ENHANCE ETHYLENE PRODUCTION FROM MIXED C4 HYDROCARBONS AND LIGHT NAPHTHA

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ABSTRACT

In an ethylene plant, mixed C4 is the only end-product that is not in high demand. In addition, it is costly and risky to store at the plant. The coke accumulation on the furnace coils tends to increase the pressure and decrease the yield hence increase fuel consumption. Consequently, ethylene production plants that use naphtha as a feedstock constantly suffer from these drawbacks. Therefore, this study aims to reduce the cost and risk of the storage of the C4 and reduce the coke deposition. The objectives were achieved by the recycling of mixed C4 to improve the ethylene and propylene yields and the addition of CO2 in the feedstock to minimize the coke deposition on the furnace coils. The recycling study consisted of two stages/processes. In the first process, the feed contained 100% naphtha, while the second process contained 85% naphtha and 15% mixed C4 as a recycled feed. During the study, a data from several units of the ethylene plant was recorded on a daily basis for 60 days (maximum operating days for each operating furnace) in order to select the highest ethylene yield. The results showed that there were higher ethylene and propylene yields after the recycling of mixed C4, with a remarkable/significant increase in coke accumulation on the furnace coils with respect to the coke accumulation during 100% naphtha cracking. In the third process, the addition of CO2 to feedstock during naphtha cracking in an attempt to decrease coke accumulation was carried out by modeling and optimization of the key operating conditions by training a real data collected during 60 days using mathematical model ordinary differential equations (ODEs) falling under the ANN approach. It was found that the addition of CO2 improves the yield of ethylene and propylene up to 15 %, decreased coke deposition on the furnace coils (form 5.5mm to 2.4mm coke thickness), hence less energy was required to operate the furnace. The addition also minimised the operation and the maintenance costs. The results from the proposed model also showed that the run time of the furnace with the addition of CO2 was almost twice (from 45 days to 120 days) the run time with adding steam. Based on these results, this study has proven that the recycling of C4 mix accompanied with CO2 has noticeable positive results on the production of ethylene from the naphtha thermal cracking process.

ABSTRAK

Dalam loji ethylene, campuran C4 merupakan satu-satunya produk akhir yang tidak mempunyai permintaan yang tinggi. Di samping itu, kos penyimpanannya di loji adalah sangat mahal dan berisiko tinggi. Pengumpulan coke pada gegelung relau cenderung untuk meningkatkan tekanan dan mengurangkan hasil yang akibatnya boleh menyebabkan peningkatan penggunaan bahan api. Sebagai kesannya, kelemahan ini sentiasa dihadapi oleh loji pengeluaran ethylene yang menggunakan naphtha sebagai bahan mentah. Oleh itu, kajian ini bertujuan untuk mengurangkan kos dan risiko penyimpanan C4 dan mengurangkan pemendapan coke. Objektif-objektif kajian dicapai dengan menggunakan kaedah kitar semula campuran C4 bagi meningkatkan hasil ethylene dan propylene selain menambahkan CO2 dalam bahan mentah bagi mengurangkan pemendapan coke pada gegelung relau. Kajian kitar semula ini terdiri daripada dua proses. Dalam proses pertama, bahan mentah yang mengandungi 100% naphtha digunakan, manakala proses kedua menggunakan bahan mentah yang mengandungi campuran 85% naphtha dan 15% C4. Sewaktu kajian dijalankan, data daripada beberapa unit loji ethylene direkodkan setiap hari selama 60 hari (waktu perkhidmatan maksimum untuk relau yang beroperasi) untuk memilih hasil ethylene tertinggi. Dapatan kajian menunjukkan hasil ethylene dan propylene lebih tinggi selepas proses kitar semula campuran C4, dengan peningkatan pengumpulan coke yang signifikan pada gegelung relau semasa 100% keretakan naphtha berlaku. Dalam proses ketiga, dalam usaha untuk mengurangkan pengumpulan coke, penambahan CO2 kepada bahan asas semasa keretakan naphtha telah dijalankan dengan menggunakan model matematik persamaan pembezaan (PPB) di bawah pendekatan ANN menggunakan data sebenar yang dikumpul selama 60 hari dalam proses pertama dan kedua. Didapati terdapat peningkatan hasil ethylene dan propylene sehingga 15% dengan penambahan CO2, serta pengurangan pemendapan coke pada gegelung relau menyebabkan pengurangan tenaga dalam mengendalikan relau(menghasilkan 5.5mm dan 2.4mm ketebalan coke) sekaligus mengurangkan kos operasi dan penyelenggaraan. Peningkatan itu juga meminimumkan kos-kos operasi dan penyelenggaraan. Hasil kajian daripada model yang dicadangkan juga menunjukkan bahawa jangkamasa larian relau dengan penambahan CO2 dan wap menjadi hampir dua kali ganda (dari 45 hari ke 120 hari). Berdasarkan keputusan ini, kajian ini telah membuktikan bahawa kitar semula campuran C4 disertai dengan CO2 mempunyai hasil yang positif kepada pengeluaran ethylene daripada proses keretakan haba naphtha.

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LIST OF ABBREVIATIONS

ANN	-	Artificial neural network
AP	-	Alarm Pressure
ASTM	-	American Society for Testing and Materials
BTX	-	Benzene, tolunen, xylene
C	-	Concentration of coke (mol/m^3)
C1	-	Methane product
C2H2	-	Acetylene product
C_2H_4	-	Ethylene product
C3	-	Propylene product
C_4	-	Mixed C4 product
CGC	-	Cracked gas compressor
CO_2	-	Carbon dioxide
C_p	-	Heat capacity (J/mol K)
d_t	-	Coil diameter (m)
FCC	-	Fluid catalytic cracking
F_i	-	Molar flow rate of component I (mole/s)
F_r	-	Friction factor
G	-	Total mass flow rate (Kg/m^2s)
H	-	Hydrogen
k_i	-	Rate coefficient of reaction i (1/s or m^3/mol s)
MAP	-	Methyl acetylene and propadiene
M_c	-	Coke molecular weight (Kg/mol)
Mm	-	Average molecular weight (Kg/mol)
OCT	-	Olefins conversion technology
ODC	-	Design of Experiment
Pt	-	Total pressure (Pa)
Q	-	Heat flux (W/m^2)

R	-	Universal gas constant (J/mol K)
R_b	-	Radius of the tube bend (m)
Rc	-	Rate of coking (mol/m^2s)
Re	-	Reynolds number
r_i	-	Rate of reaction i (mol/m^2s)
RSM	-	Response surface methodogy
S_{ij}	-	Stoichiometric coefficient of component j in ith reaction
TLE	-	Transfer line exchangers
T	-	Time (s)
tc	-	Coke thickness (m)
z	-	Axial reactor coordinate (m)

LIST OF SYMBOLS

ΔH	-	Heat of reaction (KJ/mol)
η	-	Conversion factor (atm/Pa)
Z	-	Parameter of tube bend
Λ	-	Angle of bend
α	-	Coking factor
ρC	-	Coke specific gravity (Kg/m^3)

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CHAPTER 1

INTRODUCTION

1.1 Introduction

1.1.1 Ethylene Production Overview

Ethylene is generally a hydrocarbon, which is presented by the formula: H2C=CH2. It is the lightest olefin, and is a flammable gas produced primarily from petroleum feedstock by thermal cracking within steam. Ethylene has almost no direct endues, but has an almost exclusive role as an intermediate during the manufacture of other chemicals. This is especially true for plastics (Zhao *et al.*, 2010). Figure 1.1 below shows a simple three dimensional visualization of ethylene.

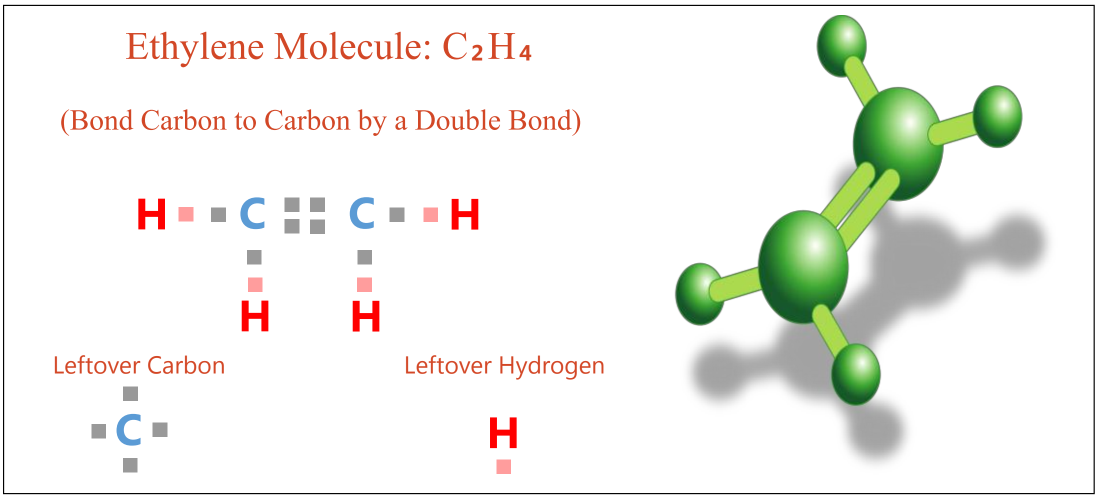


Figure 1.1 A three dimensional visualization of ethylene

Ethylene can be directly polymerized for the production of polyethylene, which is one of the most widely used plastics in the world. Ethylene can also be chlorinated for the production of 1,2-dichloroethane, which is a precursor to polyvinyl chloride, a type of plastic. It can also be combined with benzene for ethy-l benzene production, which is used during the manufacturing of polystyrene, and is considered as an important type of plastic. Smaller amounts of ethylene are oxidized in the production of chemicals, which include ethylene oxide, polyvinyl acetate, and ethanol. The quality of ethylene is based on users' requirements in downstream processes. While there is no particular chemical grade ethylene, the content of ethylene usually exceeds 99.7%. Oxygen, sulfur, hydrogen, acetylene, carbon dioxide and carbon monoxide are the most problematic impurities that must be controlled cautiously (Zhao *et al.*, 2010; Freitez *et al.*, 2011; Alvarado and Gracia, 2010; Rahimpour *et al.*, 2012). Among the most industrially produced organic materials is ethylene. The current production on a global scale is approximately 146,106,691 million tons a year, and is projected to increase in the future. A standard modern plant has the ability to produce over one million tons a year. Feedstock to a standard ethylene plant may range from a light ethane or propane mixture to heavier naphtha and vacuum gas oils. The main use of ethylene is for the production of polymers as well as ethylene derivatives like ethylene oxide and glycol. A standard ethylene plant may produce several other important chemicals, including butadiene, propylene and pyrolysis gasoline (Riverol and Pilipovik, 2007; Choudhary *et al.*, 2006). Table 1.1 shows the national ethylene capacities produced for the years 2013 and 2014 in a list of countries that contain ethylene plants.

Table 1.1 : National ethylene capacities produced for the years 2014

Country	Jan. 1, 2014	Jan. 1, 2013	Change, tpy	Country	Jan. 1, 2014	Jan. 1, 2013	Change, tpy
	--Ethylene capacity, tpy--			--Ethylene capacity, tpy--			
Algeria	133,000	133,000	-	Malaysia	1,723,000	1,649,000	74,000
Argentina	838,500	838,500	-	Mexico	1,384,000	1,384,000	-
Australia	502,000	502,000	-	Netherlands	3,965,000	3,965,000	-
Austria	500,000	500,000	-	Nigeria	300,000	300,000	-
Azerbaijan	330,000	330,000	-	North Korea	60,000	60,000	-
Belarus	193,000	193,000	-	Norway	550,000	550,000	-
Belgium	2,460,000	2,460,000	-	Poland	700,000	700,000	-
Brazil	3,500,000	3,500,000	-	Portugal	330,000	330,000	-
Bulgaria	400,000	400,000	-	Qatar	1,220,000	1,030,000	190,000
Canada	5,530,794	5,531,000	-206	Romania	844,000	844,000	-
Chile	45,000	7,348,000	-	Russia	3,490,000	3,490,000	-
China	11,778,000	7,348,000	4,430,000	Saudi Arabia	10,700,000	9,400,000	1,300,000
China, Taiwan	4,006,000	3,621,000	385,000	Serbia and Montenegro	200,000	200,000	-
Colombia	100,000	100,000	-	Singapore	2,780,000	1,960,000	800,000
Croatia	90,000	90,000	-	Slovakia	220,000	220,000	-
Czech Republic	544,000	544,000	-	South Africa	585,000	585,000	-
Egypt	330,000	330,000	-	South Korea	5,630,000	5,630,000	-
Finland	330,000	330,000	-	Spain	1,430,000	1,430,000	-
France	3,373,000	3,373,000	-	Sweden	625,000	625,000	-
Germany	5,757,000	5,757,000	-	Switzerland	33,000	33,000	-
Greece	20,000	20,000	-	Thailand	2,272,000	2,272,000	-
Hungary	660,000	660,000	-	Turkey	520,000	520,000	-
India	2,515,000	2,515,000	-	Ukraine	630,000	630,000	-
Indonesia	600,000	520,000	80,000	UAE	600,000	600,000	-
Iran	4,734,000	4,734,000	-	UK	2,855,000	2,855,000	-
Israel	200,000	200,000	-	US	27,554,206	28,492,000	-937,794
Italy	2,170,000	2,170,000	-	Uzbekistan	140,000	140,000	-
Japan	7,265,000	7,265,000	-	Venezuela	600,000	600,000	-
Kazakhstan	130,000	130,000	-				
Kuwait	1,650,000	1,650,000	-				
Libya	350,000	350,000	-	Total	146,106,691	143,402,426	2,614,265

In the past couple of years, ethylene plants have been transformed into highly integrated, flexible and reliable processing systems that are able to profitably adapt to the changing availability of raw material and market demands for olefin products.

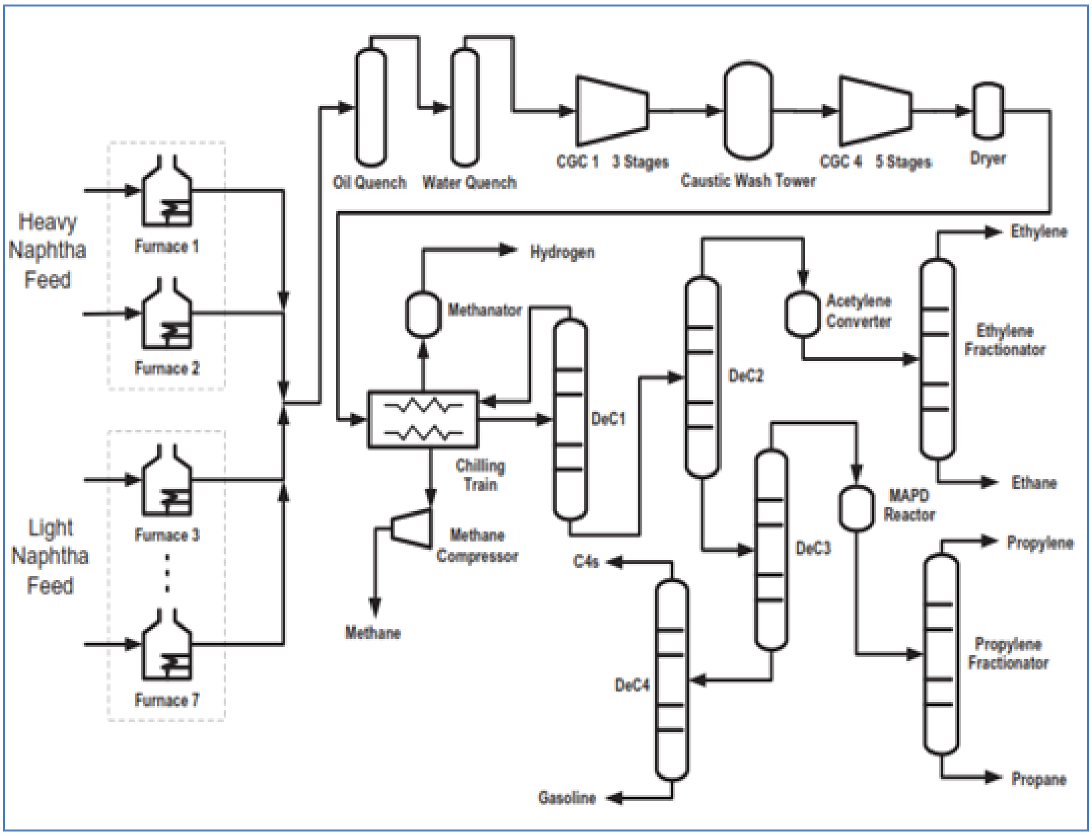
Advanced process control technology is utilized in olefin plants for the flexibility to cope with changing supply and demand (Asplin *et al.*, 2000).

Common process characteristics of a general ethylene process are short residence time within the furnace, feedstock flexibility, high selectivity, easy start-up, operational reliability and safety, and energy efficiency (Fu and Xu, 2013). Process analytics is a core problem for process control by monitoring online the numerous process streams in the production of ethylene and propylene. Process analytics generally maximizes yields and ensures a certain quality of products based on product quality specifications.

Regardless of the process type, all ethylene plants need process analytical equipment to obtain reliable and effective process data for process control, product quality, and plant safety.

1.1.2 Process Overview

A standard ethylene plant flowsheet is depicted in Figure 1.3. Two types of feedstock are applied in the plant in the thermal cracking process, which are light naphtha and heavy naphtha (Wang and He, 2000; Karimzadeh *et al.*, 2009; Masoumi *et al.*, 2006, Van Goethem *et al.*, 2010). There are a total of 10 furnaces within the plant, two of which are used for cracking recycled ethane and propane feed. The other eight are for cracking light feed. The effluent gas mixture from furnaces, cracked gas, is sent to oil quench and water quench towers sequentially. Within the quench system, heat is removed by circulating quench water and quench oil when cracked gas is cooled and then partially condensed. The quench tower overhead vapour is then compressed within a cracked gas compression (CGC) unit of four stages. Within the third and fourth compression stage, the cracked gas is treated with caustic water in order to eliminate the acid gas produced within the cracking heaters. The cracked gas from the fifth stage compressor is primarily left to dry. It is then chilled using the refrigerant within the chilling train, during which hydrogen is separated (Rahimpour *et al.*, 2011).

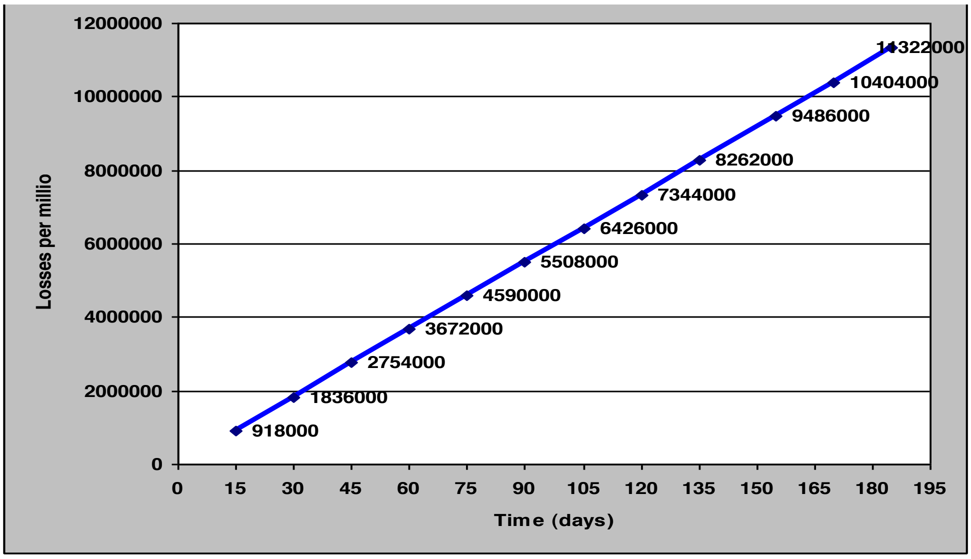


Source: Manual operating procedures ethylene plant Rasco

Figure 1.2 A standard ethylene plant flow sheet

1.2 Problem Statement

The total losses caused by the flaring of the C4 produced during six months of a collaborating organization of an ethylene plant in Libya in the year 2008 was $ 11,016,000. Over the next 2 years, there have been considerable losses by the plant due to C4 flaring. The mixed C4 production is approximately 15 MT per hour. The total production of mixed C4 a day is 15 MT * 24 hours, which is 360 MT/day. Over a period of six months, 64,800 Mt of C4 is produced. The price of C4 at that time was $170/ton. The Figure 1.3 below shows the cost analysis of the loss.



Source: (Rasco Company, 2012)

Figure 1.3 Losses of revenue due to flaring of mixed C_4

Mixed C4 is a gas with no colour at room temperature, with an odour that is similar to the characteristics of hydrocarbons. It is generally a hazardous chemical because of its flammable, reactive, and toxic nature (White, 2007).

Any remaining mixed C4 product requires more fuel to be used in the furnace. Consequently, more steam is required in the CGC compressor, with a loss in unit capacity as well. Excluding the loss in unit capacity, the energy loss (per ton) is US $33.36/hr or US $266,876/yr in a standard ethylene plant in the United States. The mixed C4 that is produced from the ethylene plant is not recoverable.

This gap has increased the motivation to conduct this work, which will attempt to recycle the mixed C4 back to the main naphtha feed, and consequently produce more ethylene and propylene. This way, not only is the C4 used, it also generates more ethylene and propylene. New technologies play a critical role in the future of any industrial process in terms of improving production, reducing costs, saving time and reducing risks. The new state of the art technologies, which are currently used on a global scale, make the processing of ethylene plants more efficient and have been successful to achieve effective results by increasing production and reducing costs. This is true for most of the products that are the output of ethylene plants, such as ethylene, ethane, propylene, and propane. All of these products are in high demand, and are extensively used in the production of other important products. Mixed C4 is the only end-product that does not have a high demand. In addition, it is costly and risky to store it at the plant, because it must be stored at a certain temperature (-11^{o}C). The cost of C_4 was USD$170/tonne.

The used mixed C_4 was at 130,000 tonnes per year. All quantity of the mixed C_4 will be used with the exception of 8 tonnes per month to save storage system in the normal operation level. More specifically, mixed C4 is currently almost entirely produced as a by-product in ethylene plants that use naphtha or gas oil steam cracking as feedst$_{oc}$k. Most of the mixed $_{C4}$ contains high amounts of butadiene. However, in high severity naphtha cracking, the mixed C4 fraction is about 9-14 wt% of the cracked products, and contains 45–50 wt% butadiene. Consequently, ethylene production plants that use naphtha feedstock are constantly suffering from many drawbacks, because mixed C4 is a product of little or no market value which is costly to store at the plant (Keyvanloo *et al.*, 2010; Ota *et al.*, 2002).

Another problem is the coking. Regular decoking is needed in certain parts of the pyrolysis section. Based on the feedstock composition, the coil configuration and the severity, decoking is needed every 14 to 100 days for steam cracking furnaces. This is a very costly routine operation, and therefore reducing coking on the furnace tubes must be taken into consideration (Liu *et al.*, 2010).

This gap has motivated the creation of the proposed model with the goal of reusing the mixed C4 by recycling it as input into the overall system in an attempt to extract ethylene from it. Therefore, this work aims at recycling the mixed C4 by-product from the debutanizer unit to the naphtha feed in an attempt to extract ethylene, which would make the entire system more efficient by increasing the overall ethylene and propylene production, and reducing the mixed C4 residue at the same time. Moreover, carbon dioxide will be added as an input with the naphtha feedstock and steam. The advantage of this is that it will reduce the rate of accumulation of coke on the coils in the furnace, and, at the same time, it will reduce the amount of fuel needed to keep the furnace at a particular temperature. Another benefit from adding CO_2 is that the run time of the furnace will be increased. Overall, this will reduce the costs needed to run the ethylene plant as a whole.

1.3 Research Aims and Objectives

The research aims and objectives of the study are presented in the following paragraphs.

1.3.1 Research Aims

The research aim of this study is to produce higher yields of ethylene and propylene.

This is achieved through recycling mixed C4 during the naphtha cracking process at an ethylene plant in Libya, in order to minimize the C4 mix in the product, hence reduce the cost and risk of the storage of the C4, and in turn increase the ethylene and propylene yields.

Furthermore, another aims is to compare the behaviour of the furnaces and cracked gas compressor as well as the fractionation columns on the ethylene and propylene yields.

1.3.2 Research Objectives

The objectives of the research are identified as follows:

1. To recycle the mixed C4 by-product produced from the ethylene plant using straight run naphtha as a feedstock.

2. To reduce the coke deposition on the coils of furnace from current situation at 5.5 mm to 2.4 mm in order to decrease the amount of fuel needed to maintain the furnace temperature.

3. To increase the run time (from the current 45 days to become 120 days)of the furnace by adding CO2as input with naphtha and steam and mitigate fouling and energy costs in the Cracked gas compressor (CGC).

4. To predict the most effective variables and optimal operating conditions based on the data obtained from the approach above, using Design of Experiments approach (DOE) through the use of MATHLAB, HYSYS.

1.4 Research Scope

The research scope of this study is identified and highlighted as shown in Table 1.2 below.

Process models are usually used for the research of an operating strategy of a plant in an optimal mode, advanced process control systems (APC), process as part of the controller. This model based controllers' performance depend on the validity of the model of the process to calculate changes from the future, when certain variables are manipulated and usually uses a cost function as an objective which needs to be minimized.

Table 1.2 : Research scope of the study

Operational Units	Naphtha Cracking Furnace	Research Scope
	Cracked Gas Compressor	
Fractionation Tower	DeMethenizer tower	
	DeEthenizer tower	
	Ethylene tower	
	DePropanizer tower	
	Propylene tower	
	DeButanizer tower	
Add CO2	Run time of the furnace	
	Yield of ethylene and propylene	
	Coke thickness	
	Furnace temperature	
	Cost and energy saving	
	Fouling in CGC	

This research work is aimed at upgrading the mixed C4 hydrocarbon by-product from the ethylene plant by recycling the residue of mixed C4 to the main feed line. The proposed plan is to be achieved by carrying out a mechanical modification of a pipeline connecting the debuinizer unit to the main feed line of straight run naphtha SRN (Gál and Lakatos, 2008; van Goethem *et al.*, 2013).

Another step is to add CO2 to the main feed in order to minimize the amount of fuel required to maintain furnace temperature which is currently at 810 – 850 degrees Celsius, increase the run time of the furnace and enhance the yield of ethylene and propylene which will be result in cost and energy saving.

The two main operational units of the ethylene plant that will be involved in this study are the furnace and the cracked gas compressor (CGC).

1.5 Collaborating Partner

This research work is limited to a particular ethylene plant in Libya, where the proposed model will be created, and where all of the experiments will be conducted.

1.5.1 Organization

Ras Lanuf Oil and Gas Processing Company (Rasco) is a subsidiary of the state-owned National Oil Corporation of Libya (NOC). Rasco operates the Ras Lanuf Refine.

1.5.2 Products

Ra's Lanuf is a topping and reforming oil refinery. It became operational in 1984 and produces an estimated 220,000 bbl/d (35,000 m3/d). It is a simple hydroskimming refinery, but its products meet market specifications due to high quality crude oil. Rasco produces fuel oil, gas oil, LPG, naphtha and kerosene. The refinery also produces petrochemicals, utilizing naphtha as a feed stock to an ethylene plant with a capacilty of 1.2 million tpy (tons per year). Its main products are ethylene (330,000 tpy), propylene (170,000 tpy), Mix C4 (130,000 tpy) and P Gasoline (335,000 tpy).

1.5.3 Background

The first construction phase for the Ra's Lanuf petrochemical complex began during April 1987. Rasco contracted Hemijska Industria Pancevo (HIP) (Yugoslavia) to manage the complex. During the first two years production was well below capacity. It began increasing in 1989 and by 1994 operated at about 85% of capacity.

The operation was impacted by UN sanctions, specifically Security Council Resolution 883 of November 11, 1993, which banned Libya from importing refinery equipment. Performance improved after the UN suspended sanctions in April 1999. The ethylene cracker was closed for a four-week maintenance in May 1999. The second phase was scheduled to finish in 1994, with Monenco as manager. However, the venture ran into numerous obstacles. In 1985, Tecnimont won a $50 million management contract, but when the contract expired in 1990, Rasco appointed Monenco. In October 1989, the first contract was awarded to a consortium consisting of Energoinvest, HIP, INA-Project and Brown & Root. In 1990, Brown & Root ended its participation and was replaced by Technip. In February 1991, Hyundai Engineering and Construction was awarded a $200 million contract for the polyethlene unit, with John Brown Engineering acting as sub-contractor. Included in the contract was a hydrogen and ethylene purification unit. By the end of 1992, Uhde GmbH (German subsidiary of ThyssenKrupp) won the contract. In 1993, Rasco terminated the construction contract due to the consortia failure to fulfil its terms.

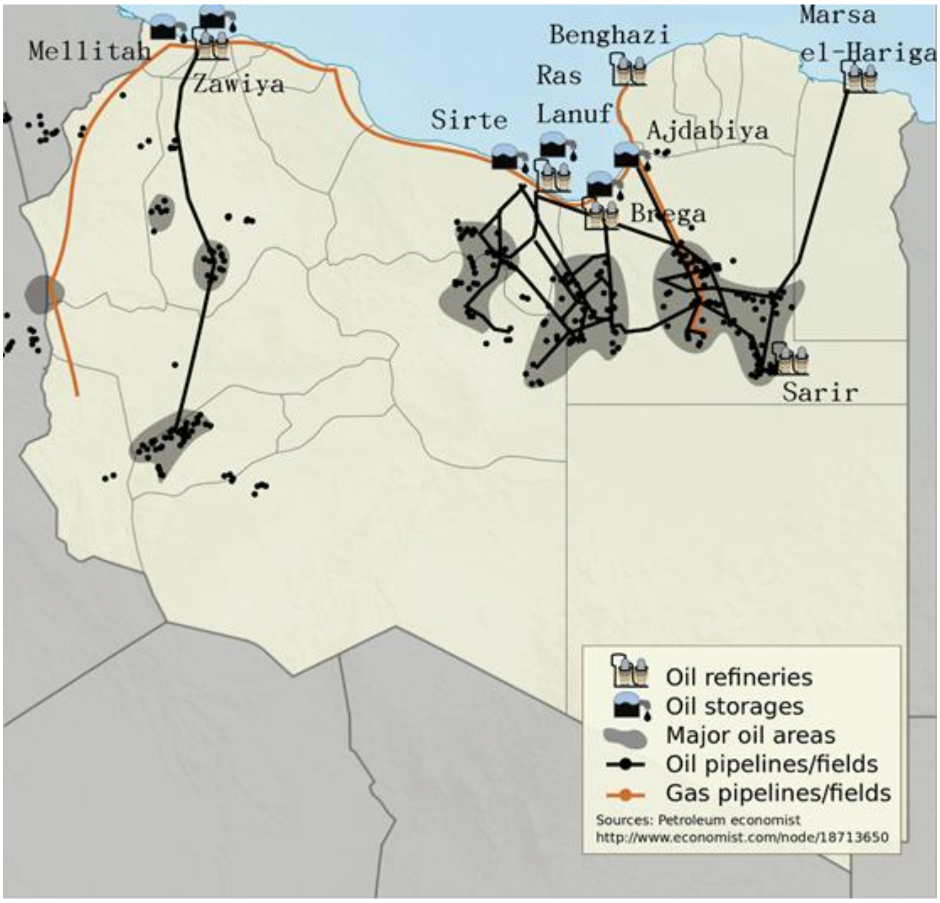


Figure 1.4 Location of the collaborating partner

REFERENCES

Albright, L.F. (2002). Comments on "Kinetic Modeling of Coke Formation during Steam Cracking". *Industrial & Engineering Chemistry Research*. 41(24): 6210-6212.

Alvarado, F.D. and Gracia, F.(2010). Steam reforming of ethanol for hydrogen production: Thermodynamic analysis including different carbon deposits representation. *Chemical Engineering Journal*. 165(2): 649-657.

Asplin, J.E., Chen, T.J., Fung, S.C., Henry, B.E., Janssen, M.J., and Wachter, W.A. (2000). *U.S. Patent No. 6, 118, 035*. Washington, DC: U.S. Patent and Trademark Office.

Cai, H., Krzywicki, A. and Oballa, M.C.(2002). Coke formation in steam crackers for ethylene production. C*hemical Engineering and Processing: Process Intensification*. 41(3): 199-214.

Choudhary, V.R., Mondal, K.C. and Mulla, S.A.(2006). Non-catalytic pyrolysis of ethane to ethylene in the presence of CO2 with or without limited O2. *Journal of Chemical Sciences*. 118(3): 261-267.

Corma, A., Melo, F., Sauvanaud, L. and Ortega, F.J.(2004). Different process schemes for converting light straight run and fluid catalytic cracking naphthas in a FCC unit for maximum propylene production. *Applied Catalysis A: General*. 265(2), 195-206.

Davis, S.G., Joshi, A.V., Wang, H. and Egolfopoulos, F.(2005). An optimized kinetic model of H2/CO combustion. *Proceedings of the Combustion Institute*. 30(1): 1283-1292.

Farniaei, M., Abbasi, M., Rasoolzadeh, A. and Rahimpour, M.R.(2011). Performance enhancement of thermally coupling of methanol synthesis, DME synthesis and cyclohexane dehydrogenation processes: Employment of water and hydrogen perm-selective membranes via different recycle streams. *Chemical Engineering and Processing: Process Intensification*. 85: 24-37.

Froment, G.F.(1981). Thermal cracking for olefins production. Fundamentals and their application to industrial problems. *Chemical Engineering Science*. 36(8): 1271-1282.

Fu, J. and Xu, Q. (2013). Simultaneous study on energy consumption and emission generation for an ethylene plant under different start-up strategies. *Computers & Chemical Engineering*. 56: 68-79.

Gál, T. and Lakatos, B.G. (2008). Re-pyrolysis of recycled hydrocarbon gas-mixtures: A simulation study. *Chemical Engineering and Processing: Process Intensification*. 47(4): 603-612.

Gao, G.Y., Wang, M., Ramshaw, C., Li, X.G. and Yeung, H. (2009). Optimal operation of tubular reactors for naphtha cracking by numerical simulation. *Asia-Pacific Journal of Chemical Engineering*. 4(6): 885-892.

Geng, Z., Cui, Y., Xia, L., Zhu, Q. and Gu, X.(2012). Compromising adjustment solution of primary reaction coefficients in ethylene cracking furnace modeling. *Chemical Engineering Science*. 80: 16-29.

Kantorowicz, S.I.(2002). May. C4 processing options to upgrade steam cracker and FCC streams. In *Lecture presented at the Second Asian Petrochemicals Technology Conference* (pp. 7-8).

Karimzadeh, R., Godini, H.R. and Ghashghaee, M. (2009). Flowsheeting of steam cracking furnaces. *Chemical Engineering Research and Design*. 87(1): 36-46.

Karimzadeh, R., H.R. Godini, and M. Ghashghaee. (2009). Flowsheeting of steamcracking furnaces. Chemical Engineering Research and Design 87: p. 36-46.

Keyvanloo, K., Towfighi, J., Sadrameli, S.M. and Mohamadalizadeh, A. (2010). Investigating the effect of key factors, their interactions and optimization of naphtha steam cracking by statistical design of experiments. *Journal of Analytical and Applied Pyrolysis*. 87(2): 224-230.

Kumar, P. and Kunzru, D. (1985). Kinetics of coke deposition in naphtha pyrolysis. *The Canadian Journal of Chemical Engineering*. 63(4): 598-604.

Kumar, P. and Kunzru, D. (1985). Modeling of naphtha pyrolysis. *Industrial & Engineering Chemistry Process Design and Development*. 24(3): 774-782.

Liu, C., Zhang, J., Xu, Q. and Li, K.(2010). Cyclic scheduling for best profitability of industrial cracking furnace system. *Computers & Chemical Engineering*, 34(4): 544-554.

Masoumi, M., Shahrokhi, M., Sadrameli, M. and Towfighi, J. (2006). Modeling and control of a naphtha thermal cracking pilot plant. *Industrial & Engineering Chemistry Research*. 45(10): 3574-3582.

Mohamadalizadeh, A., Towfighi, J. and Karimzadeh, R. (2008). Modeling of catalytic coke formation in thermal cracking reactors. *Journal of Analytical and Applied Pyrolysis*. 82(1): 134-139.

Ota, Y., Namatame, K., Hamataka, H., Nakagawa, K., Abe, H., Cervantes, A., Tjoa, I.B. and Valli, F. (2002). Optimization of Naphtha feedstock blending for integrated olefins-aromatics plant production scheduling. *Computer Aided Chemical Engineering*. 10: 739-744.

Rahimpour, M.R., Dehnavi, M.R., Allahgholipour, F., Iranshahi, D. and Joker, S.M. (2012). Assessment and comparison of different catalytic coupling exothermic and endothermic reactions: A review. *Applied Energy*. 99: 496-512.

Redwan, D.S., Lee, A.K.K. and Aitani, A.M. (1990). Changes in crushing strength of hydrocarbon steam-reforming catalyst along the reactor tube under operating conditions. *Journal of Chemical Technology and Biotechnology*. 47(4): 307-317.

Ren, T., Patel, M. and Blok, K.(2006). Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes. *Energy*. 31(4): 425-451.

Riverol, C. and Pilipovik, M.V.(2007). Optimization of the pyrolysis of ethane using fuzzy programming. *Chemical Engineering Journal*. 133(1): 133-137.

Shahrokhi, M. and Nejati, A. (2002). Optimal temperature control of a propane thermal cracking reactor. *Industrial & Engineering Chemistry Research*. 41(25): 6572-6578.

Sundaram, K.M. and Froment, G.F.(1977). Modeling of thermal cracking kinetics-II: Cracking of iso-butane, of n-butane and of mixtures ethane-propane-n-butane. *Chemical Engineering Science*. 32(6): 609-617.

Sundaram, K.M. and Froment, G.F.(1977). Modeling of thermal cracking kinetics-I: Thermal cracking of ethane, propane and their mixtures. *Chemical Engineering Science*. 32(6): 601-608.

Sundaram, K.M., Shreehan, M.M. and Olszewski, E.F.(2001). Ethylene. Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.

Towfighi, J. and Karimzadeh, R. (1993). Development of a mechanistic model for pyrolysis of naphtha. In *Process Industries Power the Pacific Rim: Sixth Conference of the Asia Pacific Confederation of Chemical Engineering; Twenty-first Australasian Chemical Engineering Conference.Official Proceedings of Combined Conference 1993* (p. 331). Institution of Engineers, Australia.

Van Geem, K.M., Reyniers, M.F. and Marin, G.B. (2005). Two severity indices for scale-up of steam cracking coils. *Industrial & Engineering Chemistry Research*. 44(10): 3402-3411.

van Goethem, M.W., Barendregt, S., Grievink, J., Verheijen, P.J., Dente, M. and Ranzi, E. (2013). A kinetic modelling study of ethane cracking for optimal ethylene yield. *Chemical Engineering Research and Design*. 91(6): 1106-1110.

Van Speybroeck, V., Hemelsoet, K., Minner, B., Marin, G.B. and Waroquier, M.(2007). Modeling elementary reactions in coke formation from first principles. *Molecular Simulation*. 33(9-10): 879-887.

Wang, K.L.C., Li, H. and Ecker, J.R.(2002). Ethylene biosynthesis and signaling networks. *The Plant Cell*. 14(suppl 1): S131-S151.

Wauters, S. and Marin, G.B. (2002). Kinetic modeling of coke formation during steam cracking. *Industrial & Engineering Chemistry Research*. 41(10): 2379-2391.

White, W.C.(2007). Butadiene production process overview. *Chemico-Biological Interactions*. 166(1): 10-14.

Yancheshmeh, M.S., Haghighi, S.S., Gholipour, M.R., Dehghani, O., Rahimpour, M.R. and Raeissi, S.(2013). Modeling of ethane pyrolysis process: A study on effects of steam and carbon dioxide on ethylene and hydrogen productions. *Chemical Engineering Journal*. 215: 550-560.

Yancheshmeh, S., Seifzadeh Haghighi, S., Gholipour, M. R., Dehghani, O., Rahimpour, M. R., & Raeissi, S. (2013). Modeling of ethane pyrolysis process: A study on effects of steam and carbon dioxide on ethylene and hydrogen productions. Chemical Engineering Journal, 215, 550-560.

Zámostný, P., Karaba, A., Olahová, N., Petrů, J., Patera, J., Hájeková, E., Bajus, M. and Bělohlav, Z. (2014). Generalized model of n-heptane pyrolysis and steam cracking kinetics based on automated reaction network generation. *Journal of Analytical and Applied Pyrolysis*. 109: 159-167.

Zhang, Z. and Albright, L.F. (2010). Pretreatments of coils to minimize coke formation in ethylene furnaces. *Industrial & Engineering Chemistry Research*. 49(4): 1991-1994.

Zhao, P.F., Ji, S.F., Wei, N., Liu, H., and Li, C.Y. (2010). Preparation, characterization and hydrodesulphurization catalytic performance of AL-Ni2 P/SAB-15 catalysts. *Chinese Journal of Inorganic Chemistry*. 26(12): 2273-2279.