRC_t1  = IS_CO_t1 * 1 + IS_CO2_t1 * 1 + IS_CH4_t1 * 1 + IS_C3H8O3_t1 * 3;
AH_SRC_t1   =               IS_H2_t1  * 2 + IS_CH4_t1 * 4 + IS_C3H8O3_t1 * 8;
AO_SRC_t1   = IS_CO_t1 * 1 + IS_CO2_t1 * 2                + IS_C3H8O3_t1 * 3;

IS_CO_t2          = 530;
IS_CO2_t2         = 2000;
IS_H2_t2          = 15000;
IS_CH4_t2         = 2000;
IS_C3H8O3_t2      = 4000;
AC_SRC_t2  = IS_CO_t2 * 1 + IS_CO2_t2 * 1 + IS_CH4_t2 * 1 + IS_C3H8O3_t2 * 3;
AH_SRC_t2   =               IS_H2_t2  * 2 + IS_CH4_t2 * 4 + IS_C3H8O3_t2 * 8;
AO_SRC_t2   = IS_CO_t2 * 1 + IS_CO2_t2 * 2                + IS_C3H8O3_t2 * 3;
!Required demand by each participating plant for each operation period;
!DMD STANDS FOR DEMAND BY FACTORIES;
! Calculation of number of CHO atoms in demand streams;
CH3OH_DEMAND_t1      = 10000;
H2_Demand_t1         = 5000;
C3H8O2_DEMAND_t1     = 2000;
C3H4O_DEMAND_t1      = 2000;
AC_DMD_t1   = CH3OH_DEMAND_t1 * 1                    + 3 * C3H8O2_DEMAND_t1  + 3 *
C3H4O_DEMAND_t1 ;
AH_DMD_t1   = CH3OH_DEMAND_t1 * 4 + 2 * H2_DEMAND_t1 + 8 * C3H8O2_DEMAND_t1  + 4 *
C3H4O_DEMAND_t1 ;
AO_DMD_t1   = CH3OH_DEMAND_t1 * 1                    + 2 * C3H8O2_DEMAND_t1  + 1 *
C3H4O_DEMAND_t1 ;

CH3OH_DEMAND_t2      = 7500;
H2_Demand_t2         = 11000;
C3H8O2_DEMAND_t2     = 1000;
C3H4O_DEMAND_t2      = 1000;
AC_DMD_t2   = CH3OH_DEMAND_t2 * 1                    + 3 * C3H8O2_DEMAND_t2  + 3 *
C3H4O_DEMAND_t2 ;
AH_DMD_t2   = CH3OH_DEMAND_t2 * 4 + 2 * H2_DEMAND_t2 + 8 * C3H8O2_DEMAND_t2  + 4 *
C3H4O_DEMAND_t2 ;
AO_DMD_t2   = CH3OH_DEMAND_t2 * 1                    + 2 * C3H8O2_DEMAND_t2  + 1 *
C3H4O_DEMAND_t2 ;
!Atomic balanced equations to determine minimum benchmark for required and discharged
chemical species;
!NET STANDS FOR NET RESULT BETWEEN INTERNAL SOURCES AND DEMAND;
AC_NET_t1   = AC_SRC_t1 - AC_DMD_t1;
AH_NET_t1   = AH_SRC_t1 - AH_DMD_t1;
AO_NET_t1   = AO_SRC_t1 - AO_DMD_t1;

AC_NET_t2  = AC_SRC_t2 - AC_DMD_t2;
AH_NET_t2  = AH_SRC_t2 - AH_DMD_t2;
AO_NET_t2   = AO_SRC_t2 - AO_DMD_t2;

!Molecular balanced equations for each operation period to determine required flowrates of
external sources and discharged chemical species;
!EX STANDS FOR EXTERNAL SOURCES REQUIRED BY EIP TO ACHIEVE DEMAND REQUESTED BY THE
FACTORIES;
AC_NET_t1 + 3 * EX_C3H8O3_t1 + 3 * F_C3H8O3_IFS_t1 - 3 * F_C3H8O3_ITS_t1  - 3 * DI_C3H8O3
_t1  + 1 * EX_CH4_t1 + 1 * F_CH4_IFS_t1 - 1 * F_CH4_ITS_t1 - 1 * DI_CH4_t1 + 0 * EX_H2_t1
+ 0 * F_H2_IFS_t1 - 0 * F_H2_ITS_t1 - 0 * DI_H2_t1 + 1 * EX_CO_t1 + 1 * F_CO_IFS_t1 - 1 *
F_CO_ITS_t1  - 1 * DI_CO_t1 + 0 * EX_H2O_t1 - 0 * DI_H2O_t1 - 1 * D_CO2_t1 = 0;
AH_NET_t1 + 8 * EX_C3H8O3_t1 + 8 * F_C3H8O3_IFS_t1 - 8 * F_C3H8O3_ITS_t1  - 8 * DI_C3H8O3
```

```
_t1  + 4 * EX_CH4_t1 + 4 * F_CH4_IFS_t1 - 4 * F_CH4_ITS_t1 - 4 * DI_CH4_t1 + 2 * EX_H2_t1
+ 2 * F_H2_IFS_t1 - 2 * F_H2_ITS_t1 - 2 * DI_H2_t1 + 0 * EX_CO_t1 + 0 * F_CO_IFS_t1 - 0 *
F_CO_ITS_t1  - 0 * DI_CO_t1 + 2 * EX_H2O_t1 - 2 * DI_H2O_t1 - 0 * D_CO2_t1 = 0;
AO_NET_t1 + 3 * EX_C3H8O3_t1 + 3 * F_C3H8O3_IFS_t1 - 3 * F_C3H8O3_ITS_t1  - 3 * DI_C3H8O3
_t1  + 0 * EX_CH4_t1 + 0 * F_CH4_IFS_t1 - 0 * F_CH4_ITS_t1 - 0 * DI_CH4_t1 + 0 * EX_H2_t1
+ 0 * F_H2_IFS_t1 - 0 * F_H2_ITS_t1 - 0 * DI_H2_t1 + 1 * EX_CO_t1 + 1 * F_CO_IFS_t1 - 1 *
F_CO_ITS_t1  - 1 * DI_CO_t1 + 1 * EX_H2O_t1 - 1 * DI_H2O_t1 - 2 * D_CO2_t1 = 0;

AC_NET_t2 + 3 * EX_C3H8O3_t2 + 3 * F_C3H8O3_IFS_t2 - 3 * F_C3H8O3_ITS_t2  - 3 * DI_C3H8O3
_t2  + 1 * EX_CH4_t2 + 1 * F_CH4_IFS_t2 - 1 * F_CH4_ITS_t2 - 1 * DI_CH4_t2 + 0 * EX_H2_t2
+ 0 * F_H2_IFS_t2 - 0 * F_H2_ITS_t2 - 0 * DI_H2_t2 + 1 * EX_CO_t2 + 1 * F_CO_IFS_t2 - 1 *
F_CO_ITS_t2  - 1 * DI_CO_t2 + 0 * EX_H2O_t2 - 0 * DI_H2O_t2 - 1 * D_CO2_t2 = 0;
AH_NET_t2 + 8 * EX_C3H8O3_t2 + 8 * F_C3H8O3_IFS_t2 - 8 * F_C3H8O3_ITS_t2  - 8 * DI_C3H8O3
_t2  + 4 * EX_CH4_t2 + 4 * F_CH4_IFS_t2 - 4 * F_CH4_ITS_t2 - 4 * DI_CH4_t2 + 2 * EX_H2_t2
+ 2 * F_H2_IFS_t2 - 2 * F_H2_ITS_t2 - 2 * DI_H2_t2 + 0 * EX_CO_t2 + 0 * F_CO_IFS_t2 - 0 *
F_CO_ITS_t2  - 0 * DI_CO_t2 + 2 * EX_H2O_t2 - 2 * DI_H2O_t2 - 0 * D_CO2_t2 = 0;
AO_NET_t2 + 3 * EX_C3H8O3_t2 + 3 * F_C3H8O3_IFS_t2 - 3 * F_C3H8O3_ITS_t2  - 3 * DI_C3H8O3
_t2  + 0 * EX_CH4_t2 + 0 * F_CH4_IFS_t2 - 0 * F_CH4_ITS_t2 - 0 * DI_CH4_t2 + 0 * EX_H2_t2
+ 0 * F_H2_IFS_t2 - 0 * F_H2_ITS_t2 - 0 * DI_H2_t2 + 1 * EX_CO_t2 + 1 * F_CO_IFS_t2 - 1 *
F_CO_ITS_t2  - 1 * DI_CO_t2 + 1 * EX_H2O_t2 - 1 * DI_H2O_t2 - 2 * D_CO2_t2 = 0;

@free(AC_NET_t1);
@free(AH_NET_t1);
@free(AO_NET_t1);
@free(AC_NET_t2);
@free(AH_NET_t2);
@free(AO_NET_t2);
D_CO2_t1  > 0;
EX_H2O_t1 > 0;
DI_H2O_t1 > 0;
D_CO2_t2  > 0;
EX_H2O_t2 > 0;
DI_H2O_t2 > 0;

EX_C3H8O3_t1    > 0;
DI_C3H8O3_t1    > 0;
F_C3H8O3_IFS_t1 > 0;
F_C3H8O3_ITS_t1 > 0;
EX_C3H8O3_t2    > 0;
DI_C3H8O3_t2    > 0;
F_C3H8O3_IFS_t2 > 0;
F_C3H8O3_ITS_t2 > 0;

EX_CO_t1    > 0;
DI_CO_t1    > 0;
F_CO_IFS_t1 > 0;
F_CO_ITS_t1 > 0;
EX_CO_t2    > 0;
DI_CO_t2    > 0;
F_CO_IFS_t2 > 0;
F_CO_ITS_t2 > 0;

EX_H2_t1    > 0;
DI_H2_t1    > 0;
F_H2_IFS_t1 > 0;
F_H2_ITS_t1 > 0;
EX_H2_t2    > 0;
DI_H2_t2    > 0;
F_H2_IFS_t2 > 0;
F_H2_ITS_t2 > 0;

EX_CH4_t1    > 0;
DI_CH4_t1    > 0;
F_CH4_IFS_t1 > 0;
F_CH4_ITS_t1 > 0;
EX_CH4_t2    > 0;
DI_CH4_t2    > 0;
```

```
F_CH4_IFS_t2 > 0;
F_CH4_ITS_t2 > 0;

!overall mass balanced equation;
!OVR STANDS FOR THE OVERALL EQUATION FOR THE WHOLE EIP;
(EX_C3H8O3_t1 + IS_C3H8O3_t1 + F_C3H8O3_IFS_t1 - F_C3H8O3_ITS_t1 - DI_C3H8O3_t1) +
(IS_CO_t1 + EX_CO_t1+ F_CO_IFS_t1 - F_CO_ITS_t1   -DI_CO_t1) + (IS_CO2_t1 - D_CO2_t1) +
(IS_H2_t1 + EX_H2_t1+ F_H2_IFS_t1 - F_H2_ITS_t1 - H2_DEMAND_t1-DI_H2_t1) + (IS_CH4_t1 +
EX_CH4_t1+ F_CH4_IFS_t1 - F_CH4_ITS_t1 -DI_CH4_t1) + (EX_H2O_t1-DI_H2O_t1) =
CH3OH_DEMAND_t1 + C3H8O2_DEMAND_t1 + C3H4O_DEMAND_t1;
OVR_C3H8O3_t1  = (EX_C3H8O3_t1 + IS_C3H8O3_t1 + F_C3H8O3_IFS_t1 - F_C3H8O3_ITS_t1   -
DI_C3H8O3_t1);
OVR_CO_t1      = (IS_CO_t1     + EX_CO_t1 + F_CO_IFS_t1 - F_CO_ITS_t1       - DI_CO_t1);
OVR_CO2_t1     = (IS_CO2_t1    - D_CO2_t1);
OVR_H2_t1      = (IS_H2_t1     + EX_H2_t1     - H2_DEMAND_t1 + F_H2_IFS_t1 - F_H2_ITS_t1-
DI_H2_t1);
OVR_CH4_t1     = (IS_CH4_t1    + EX_CH4_t1 + F_CH4_IFS_t1 - F_CH4_ITS_t1     -DI_CH4_t1);
OVR_H2O_t1     = (EX_H2O_t1                    -DI_H2O_t1);
OVR_C3H8O2_t1  = (C3H8O2_DEMAND_t1);
OVR_C3H4O_t1   = C3H4O_DEMAND_t1;

(EX_C3H8O3_t2 + IS_C3H8O3_t2+ F_C3H8O3_IFS_t2 - F_C3H8O3_ITS_t2 -DI_C3H8O3_t2) + (IS_CO_t2
+ EX_CO_t2+ F_CO_IFS_t2 - F_CO_ITS_t2 -DI_CO_t2) + (IS_CO2_t2 - D_CO2_t2) + (IS_H2_t2 +
EX_H2_t2+ F_H2_IFS_t2 - F_H2_ITS_t2 - H2_DEMAND_t2-DI_H2_t2) + (IS_CH4_t2 + EX_CH4_t2+
F_CH4_IFS_t2 - F_CH4_ITS_t2 -DI_CH4_t2) + (EX_H2O_t2-DI_H2O_t2) = CH3OH_DEMAND_t2 + C3H8O2
_DEMAND_t2 + C3H4O_DEMAND_t2;
OVR_C3H8O3_t2  = (EX_C3H8O3_t2 + IS_C3H8O3_t2+ F_C3H8O3_IFS_t2 - F_C3H8O3_ITS_t2 -
DI_C3H8O3_t2);
OVR_CO_t2      = (IS_CO_t2     + EX_CO_t2+ F_CO_IFS_t2 - F_CO_ITS_t2   -DI_CO_t2);
OVR_CO2_t2     = (IS_CO2_t2    - D_CO2_t2);
OVR_H2_t2      = (IS_H2_t2     + EX_H2_t2 + F_H2_IFS_t2 - F_H2_ITS_t2 - H2_DEMAND_t2-DI_H2
_t2);
OVR_CH4_t2     = (IS_CH4_t2    + EX_CH4_t2 + F_CH4_IFS_t1 - F_CH4_ITS_t1 -DI_CH4_t2);
OVR_H2O_t2     = (EX_H2O_t2-DI_H2O_t2);
OVR_C3H8O2_t2  = (C3H8O2_DEMAND_t2);
OVR_C3H4O_t2   = C3H4O_DEMAND_t2;

@FREE(OVR_C3H8O3_t1);
@FREE(OVR_CO_t1);
@FREE(OVR_CO2_t1);
@FREE(OVR_H2_t1);
@FREE(OVR_CH4_t1);
@FREE(OVR_H2O_t1);
@FREE(CH3OH_DEMAND_t1);
@FREE(H2_DEMAND_t1);
@FREE(OVR_C3H8O2_t1);
@FREE(C3H8O2_DEMAND_t1);

@FREE(OVR_C3H8O3_t2);
@FREE(OVR_CO_t2);
@FREE(OVR_CO2_t2);
@FREE(OVR_H2_t2);
@FREE(OVR_CH4_t2);
@FREE(OVR_H2O_t2);
@FREE(CH3OH_DEMAND_t2);
@FREE(H2_DEMAND_t2);
@FREE(OVR_C3H8O2_t2);
@FREE(C3H8O2_DEMAND_t2);



! determine the required reactions to achieve the participating plant demands
! X STANDS FOR STOICHMETRIC COEFFICIENT FOR A SET OF EQUATIONS DETERMINED BY THE EIP
AND NUMBER OF COMPONENTS PARTICIPATING;
x5_t1   + x8_t1   + x9_t1                                                  = OVR_C3H8O3
 t1;
x1_t1   - x3_t1   + x6_t1   - x7_t1                                        = OVR_CO_t1;
```

```
x2_t1   - x4_t1   - 3*x5_t1 - x6_t1   + x7_t1                                  = OVR_CO2_t1;
2*x1_t1 + 3*x2_t1 - 3*x3_t1 - 4*x4_t1 - 7*x5_t1 - x6_t1   + x7_t1 + x8_t1    = OVR_H2_t1;
-1*x2_t1+ x3_t1   + 2*x4_t1 + 3*x5_t1 + x6_t1    - x7_t1  - x8_t1 - 2*x9_t1 = OVR_H2O_t1;
x3_t1   + x4_t1                                                               = OVR_CH4_t1;
x1_t1   + x2_t1                                                               =
CH3OH_DEMAND_t1;
x8_t1                                                                         = C3H8O2
_DEMAND_t1;
x9_t1                                                                         =
C3H4O_DEMAND_t1;

x5_t2   + x8_t2   + x9_t2                                                     = OVR_C3H8O3
_t2;
x1_t2   - x3_t2   + x6_t2   - x7_t2                                           = OVR_CO_t2;
x2_t2   - x4_t2   - 3*x5_t2 - x6_t2   + x7_t2                                 = OVR_CO2_t2;
2*x1_t2 + 3*x2_t2 - 3*x3_t2 - 4*x4_t2 - 7*x5_t2 - x6_t2   + x7_t2 + x8_t2    = OVR_H2_t2;
-1*x2_t2+ x3_t2   + 2*x4_t2 + 3*x5_t2 + x6_t2    - x7_t2  - x8_t2 - 2*x9_t2 = OVR_H2O_t2;
x3_t2   + x4_t2                                                               = OVR_CH4_t2;
x1_t2   + x2_t2                                                               =
CH3OH_DEMAND_t2;
x8_t2                                                                         = C3H8O2
_DEMAND_t2;
x9_t2                                                                         =
C3H4O_DEMAND_t2;


x1_t1>0;
x2_t1>0;
x3_t1>0;
x4_t1>0;
x5_t1>0;
x6_t1>0;
x7_t1> 0;
x6_t1 + x7_t1 < 1;
x8_t1>0;
x9_t1>0;

x1_t2>0;
x2_t2>0;
x3_t2>0;
x4_t2>0;
x5_t2>0;
x6_t2>0;
x7_t2> 0;
x6_t2 + x7_t2 < 1;
x8_t2>0;
x9_t2>0;

!CHOSYN Reactions;
!chemical species flowrate per each reaction;
!during t1 operation;


F_H2_x1_P1    = 2*x1_t1;
F_CO_x1_P1    = x1_t1;
F_CH3OH_x1_P1 = x1_t1 ;

F_H2_x2_P1    = 3*x2_t1;
F_CO2_x2_P1   = x2_t1;
F_CH3OH_x2_P1 = x2_t1;
F_H2O_x2_P1   = x2_t1;

F_CH4_x3_P1    = x3_t1;
F_H2O_x3_P1    = x3_t1;
F_H2_x3_P1     = 3*x3_t1;
F_CO_x3_P1     = x3_t1;
```

```
F_CH4_x4_P1     = x4_t1;
F_H2O_x4_P1     = 2*x4_t1;
F_H2_x4_P1      = 4*x4_t1;
F_CO2_x4_P1     = x4_t1;

F_C3H8O3_x5_P1 = x5_t1;
F_H2O_x5_P1     = 3*x5_t1;
F_H2_x5_P1      = 7*x5_t1;
F_CO2_x5_P1     = 3*x5_t1;

F_H2O_x6_P1     = x6_t1;
F_CO_x6_P1      = x6_t1;
F_H2_x6_P1      = x6_t1;
F_CO2_x6_P1     = x6_t1;

F_H2_x7_P1    =   x7_t1;
F_CO2_x7_P1   =  x7_t1;
F_H2O_x7_P1   =  x7_t1;
F_CO_x7_P1     = x7_t1;

F_C3H8O3_x8_P1 = x8_t1;
F_H2_x8_P1    =   x8_t1;
F_C3H8O2_x8_P1 = x8_t1;
F_H2O_x8_P1    = x8_t1;

F_C3H8O3_x9_P1 = x9_t1;
F_H2O_x9_P1     = 2*x9_t1;
F_C3H4O_x9_P1  = x9_t1;

!During t2 operation;

F_H2_x1_P2     = 2*x1_t2;
F_CO_x1_P2     = x1_t2;
F_CH3OH_x1_P2 = x1_t2 ;

F_H2_x2_P2     = 3*x2_t2;
F_CO2_x2_P2   = x2_t2;
F_CH3OH_x2_P2 = x2_t2;
F_H2O_x2_P2   = x2_t2;

F_CH4_x3_P2     = x3_t2;
F_H2O_x3_P2     = x3_t2;
F_H2_x3_P2     = 3*x3_t2;
F_CO_x3_P2     = x3_t2;

F_CH4_x4_P2     = x4_t2;
F_H2O_x4_P2     = 2*x4_t2;
F_H2_x4_P2      = 4*x4_t2;
F_CO2_x4_P2     = x4_t2;

F_C3H8O3_x5_P2 = x5_t2;
F_H2O_x5_P2     = 3*x5_t2;
F_H2_x5_P2      = 7*x5_t2;
F_CO2_x5_P2     = 3*x5_t2;

F_H2O_x6_P2     = x6_t2;
F_CO_x6_P2      = x6_t2;
F_H2_x6_P2      = x6_t2;
F_CO2_x6_P2     = x6_t2;

F_H2_x7_P2    =   x7_t2;
F_CO2_x7_P2   =  x7_t2;
F_H2O_x7_P2   =  x7_t2;
F_CO_x7_P2     = x7_t2;

F_C3H8O3_x8_P2 = x8_t2;
F_H2_x8_P2      = x8_t2;
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F_C3H8O2_x8_P2 = x8_t2;
F_H2O_x8_P2    = x8_t2;

F_C3H8O3_x9_P2 = x9_t2;
F_H2O_x9_P2    = 2*x9_t2;
F_C3H4O_x9_P2  = x9_t2;

!Component Material Balance;
!during t1 operation;
 F_CO_x1_P1     - F_CO_x3_P1     + F_CO_x6_P1     - F_CO_x7_P1 - IS_CO_t1     - EX_CO_t1 -
F_CO_IFS_t1 + F_CO_ITS_t1       + DI_CO_t1 =0;
 F_H2_x1_P1     + F_H2_x2_P1     - F_H2_x3_P1     - F_H2_x4_P1 - F_H2_x5_P1 - F_H2_x6_P1 +
F_H2_x7_P1 + F_H2_x8_P1 - IS_H2_t1     - EX_H2_t1     + H2_DEMAND_t1 - F_H2_IFS_t1 + F_H2
_ITS_t1+DI_H2_t1 =0;
 F_CH4_x3_P1    + F_CH4_x4_P1    - IS_CH4_t1    - EX_CH4_t1 - F_CH4_IFS_t1 + F_CH4_ITS_t1
+DI_CH4_t1 =0;
 F_C3H8O3_x5_P1 + F_C3H8O3_x8_P1 + F_C3H8O3_x9_P1 - EX_C3H8O3_t1 - IS_C3H8O3_t1 - F_C3H8O3
_IFS_t1 + F_C3H8O3_ITS_t1  + DI_C3H8O3_t1 =0;

 F_CH3OH_x1_P1  + F_CH3OH_x2_P1 - CH3OH_DEMAND_t1 =0;
F_C3H8O2_x8_P1 - C3H8O2_DEMAND_t1 =0;
F_C3H4O_x9_P1  - C3H4O_DEMAND_t1 =0;

 -F_H2O_x2_P1 + F_H2O_x3_P1 + F_H2O_x4_P1 + F_H2O_x5_P1 + F_H2O_x6_P1 - F_H2O_x7_P1 -
F_H2O_x8_P1 - F_H2O_x9_P1 - EX_H2O_t1    +DI_H2O_t1 =0;
F_CO2_x2_P1 - F_CO2_x4_P1 - F_CO2_x5_P1 - F_CO2_x6_P1 + F_CO2_x7_P1 - IS_CO2_t1    + D_CO2
_t1  =0;


!during t2 operation;
F_CO_x1_P2     - F_CO_x3_P2+ F_CO_x6_P2          - F_CO_x7_P2 - IS_CO_t2     - EX_CO_t2-
F_CO_IFS_t2 + F_CO_ITS_t2  +DI_CO_t2 =0;
F_H2_x1_P2     + F_H2_x2_P2     - F_H2_x3_P2     - F_H2_x4_P2 - F_H2_x5_P2 - F_H2_x6_P2 +
F_H2_x7_P2 + F_H2_x8_P2 - IS_H2_t2     - EX_H2_t2 - F_H2_IFS_t2 + F_H2_ITS_t2 + H2
_DEMAND_t2+DI_H2_t2 =0;
F_CH4_x3_P2    + F_CH4_x4_P2    - IS_CH4_t2    - EX_CH4_t2 - F_CH4_IFS_t1 + F_CH4_ITS_t1 +
DI_CH4_t2 =0;
F_C3H8O3_x5_P2 + F_C3H8O3_x8_P2 + F_C3H8O3_x9_P2 - EX_C3H8O3_t2 - IS_C3H8O3_t2 - F_C3H8O3
_IFS_t2 + F_C3H8O3_ITS_t2 +DI_C3H8O3_t2 =0;

F_CH3OH_x1_P2  + F_CH3OH_x2_P2 - CH3OH_DEMAND_t2 =0;
F_C3H8O2_x8_P2 - C3H8O2_DEMAND_t2 =0;
F_C3H4O_x9_P2  - C3H4O_DEMAND_t2 =0;

 -F_H2O_x2_P2 + F_H2O_x3_P2 + F_H2O_x4_P2 + F_H2O_x5_P2 + F_H2O_x6_P2 - F_H2O_x7_P2 -
F_H2O_x8_P2 - F_H2O_x9_P2 - EX_H2O_t2+DI_H2O_t2 =0;
F_CO2_x2_P2 - F_CO2_x4_P2 - F_CO2_x5_P2 - F_CO2_x6_P2 + F_CO2_x7_P2 - IS_CO2_t2    + D_CO2
_t2 =0;



!Storage and dispatch system mass balanced equation;
!CO;
F_CO_I_storege = F_CO_ITS_t1 + F_CO_ITS_t2  - F_CO_IFS_t1 - F_CO_IFS_t2  ;
!F_CO_ITS_t1 < 2000;
!F_CO_ITS_t2  < 2000;
F_CO_ITS_t1  = F_CO_IFS_t2 ;
F_CO_ITS_t2  =  F_CO_IFS_t1  ;

!F_CO_I_storege_t1 = F_CO_ITS_t1 ;
!F_CO_I_storege_t2 = F_CO_ITS_t1 + F_CO_ITS_t2 - F_CO_IFS_t2  ;
!F_CO_I_storege_t3 = F_CO_ITS_t1 + F_CO_ITS_t2 - F_CO_IFS_t2 - F_CO_IFS_t3  ;



!H2;
F_H2_I_storege = F_H2_ITS_t1 + F_H2_ITS_t2 - F_H2_IFS_t1 - F_H2_IFS_t2 ;
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!F_H2_ITS_t1 < 2000;
!F_H2_ITS_t2 < 2000;
F_H2_ITS_t1 = F_H2_IFS_t2 ;
F_H2_ITS_t2 = F_H2_IFS_t1;
!Ch4;
F_CH4_I_storege = F_CH4_ITS_t1 + F_CH4_ITS_t2  - F_CH4_IFS_t1 - F_CH4_IFS_t2  ;
!C3h8o3;
F_C3h8o3_I_storege = F_C3H8O3_ITS_t1 + F_C3H8O3_ITS_t2  - F_C3H8O3_IFS_t1 - F_C3H8O3
_IFS_t2  ;
!F_C3H8O3_ITS_t1  < 1000;
!F_C3H8O3_ITS_t2 < 1000;
F_C3H8O3_ITS_t1  = F_C3H8O3_IFS_t2;
F_C3H8O3_ITS_t2 =F_C3H8O3_IFS_t1 ;


!Cost analysis;

!COST CALCULATIONS in $/kg for purchased and sold chemical species;
COST_C3H8O3_t1    = EX_C3H8O3_t1 * 115  ;
COST_CH4_t1       = EX_CH4_t1    * 115.84 ;
COST_H2_t1        = EX_H2_t1     * 3      ;
COST_CO_t1        = EX_CO_t1     * 120    ;
PROFIT_CH3OH_t1   = CH3OH_DEMAND_t1  * 35;
PROFIT_C3H8O2_t1  = C3H8O2_DEMAND_t1 * 380 ;
PROFIT_C3H4O_t1   = C3H4O_DEMAND_t1  * 168 ;

COST_C3H8O3_t2    = EX_C3H8O3_t2 * 115.2  ;
COST_CH4_t2       = EX_CH4_t2    * 115.84 ;
COST_H2_t2        = EX_H2_t2     * 3.1      ;
COST_CO_t2        = EX_CO_t2     * 120    ;
PROFIT_CH3OH_t2   = CH3OH_DEMAND_t2  * 35  ;
PROFIT_C3H8O2_t2  = C3H8O2_DEMAND_t2 * 380 ;
PROFIT_C3H4O_t2   = C3H4O_DEMAND_t2  * 168 ;


!Capital cost calculations using factorial method;
EQUIP_cost_1 = (0.31 * (x1_t1*I1) * 32) + (2.31 * x1_t2*(1-I1) * 32)    ;
EQUIP_cost_2 = (0.49  * (x2_t1*I2) * 32) + (3.4  * x2_t2*(1-I2) * 32);
EQUIP_cost_3 = (0.29 * (x3_t1*I3)  * 3)+ (2.33 * x3_t2*(1-I3)  * 3)  ;
EQUIP_cost_4 = (0.29 * (x4_t1*I4)  * 4)+ (2.33 * x4_t2*(1-I4)  * 4)  ;
EQUIP_cost_5 = (0.66 * (x5_t1*I5)  * 7)+ (4.64 * x5_t2*(1-I5)  * 7)  ;
EQUIP_cost_6 = (0.1  * (x6_t1*I6))    + (0.1  * x6_t2*(1-I6) )      ;
EQUIP_cost_7 = (0.1  * (x7_t1*I7) * 28)    + (0.1  * x7_t2*(1-I7) * 28);
EQUIP_cost_8 = (0.28 * (x8_t1*I8) * 76)+ (2.13 * x8_t2*(1-I8) * 76)  ;
EQUIP_cost_9 = (0.21 * (x9_t1*I9) * 56) + (1.52 * x9_t2*(1-I9) * 56)  ;

PPC_1 = 3.47*EQUIP_cost_1;
IPC_1 = 0.45* PPC_1;
Fixed_cost_1 = PPC_1+IPC_1;
Capital_cost_1 = Fixed_cost_1*1.18;

PPC_2 = 3.47*EQUIP_cost_2;
IPC_2 = 0.45* PPC_2;
Fixed_cost_2 = PPC_2+IPC_2;
Capital_cost_2 = Fixed_cost_2*1.18;

PPC_3          = 3.47*       EQUIP_cost_3;
IPC_3          = 0.45*              PPC_3;
Fixed cost 3   =        PPC 3+      IPC 3;
Capital_cost_3 = Fixed_cost_3*1.18;

PPC_4          = 3.47*       EQUIP_cost_4;
IPC 4          = 0.45*              PPC 4;
Fixed cost 4   =        PPC 4+      IPC 4;
Capital_cost_4 = Fixed_cost_4*1.18;

PPC_5          = 3.47*       EQUIP_cost_5;
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IPC_5          = 0.45*              PPC_5;
Fixed cost 5   =        PPC 5+      IPC 5;
Capital_cost_5 = Fixed_cost_5*1.18;

PPC_6          = 3.47*       EQUIP_cost_6;
IPC 6          = 0.45*              PPC 6;
Fixed cost 6   =        PPC 6+      IPC 6;
Capital_cost_6 = Fixed_cost_6*1.18;

PPC_7          = 3.47*       EQUIP_cost_7;
IPC 7          = 0.45*              PPC 7;
Fixed cost 7   =        PPC 7+      IPC 7;
Capital_cost_7 = Fixed_cost_7*1.18;


PPC_8          = 3.47*       EQUIP_cost_8;
IPC 8          = 0.45*              PPC 8;
Fixed cost 8   =        PPC 8+      IPC 8;
Capital_cost_8 = Fixed_cost_8*1.18;

PPC_9          = 3.47*       EQUIP_cost_9;
IPC 9          = 0.45*              PPC 9;
Fixed cost 9   =        PPC 9+      IPC 9;
Capital_cost_9 = Fixed_cost_9*1.18;



capital_cost = Capital_cost_1 + Capital_cost_2 + Capital_cost_3 + Capital_cost_4 +
Capital_cost_5 + Capital_cost_6 + Capital_cost_7 + Capital_cost_8 + Capital_cost_9 ;

x1_t1        > x1_t2*I1;
x1_t1*(1-I1) < x1_t2;
x2_t1        > x2_t2*I2;
x2_t1*(1-I2) < x2_t2;
x3_t1        > x3_t2*I3;
x3_t1*(1-I3) < x3_t2;
x4_t1        > x4_t2*I4;
x4_t1*(1-I4) < x4_t2;
x5_t1        > x5_t2*I5;
x5_t1*(1-I5) < x5_t2;
x6_t1        > x6_t2*I6;
x6_t1*(1-I6) < x6_t2;
x7_t1        > x7_t2*I7;
x7_t1*(1-I7) < x7_t2;
x8_t1        > x8_t2*I8;
x8_t1*(1-I8) < x8_t2;
x9_t1        > x9_t2*I9;
x9_t1*(1-I9) < x9_t2;
@bin (I1);
@bin (I2);
@bin (I3);
@bin (I4);
@bin (I5);
@bin (I6);
@bin (I7);
@bin (I8);
@bin (I9);

!production cost calculations for each operation period;
Production_cost_1_t1 = 19.52 * x1_t1  ;
Production_cost_2_t1 = 32.32 * x2_t1  ;
Production_cost_3_t1 = 1.98  * x3_t1  ;
Production_cost_4_t1 = 2.64  * x4_t1  ;
Production_cost_5_t1 = 18.2  * x5_t1  ;
Production_cost_6_t1 = 0.1   * x6_t1  ;
Production_cost_7_t1 = 2.8   * x7_t1  ;
Production_cost_8_t1 = 64.6  * x8_t1  ;
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Production_cost_9_t1 = 23.52 * x9_t1  ;
production_cost_t1 = 0.5*( Production_cost_1_t1 + Production_cost_2_t1 + Production_cost_3
_t1 + Production_cost_4_t1 + Production_cost_5_t1 + Production_cost_6_t1 +
Production_cost_7_t1 + Production_cost_8_t1 +Production_cost_9_t1);

Production_cost_1_t2 = 19.52 * x1_t2  ;
Production_cost_2_t2 = 32.32 * x2_t2  ;
Production_cost_3_t2 = 1.98  * x3_t2  ;
Production_cost_4_t2 = 2.64  * x4_t2  ;
Production_cost_5_t2 = 18.2  * x5_t2  ;
Production_cost_6_t2 =  0.1  * x6_t2  ;
Production_cost_7_t2 =  2.8  * x7_t2  ;
Production_cost_8_t2 = 64.6  * x8_t2  ;
Production_cost_9_t2 = 23.52 * x9_t2  ;
production_cost_t2 = 0.5*( Production_cost_1_t2 + Production_cost_2_t2 + Production_cost_3
_t2 + Production_cost_4_t2 + Production_cost_5_t2 + Production_cost_6_t2 +
Production_cost_7_t2 + Production_cost_8_t2 +Production_cost_9_t2);

!sales, ROI calculations;
AFC = 0.1* capital_cost;
sales_t1 = (PROFIT_CH3OH_t1 + PROFIT_C3H8O2_t1 + PROFIT_C3H40_t1 - COST_C3H8O3_t1 -
COST_CH4_t1 - COST_H2_t1 - (COST_CO_t1))*0.5;
sales_t2 = (PROFIT_CH3OH_t2 + PROFIT_C3H8O2_t2 + PROFIT_C3H40_t2 - COST_C3H8O3_t2 -
COST_CH4_t2 - COST_H2_t2 - COST_CO_t2)*0.5;
sales = ((sales_t1 + sales_t2 -(production_cost_t1 + production_cost_t2 + AFC))*(1-0.25))
+ AFC ;
ROI = ( sales/ Capital_cost) * 100 ;
!Max = Annual_sales;
!Min = D_CO2_t1 + D_CO2_t2;
Min = DI_H2O_t1 + DI_H2O_t2+ D_CO2_t1 + D_CO2_t2;
ROI > 15;
!Max = ROI;

Annual_sales = sales * 24*300;
!Annual_sales_t2 = sales_t2 * 24*300;
Total_production_cost_t1 = production_cost_t1 * 24*300;
Total_production_cost_t2 = production_cost_t2 * 24*300;
Total_capital_cost = capital_cost * 24 * 300;
!SASWROIM = Annual_sales * (1 + ((0.1*((2990- D_CO2)/(2990-0))) + (0.1*((-4000 - EX_H2O)/
(-4000-0))) + (0.1*((35 - Total_PSI)/(35-2)))))/Total_Capital_cost;
!Max = Annual_sales;
!Min = Total_PSI;
!Min = EX_C3H8O3 + EX_CH4;
!min = Total_capital_cost;
!EX_H2 < -3000;

! Objective function;
Min = DI_H2O_t1 + DI_H2O_t2+ D_CO2_t1 + D_CO2_t2;

@FREE(COST_C3H8O3_t1);
@FREE(PROFIT_CH3OH_t1);
@FREE(COST_CH4_t1);
@FREE( COST_H2_t1) ;
@FREE( COST_CO_t1) ;
D_CO2_t1 > 0;
@FREE(COST_C3H8O3_t2);
@FREE(PROFIT_CH3OH_t2);
@FREE(COST_CH4_t2);
@FREE( COST_H2_t2) ;
@FREE( COST_CO_t2) ;
D_CO2_t2 > 0;
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