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Simulation and optimization of fluid catalytic cracking processes for environmentally friendly light products

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UNIVERSITY OF THE
WITWATERSRAND,
JOHANNESBURG

Simulation and optimization of Fluid Catalytic Cracking processes for environmentally friendly light Products.

MSc RESEARCH DISSERTATION

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Submitted to

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Supervisors:

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10 December 2018

To the women who believed in me.

Be curious always! For knowledge will not acquire you; you must acquire it

~ Sudie Back

DECLARATION

This dissertation is the result of my own work and includes nothing, which is the outcome of work done in collaboration except where specifically indicated in the text. It has not been previously submitted, in part or whole, to any university of the institution for any degree, diploma, or other qualification.

Signed:_____

Date:_____

Moyo, Nomzamo Qaziwe (NQ)

SUMMARY

The rapid industrialization that happened in the early turn of the 18th century came with a lot of positives, and these include the invention of engines which became the back bone of a number of industrial equipment. In the 20th century the draw backs of the continuous industrialization came to light, the hole in the ozone layer was discovered, this led to industrialists being urged to try and find better ways to achieve production whilst decreasing their carbon foot print.

Refinery emissions contributed greatly to the carbon foot print, and it is worth investigating ways to reduce the amount of emissions. The Fluid Catalytic Cracking (FCC) unit, which is the heart of most refineries, is one such unit that contributes up to 10% of a refinery's greenhouse emissions. Due to the high emissions from the FCC unit a number of studies are being conducted to try and curb the high emissions.

This project is aimed at finding ways to reduce the amount of CO_2 that is emitted into the atmosphere as well as to optimize on the energy used. A simulation in Aspen HYSYS was built and a case study was performed to help find the optimum operating point of the FCC. A discussion of the results has been conducted and recommendations given.

ACKNOWLEDGMENTS

I would like to extend my gratitude to the following people;
My supervisor, Professor J. Mulopo, who has assisted me in every step of the way in producing this report with a critical eye on the content produced at every step. Your assistance is greatly appreciated.
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My family and friends, for the unwavering support during this time.

Without all the above mentioned this project would not have been possible.

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LIST OF ABBREVIATIONS AND ACRONYMS

FCCU	Fluid catalytic cracking unit
LPG	Light petroleum gas
COR	Catalyst to oil ratio
$\dot{W}$	Energy rate (J/kg)
H	Enthalpy
f_s	Flow system
T_σ	Temperature of the surroundings
S	Entropy
$\dot{m}$	Mass flow rate
Q	Enthalpy
N	Number of lumps
SCC	Synthetic catalytic cracker
HVGO	Heavy vacuum gas oil
$\dot{E}_{net}$	Net exergy
$\dot{E}_{produced}$	Produced exergy
$\dot{E}_{dest}$	Destroyed exergy
$\dot{E}_{cat}$	Catalyst exergy
$\dot{E}_{gasoil}$	Gasoil exergy
$\dot{E}_{st}$	Steam exergy
$\dot{E}_{cooling}$	Cooling exergy
RON	Research Octane Number
DCS	Distributed Control System

1. INTRODUCTION

From the early years of the industrial revolution a variety of fuels have been in demand. In the early years of the revolution raw materials were used directly to supply the energy needed to drive engines. However as technological advancements were made more sophisticated fuels were required to run the new equipment. At the turn of the 21st century, these sophisticated fuels also came with more stringent quality specifications values as environmental consciousness was also on the rise. Product specifications of most fuels became more stringent, these tightly measured regulations left refiners with the mammoth task of optimizing their production mechanisms at the same time meeting government regulated product specifications. The government did not only put regulations for the product specifications but also for the emissions during the production of the fuels, and this has led to the common term 'clean fuels' being used to refer to the fuel products.

In order for the refinery to make the much needed profits, as well as to meet the ever increasing fuel demand, as shown in figure 1, a number of optimization projects have been implemented. Continuous studies in the areas of optimization and reduction of greenhouse gases are being carried out to find more ways to increase the yield of more valuable products whilst using the least amount of energy.

A number of technologies have been introduced in the refinery to meet the ever increasing demand for lighter fuel products, one such technology is the fluid catalytic cracking unit (FCC), which has become the heart of the refining process.

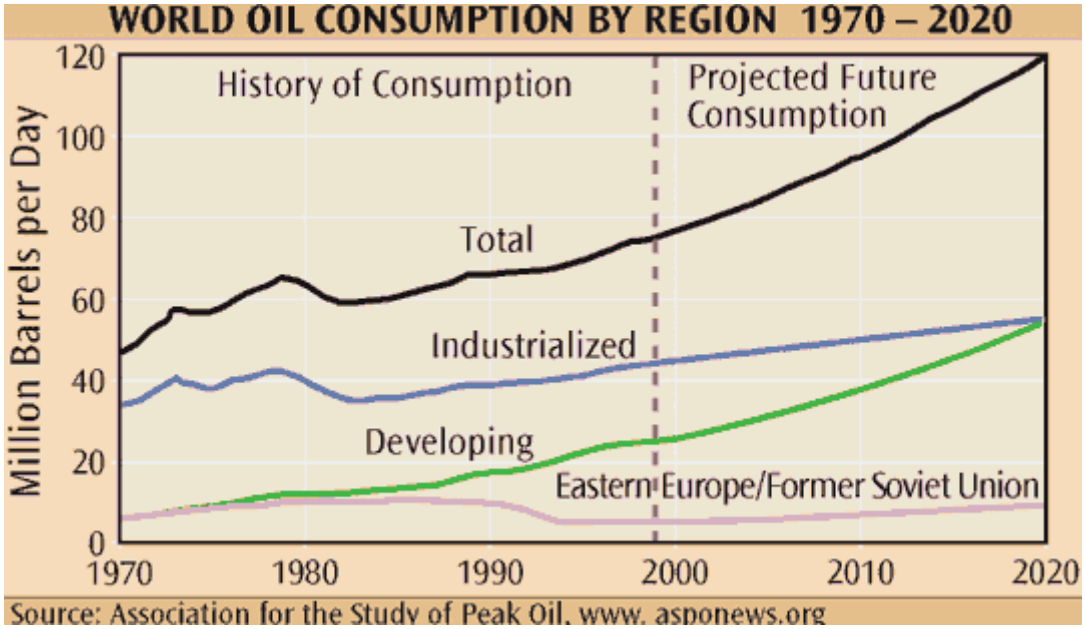


Figure 1: Oil Supply vs Demand, source: (Association for the study of peak oil. www.asponews.org)

FCC units are widely used in the petrochemicals industry in the production of light hydrocarbons from heavy hydrocarbons whose boiling point is above 350°C. The heavy hydrocarbons are broken down into lighter more profitable products such as gasoline components, middle distillates and chemicals in the presence of a catalyst in a reactor (Sadeghbeigi, 2012). Despite the FCC units addressing some of the world's demands for light products, they have the drawback of producing high volumes of CO_2 as well as consuming high volumes of energy thereby rendering the process environmentally unfriendly and expensive to run. Instabilities in oil prices is making it harder for refineries to predict their profits, when the oil price is low the refinery is less profitable. Figure 2 shows the trend of oil prices for a period of 18 years. The production of light products in FCC units has to be optimized in order for refineries to remain economically viable even when the oil rice is low, this is also in light of the National Environment Management: Air Quality Act No. 39, failure to abide by the act will result in heavy penalties.

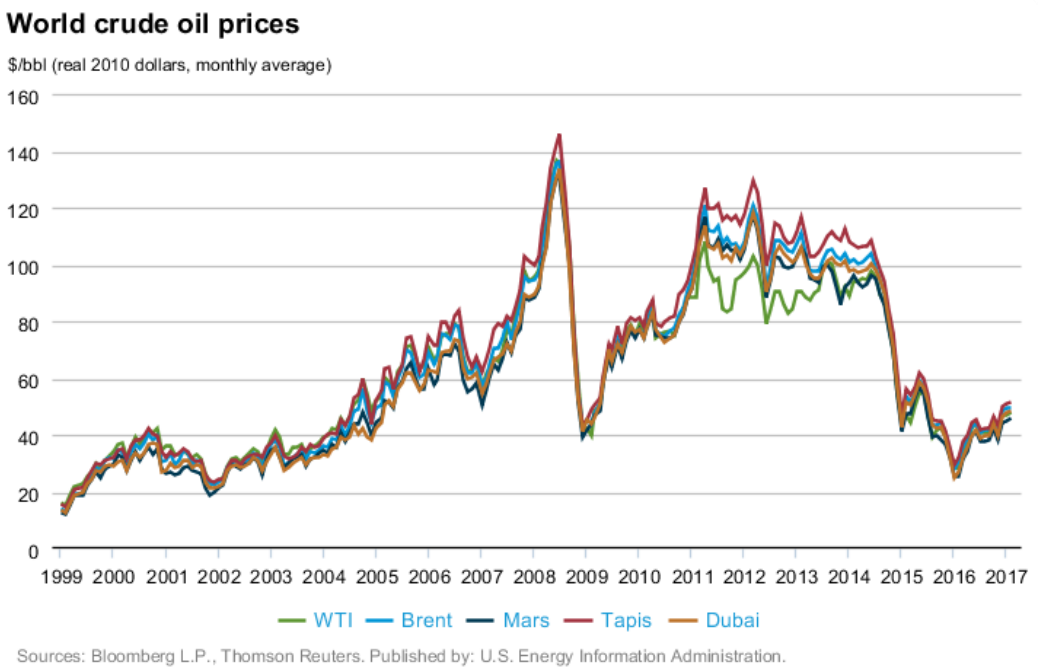


Figure 2: World oil prices, source: (Bloomberg L. P, Thomson Reuters.)

As the acts and laws governing emissions are becoming more stringent and the penalties for non-compliance are increasing, this in turn affects business net profit margins. New policies in addition to the already existing ones are also being passed in a bid to minimize hazardous emissions. The South African Carbon Tax Policy, is a carbon dioxide abetment policy aimed at reducing the amount of greenhouse gases emitted into the atmosphere, as the tax policy is being rolled out, it is worth researching ways to reduce the amount of carbon dioxide that FCC units emit into the atmosphere through unit optimization. The idea of optimization is more lucrative to most refiners as compared to debottlenecking, as debottlenecking requires additional equipment to be put up which could cost billions of Rands in project implementation. Typically, carbon dioxide makes up 10% of the gases exiting a flue stack in an FCC unit and this number can be reduced(Van Houwelingen, 2017).

2. PROBLEM STATEMENT

The current economic, and environmental landscapes put significant pressures on petroleum refineries to optimize and integrate the refining process. Fluid catalytic cracking units (FCCU) continue to play a key role in an integrated refinery as the primary conversion process in the production of light hydrocarbons from heavy hydrocarbons and remain by far the largest producer of gasoline and light ends in refineries (Sadeghbeigi, 2012). For many refiners, the catalytic cracker is the key to profitability in that the successful operation of the unit determines whether or not the refiner can remain competitive in today's market. Due to the complexity of the catalytic cracker, meaningful improvements should consider a broad range of process aspects which include, the reaction chemistry, feed characteristics and equipment performance. In such an endeavour, the use of simulation package such as Aspen HYSYS is critical for process simulation, further validation with plant data to identify key areas for improvements is very important. Though, there is significant previous work that addresses the issues of process dynamics and control to identify control schemes and yield behaviour for the FCC unit, this work fills the gap between the development of simple FCC simulation model and industrial application in a large-scale refinery that can be utilised in carbon dioxide production minimization and energy consumption optimization. Most models that exist were built for the design stage of the refinery, this model will be used to optimize an existing running plant.

2.1 RESEARCH OBJECTIVES

Refiners are very interested in obtaining optimal operating conditions that maximize the yield of a profitable product slate. Obtaining optimal operating conditions that maximize the yield of a profitable product slate is every refiners' objective. Optimizing the product slate to energy ratio of the FCC unit is critical in ensuring profitability of the unit in light of the ever-changing prices of the product slate. Unlike traditional chemical plants, the FCC unit generates several products that have different profit margins. Further complicating matters is that these profit margins may change depending on refinery constraints, market conditions and existing regulations. Therefore, it is

critical to understand how to manage the FCC unit under different operating scenarios. An understanding of the energy issues of the FCC reactor will enable refiners to operate the refinery optimally, in order to do this energy studies must be conducted to locate areas of energy optimization hence improving the product slate to energy ratio.

The project will focus on the following objectives;

1. For a fixed feed composition, varying of inputs in FCC operation will permit for a study of the energy response of the system, this will be achieved by holding the feed rate constant and varying the riser outlet temperature (ROT), Aspen HYSYS will be used to create a simulation of an existing plant to achieve the objective.
2. An additional objective of the project is to improve on energy efficiency of the FCC which might lead to a reduction in CO_2 produced. Previous studies have shown that a correlation exists between FCC efficiency and the amount of CO_2 produced (Yakubu, Patel and Mujtaba, 2017).

3. LITERATURE REVIEW

FCC reactors are a major conversion technology in oil refineries and they produce a majority of the world's light fuels and valuable chemicals, this includes high octane gasoline and propylene. As of the beginning of 2014, the fluid catalytic cracking process was operational in 300 of 646 refineries and more are still to be commissioned (Vogt and Weckhuysen, 2015).

FCC technology came about in the 1940s, the use of oil for lighting and heating was on the rise, as industrialization progressed more oil was needed to supply the growing number of industries. Bayton, Texas was the first company to commission a full-scale FCC unit. Further improvements were done on the unit with the introduction of a highly active catalyst in the 1960s (Perry and Green, 2007). A number of companies have contributed and continue to do further research on the FCC unit; these include Exxon Research and Development Co., Shell Oil Company and Universal Oil Products Company, these companies normally provide designs or licences for other companies. The type of design normally varies with each refinery's objectives.

3.1 PROCESS DESCRIPTION

The FCCU is used for the cracking of paraffins (C_{8+}) to lighter more valuable products. In the FCC unit high molecular weight olefins and paraffin's are converted to ethylene and propylene over a ZSM-5 zeolite catalyst, high octane gasoline is also produced in the process.

The following equipment is normally found in FCCUs:

- Pre-heat furnace
- Catalytic Cracker
- Catalyst fines system
- Flare systems

High vacuum gas oil (HVGO), which is the feed, is first sent to a surge drum under level control and is pumped to the feed preheat furnace, the water that collects at the bottom of the surge drum is constantly drained to prevent water carry over into the furnace. The feed first goes through the

convectional section of the furnace, and then through the radiation section where it is superheated to elevated temperatures. The furnace effluent flows to the riser reactor in the converter section.

In the converter, the feed is converted to lighter products, the converter is divided into four sections; the cracking riser reactor, catalyst disengager, spent catalyst stripper and the regenerator, there is continuous circulation of catalyst occurring from section to section. The catalyst stripper and disengager vessel are normally located directly above the regenerator.

In this set up the catalyst flow moves from the cracking riser, into the disengager, into the stripper and finally to the regenerator where coke deposited during the cracking reaction is burnt off.

A sloped transfer line (standpipe) is used to move the hot regenerated catalyst to the riser. The catalyst flows to the base of the riser and feed is introduced at the bottom of the riser reactor, the catalyst and the feed rise up and to the disengager into the riser cyclones, whilst the endothermic cracking takes place.

Superheated steam is used to aerate the catalyst in the standpipe and dense phase of the riser. The steam is injected along the standpipe to replace gas volume lost due to increasing pressure as the catalyst moves down the slide valve.

A short contact time is essential between the feed and the catalyst to ensure that over cracking does not occur, the riser is normally designed for less than two seconds contact time.

The riser turns from vertical to horizontal, at this point the riser enters the disengager zone and terminates at the riser cyclones. The riser cyclones are designed to make a fast separation of the product gas and the catalyst to ensure that further reactions do not occur. The riser outlet temperature is controlled by the amount of hot regenerated catalyst admitted into the riser.

The disengager houses the closed cyclone system that separates the cracked gas from the catalyst. The reaction vapours pass directly from the riser cyclone outlet in to the transition chamber and then into the upper disengager cyclone. The reaction vapours with some catalyst carry over and leave the disengager through the upper cyclones were the trace catalyst is removed.

Catalyst separated in both the riser and the disengager cyclones flows through the respective dip legs and deposits into the stripper. In the stripper, the catalyst is contacted with steam flowing upwards to remove any entrained hydrocarbons. Since the steam partial pressure is high the remaining hydrocarbons diffuse out of the catalyst pores leaving only solid coke on the spent catalyst.

The catalyst then flows into the spent catalyst well were it is fluidised with an aeration ring, tail gas is used for the aeration, superheated steam can be substituted in for the tail gas. In addition to

the tail gas fuel oil is sprayed onto the catalyst. The fuel oil, tail gas, and coke provide fuel required by the regenerator exothermic reaction.

In the regenerator air rich in oxygen is added to aid in the combustion of the coke that deposits on the catalyst, this is an exothermic reaction. The products of combustion consist of carbon monoxide, carbon dioxide, and water.

The heat generated by the exothermic reaction in the regenerator is the heat supply for the endothermic reaction that occurs in the riser. Combustion air is supplied by a compressor and enters the regenerator via a ring distributor.

The regenerated catalyst exits the regenerator through the opening in the regenerator's bottom and flows into the catalyst standpipe completing the circulation back into the riser.

3.3.1 TYPICAL CRACKING REACTIONS

A series of reactions take place when hydrocarbons come into contact with a catalyst at temperatures of 450ºC. The most significant reactions being cracking, isomerization and hydrogenation. Product distribution is highly dependent on the properties of the catalyst acid sites, as well as the catalyst strength and nature (Sadeghbeigi, 2000). Although most of the reactions taking place in the reactor are catalytic, some thermal reactions also take place when the catalytic conditions have ceased to exist. Thermal cracking promotes low order cracking reactions that result in more dry gas being produced, which lowers the profit of the unit. The following sub-topics illustrate some of the reactions that take place in the reactor (Sadeghbeigi, 2000).

As discussed earlier the cracking reactions are particularly important in breaking down the heavy components into more useful products. Isomerization is important as it forms high octane products that increase the RON of the gasoline being produced. Hydrogenation reactions saturate the unsaturated hydrocarbon reducing the cloud point in diesel products (Pashikanti and Liu, 2012). Typical reactions are given below;

Cracking reactions

Paraffins are cracked to smaller chain paraffins and olefins.

Equation 1

$$C_{10}H_{22} \rightarrow C_4H_{10} + C_6H_{12}$$

Olefins crack to smaller olefins

Equation 2

$$C_9H_{18} \rightarrow C_4H_8 + C_5H_{10}$$

Aromatic side chain scission

Equation 3

$$ArC_{10}H_{21} \rightarrow ArC_5H_9 + C_5H_{12}$$

Cyclo-parrafins are cracked to olefins and smaller ring compounds

Equation 4

$$Cyclo - C_{10}H_{20} \rightarrow C_6H_{12} + C_4H_8$$

Isomerization

Olefin bond shift

Equation 5

$$1 - C_4H_8 \rightarrow trans - 2 - C_4H_8$$

Normal olefins to iso-olefins

Equation 6

$$n - C_5H_{10} \rightarrow iso - C_5H_{10}$$

Normal paraffins to iso-parrafins

Equation 7

$$n - C_4H_{10} \rightarrow iso - C_4H_{10}$$

Cyclo-hexane to cyclo-pentane

Equation 8

$$C_6H_{12} \rightarrow C_5H_9CH_3$$

Hydrogen transfer

Equation 9

$$napthene + olefin \rightarrow aromatic + parrafin$$

Trans-alkylation

Diethyl benzenes arise as side-products of the alkylation of benzene with ethylene. Diethyl benzene, is recycled by trans-alkylation to give ethyl benzene.

Equation 10

$$C_6H_4(C_2H_5)_2 + C_6H_6 \rightarrow 2\,C_6H_5C_2H_5$$

Cyclization of olefins and naphthene's

Equation 11

$$C_6H_4(CH_3)_2 + C_6H_6 \rightarrow 2C_6H_5CH_3$$

Dehydrogenation

This reaction involves the removal of hydrogen from the hydrocarbon chain. Dehydrogenation is an important reaction because it converts alkanes, which are relatively inert and thus low-valued, to olefins, which are reactive and thus more valuable.

Equation 12

$$n - C_8H_{18} \rightarrow C_8H_{16} + H_2$$

De-alkylation

Alkylation produces light, gaseous hydrocarbons are combined to produce high-octane components of gasoline.

Equation 13

$$Iso - C_3H_7 - C_6H_5 \quad \rightarrow C_6H_6 + C_3H_6$$

Condensation

Condensation of single aromatic cores produces multiple ring aromatic cores.

Equation 14

$$Ar - CH = CH_2 + R_1CH = CHR_2 \rightarrow Ar - Ar + 2H$$

Hydrogen selectivity's

The split of each reaction can be determined by a hydrogen balance

Equation 15

$$CH_z \rightarrow a \cdot CH_x + (1 - a)CH_y$$

$$z = a \cdot x + (1 - a) \cdot y$$

The following assumptions are made with regards to the reactions:

1. The hydrogen 'sink', C_{4-} paraffins and hydrogen have a fixed distribution and will be formed regardless of the distribution of all reactions. The hydrogen: carbon ratio of 3.65 is expected.
2. Dienes always form olefins to a fixed carbon distribution. The average carbon number of the distribution is 5.17.
3. Aromatics distribution is constant over the sheet with a distribution number of 7.23
4. The average molar mass of alcohols is taken as 107g/mol.
5. The average molar mass of carbonyls in the feed is 88.5g/mol.

Table 1: Typical reactions in the FCC reactor, source:(Van Houwelingen, 2017)

Reaction	Reagent	Products	Selectivity	Notation
(1)	C5	Olefins	0.74 X5	X5 =Conversion of C5 paraffins
		C4- paraffins	0.26 X5	
		C5 paraffins (unconverted)	1- X5	
(2)	C6	Olefins	0.78 X6	X6 =Conversion of C6 paraffins
		C4- paraffins	0.22 X6	
		C6 paraffins (unconverted)	1 – X6	
(3)	C7	Olefins	0.81 X7	X7 =Conversion of C7 paraffins
		C4- paraffins	0.19 X7	
		C7 paraffins (unconverted)	1 – X7	
(4)	C8	Olefins	0.83 X8	X8 =Conversion of C8 paraffins
		C4- paraffins	0.17 X8	
		C8 paraffins (unconverted)	1 – X8	
(5)	Olefins	Dienes	0.79 Xol	Xol =Conversion of olefins
		C4- paraffins	0.21 Xol	
		Olefins (unconverted)	1-Xol	
(6)	Dienes	Aromatics	0.79 Sar Xdi	Sar = selectivity of dienes reaction towards aromatics formation (and associated C4- paraffins) ahv = heavies:C4- paraffins for reaction from dienes to heavies Xdi = dienes conversion
		Heavies	ahv (1-Sar) Xdi	
		C4- paraffins	[0.21 Sar +(1-ahv)(1-Sar)] Xdi	
		Dienes (uncoverted)	1-Xdi	
(7)	Heavies	Aromatics	Xhv	Xhv= (feed) heavies conversion to aromatics
		Heavies (unconverted)	1-Xhv	
(8)	Carbonyls	CO	0.32 Sdc	Sdc = Selectivity towards de-carbonylation
		C4- paraffins	0.68 Sdc	
		Aromatics	0.80 (1-Sdc)	
		H2O	0.20 (1-Sdc)	
(9)	Alcohols	Olefins	0.83	N/A
		H2O	0.17	

(10)	Cyclics	Aromatics	0.62	N/A
		C4- paraffins	0.38	

3.2 FCC EQUIPMENT

The reactor, regenerator and distillation column are major equipment in the FCC process. Different designs exist as per the refinery feed. The high rate of exchange between the exothermically generated catalyst and the endothermic cracking of the petroleum feedstock enables the FCC unit energy to be controlled without using auxiliary heating mechanisms (Perry and Green, 2007). This high exchange also helps to maintain the high catalyst activity.

- **Riser reactor or down comer reactor**. The heavy hydrocarbons and catalyst are fed into the reactor at high temperature. The high temperatures are such that the heavy hydrocarbons are in their gaseous form enabling a gas-solid reaction to take place on the surface of the catalyst. The reactor operates similarly to a plug flow reactor, an endothermic reaction takes place inside the reactor. The catalyst used is a zeolite catalyst; energy is absorbed by the catalyst from the hydrocarbon and this breaks the long chain hydrocarbons converting them to shorter chain hydrocarbons (lighter fuels). The difference between the riser and the down comer reactors is the method in which the feed is introduced into the reactor. In the riser, feed is introduced from the bottom and steam is used to disperse the heavy hydrocarbons. In the down comer, the heavy hydrocarbon is fed from the top and moves down the reactor by gravity.(Lopez-Isunza, 1990)

  The reactor consists of the mixing zone as well as the reaction zone. The region where the feed oil and hot catalyst come into contact in the reactor is known as the mixing zone. When building a reactor model this section is considered to be a small part of the reactor, vaporization occurs in this zone. The feed and catalyst are assumed to be at an equal temperature when exiting the mixing zone (Sildir *et al.*, 2015). It is assumed that no reaction occurs in the mixing region as the feed is still liquid, the reaction only occurs in the feeds gaseous form. The cracking reaction is normally assumed to be first order and that the riser is at pseudo-steady state. The energy balance and mass balance model equations are important when modelling the riser reactor, this allows for the ease of predictability of the outputs.

  The riser reactor is operated co-currently as this makes it more energy efficient, modelling work carried out by Lopez-Isunza et al confirmed the operation mode. A model was set up

to compare the yields of gasoline when co-current and counter current streams were introduced into the reactor. Figure 3 shows the results produced by the model.

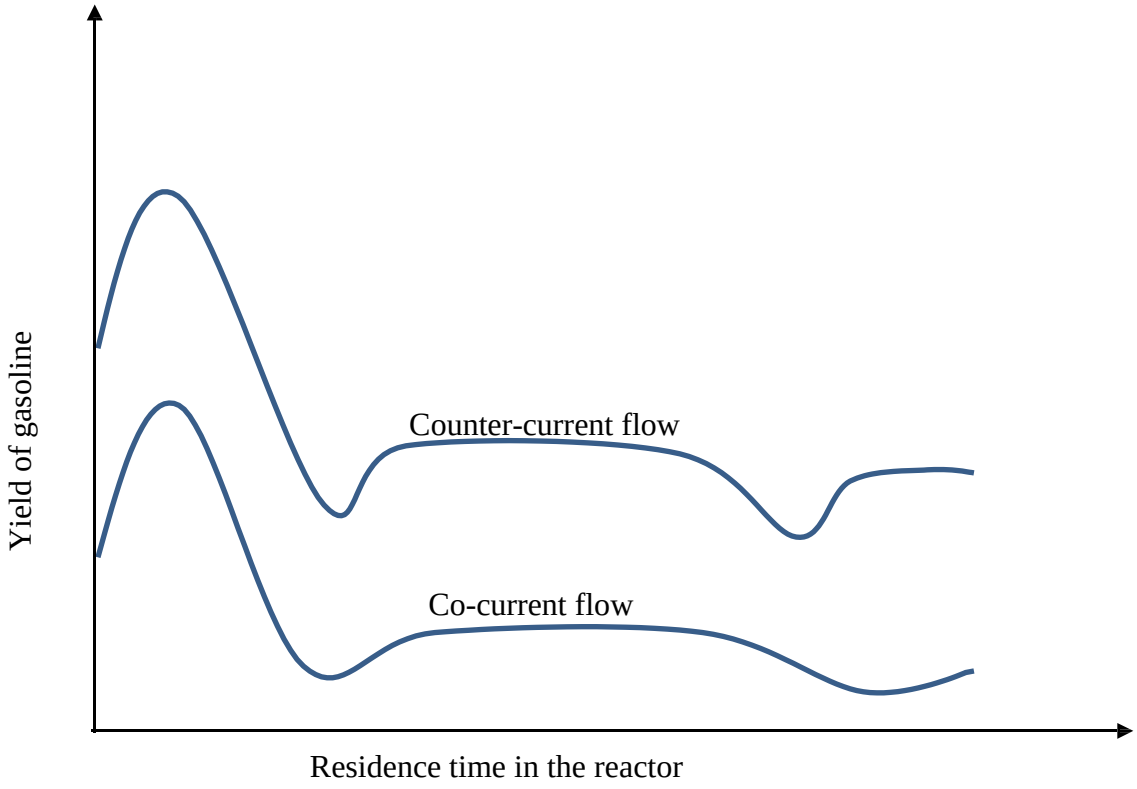


Figure 3: Co-current and counter current flow model results, source: (Lopez-Isunza, 1990)

- **The regenerator.** Carbon deposits onto the catalyst in the reactor contributing to the deactivation of the catalyst by reducing the surface area available for cracking reactions, the carbon is burnt off in an exothermic reaction in the regenerator providing the energy needed in the reactor for the endothermic reaction. (Sadeghbeigi, 2000).

  The regenerator consists of two sections the dense bed and the freeboard. The dense bed holds a majority of the catalyst and has a particle lean bubble phase and a particle rich emulsion phase. Due to a large amount of catalyst in the reactor, the residence time of the catalyst is higher in the regenerator. (Lopez-Isunza, 1990)
- **The fractionator.** The products from the catalytic cracking reactor as well as steam that is introduced are separated in the fractionator. The fractionator uses the different boiling points of the components to separate them.

The feed into conventional FCC units is made up of; paraffin's, olefins, naphthene's, aromatics, sulphur compounds, oxygen compounds, nitrogen compounds, metallic compounds, alsphatenes,

and resins. The main products that are produced are; light petroleum gas (LPG), gasoline, kerosene, jet fuel, diesel fuel, fuel oil, residual fuel oil, lube oil, asphalt and petroleum coke. Figure 4 shows the main equipment as well as the flow in the FCC process.

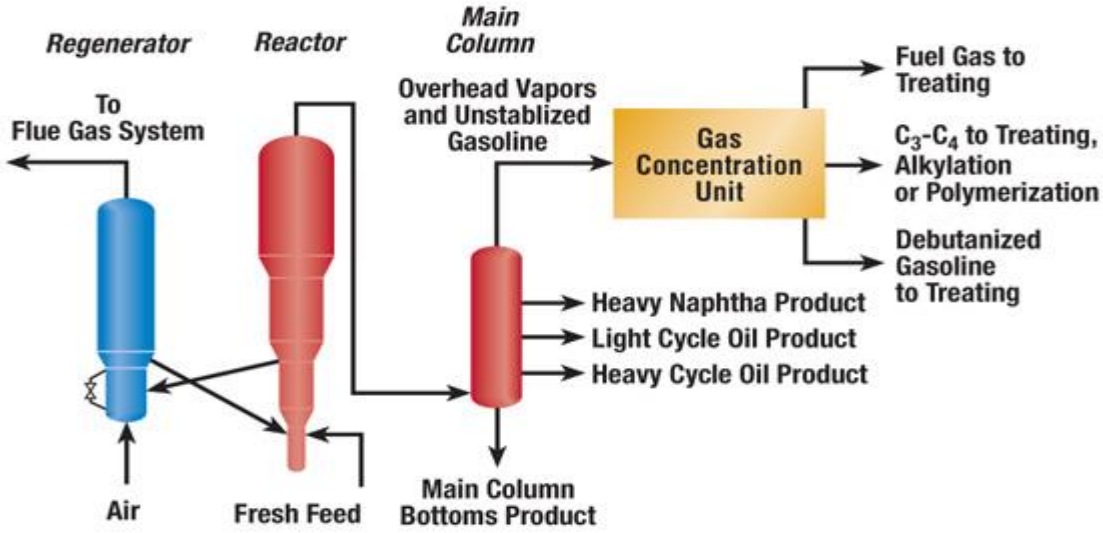


Figure 4: Schematic diagram of Riser reactor FCC Unit, source: (www.uop.com)

Modelling of an FCC reactor involves the following (Shikha Dhankhar, 1995):

- Catalyst deactivation modelling.
- Material balance modelling.
- Hydrodynamic modelling, although in some models it is believed that the velocity of the two phases is equal a slip factor is sometimes introduced and it is assumed to be constant along the reactor.
- Kinetic modelling, the different species are grouped according to their different boiling points. A lot of work has been done on the grouping, the kinetic models range from 3-19 lumps, the 4-10 lumps are commonly used for modelling purposes.(Ranzi *et al.*, 2001)(Cristina, 2015).

When modelling the FCC unit a couple of general assumptions are made (John, Patel and Mujtaba, 2017), these are:

- The feed vaporizes instantly when it comes into contact with the hot catalyst from the regenerator, the vapour and fluid move at the same velocity and there is no heat loss in the riser
- The cracking reactions quickly take place in the riser and the coke is deposited instantly, this allows for the assumption of steady state operation
- The vaporizing section is ignored in most models
- System momentum equations are sometimes ignored
- The rate of dispersion and absorption are not included in most models
- Coke deposition does not affect catalyst velocity

In previous years focus has been put on the selectivity performance and the yields of FCC units, considering the high energy cost environment of these units. A lot of opportunities have also been found in the heat integration of the FCC unit to save energy, these integrating opportunities exist inside the battery limit of the FCC and sometimes will include other processes in the refinery to maximize heat and power recovery (Wolschlag *et al.*, 2009).

The FCC unit supplies its own fuel by burning the coke that deposits on the catalyst in the regenerator. The operator can determine the severity of the coke that is burned, which will in turn, determine the extent of cracking depending on the feedstock. Adequate coke has to be burned to increase the feed conversion and produce an optimal yield pattern (Wolschlag *et al.*, 2009). However the burning of coke in the regenerator produces high volumes of CO_2. The South African government has committed to reducing these greenhouse emissions by 34% in 2020 and by 42% in 2025, hence it is in the best interests of all industries to find ways to reduce the CO_2 emitted into the atmosphere from their unit processes (Report, 2017).

3.3 UNIT CONFIGURATIONS

A number of FCC proprietary designs are have been developed for modern FCC units. Each design is available under a license that must be purchased from the design developer.

There are two different configurations for an FCC unit: the "stacked" type where the reactor and the catalyst regenerator are contained in a single vessel with the reactor above the catalyst regenerator and the "side-by-side" type where the reactor and catalyst regenerator are in two separate vessels.

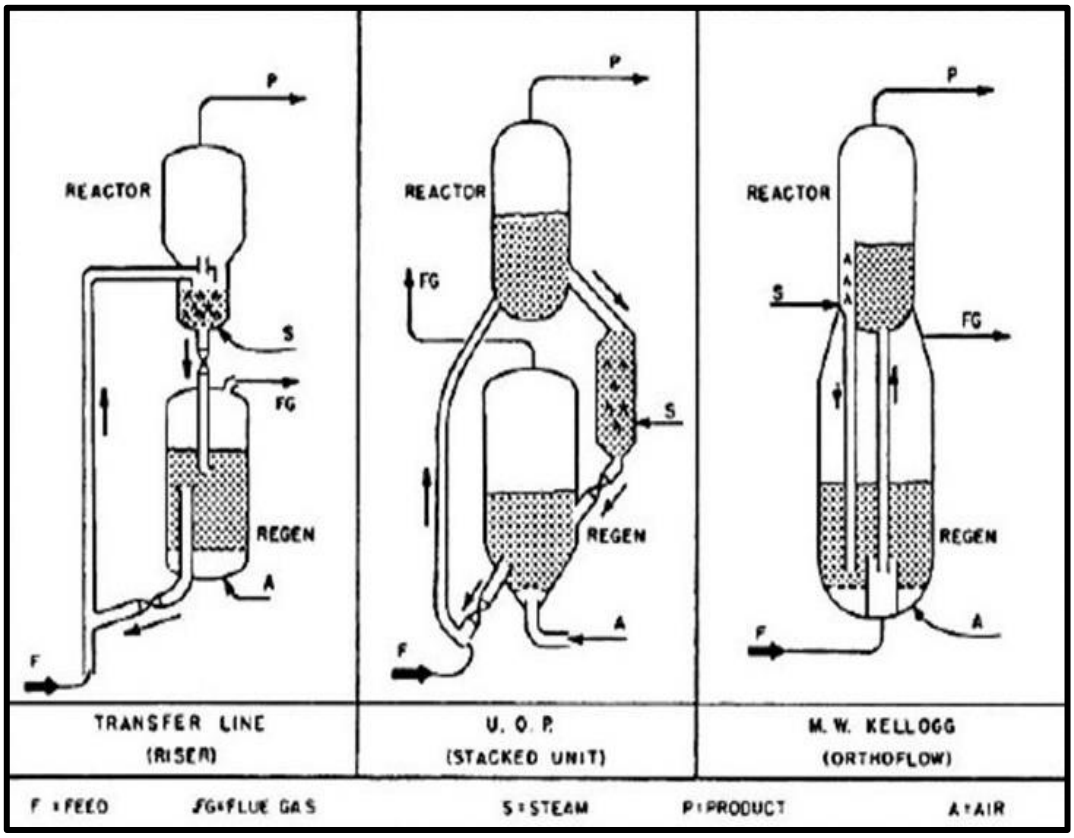


Figure 5: Stacked type reactors, source: (www.slideplayer.com)

In the stacked type FCC, the reactor is stacked on top of the regenerator. The spent catalyst slides down into the regenerator that is directly below it, a valve regulates the catalyst flow as well as the pressure in the system. The regenerated catalyst is transported back into the reactor using a transfer line. Figure 5 shows the different configurations of stacked type of reactors.

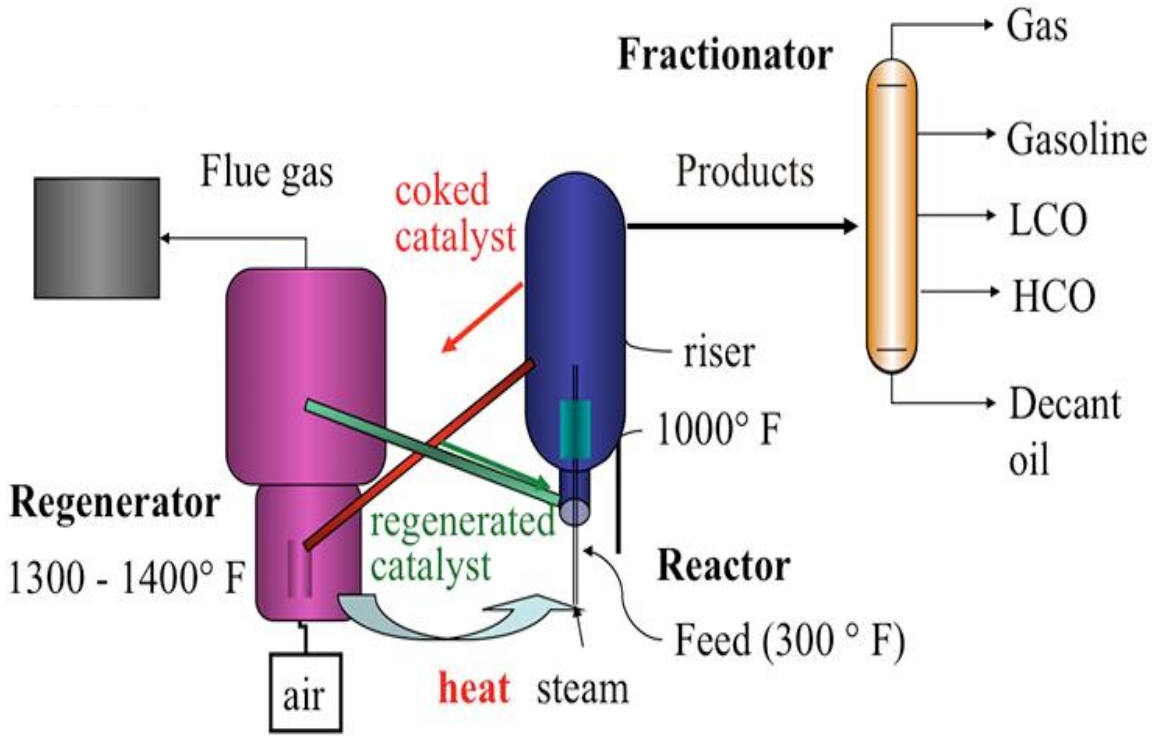


Figure 6: Side-by-side type reactor, source: (www.e-education.psu.edu)

In the side by side reactor the riser and the regenerator are placed next to each other as shown in figure 6. They are connected by transfer lines that allow the circulation of catalyst from the riser, spent catalyst, to the regenerator, and from the regenerator, regenerated catalyst, to the reactor.

3.4 PROCESS DEVELOPMENTS AND MODELLING

A lot of work has been done in the subject matter of development concerning FCC units. The FCC hardware, catalysts and operations have gone through a high evolution ever since FCC units were introduced into refineries. The following areas have changed drastically over the years (O'Connor, 2007):

- Unit size, this has also influenced cost of the unit feed per barrel into the FCC
- Product selectivity and conversion, by the development of catalysts
- Feedstock selectivity, higher carbon feed as well as high metal content feed can be fed into the system

A number of events have influenced the rapid development in FCC units. These developments have either increased the desired yields of the different units or made the FCCU more robust with regards to the feed that the unit can process.

Various models have been produced by different researchers, these models try to mimic already existing units in order to predict the unit products and reactions to varying temperatures, pressures and feed rates. These models are either based on the chemical reaction kinetics of the system or the unit models of the individual components.

3.4.1 CATALYST IMPROVEMENTS

Chemical kinetics in the reactor are driven by heterogeneous catalysis reactions, a series of events that comprise of physicochemical interaction between the solid catalyst and the hydrocarbon gases. In general the catalyst offers active reaction sites for the reactants, the reactants must then be transported to the catalyst surface forces by the action of diffusion and combined with the exposed centres in an action called chemisorption, and this combination with active centres generates products. These products must then be desorbed from the surface of the catalyst into the bulk fluid phase (Carberry, 2001). As the reaction proceeds some products are left on the surface of the catalyst and these reduce the surface area for further reactions rendering the catalyst inactive. In order to activate the catalyst a process of regeneration maybe be conducted.

Catalytic management and selection is one of the greatest aspects to a refinery, as these directly determine the yield in the reactor. The first commercial catalyst was acid treated clay containing alumina. The greatest and probably most beneficial development to refiners has been the introduction of more selective and more active catalysts such as zeolites. Zeolites have been introduced as catalysts in favour of amorphous silica-alumina (Sadeghbeigi, 2000). The nature of a catalyst promotes higher yield of some products as compared to others, in order to choose the right catalyst understanding the zeolite structure, cracking mechanism and products yields is very important (Sadeghbeigi, 2000). Figure 7 shows the typical illustration of a zeolite catalyst.

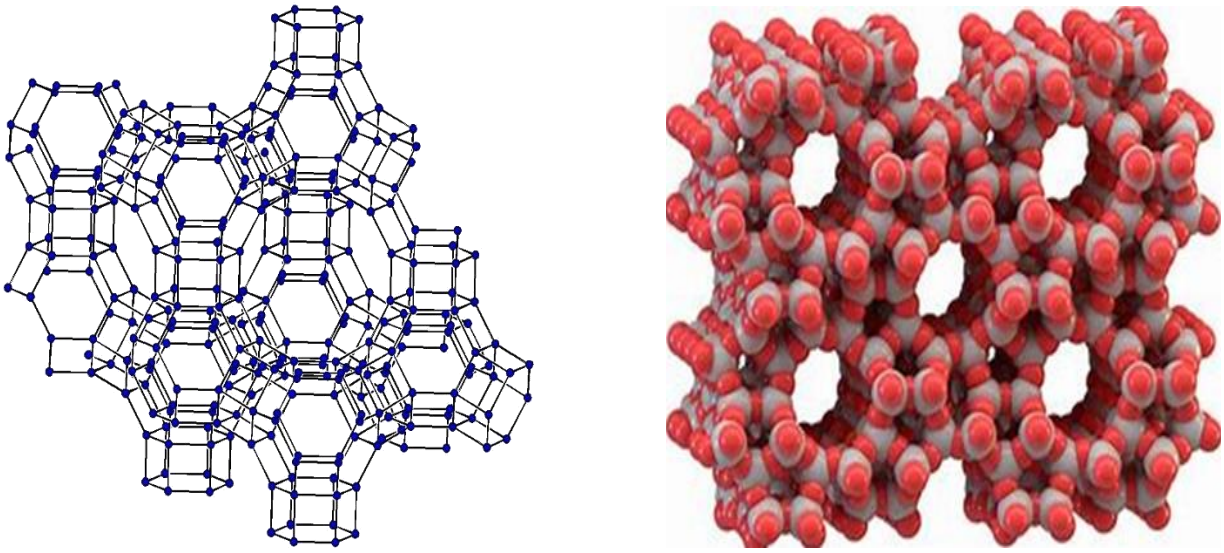


Figure 7: ZSM 5 structure, source: (nuigalway.ie and everipedia.org)

Introduction of zeolites improved the yield of octanes and light olefins as well as decreased the contact time in the reactor (O'Connor, Hakuli, and Imhof, 2004), this is relationship is shown in figure 8.

The zeolite catalyst, ZSM-5, effectiveness is decreased with hydrogen transfer activity (O'Connor, Hakuli, and Imhof, 2004).

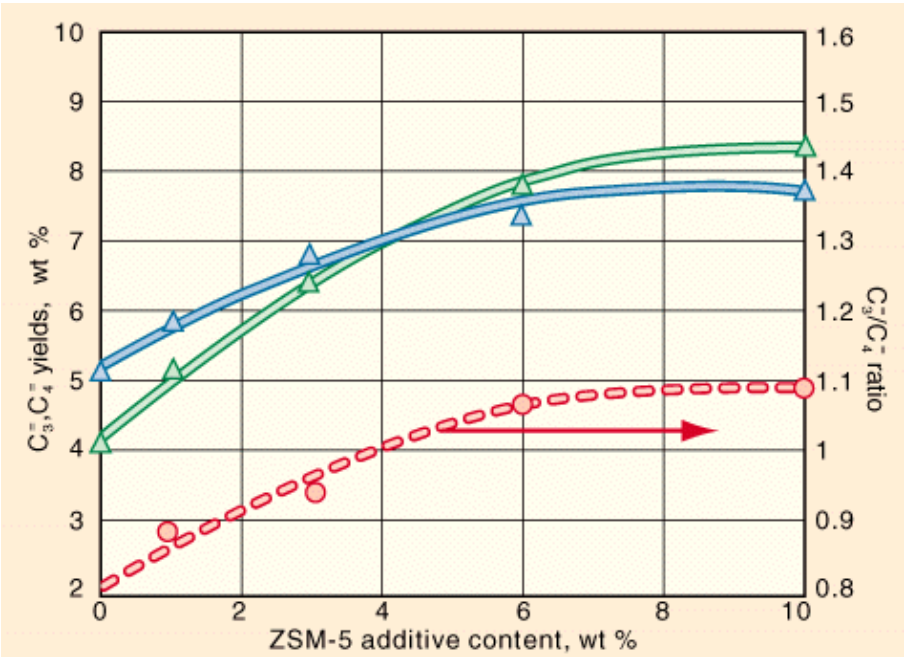


Figure 8: Propylene yield when ZSM-5 is added, Source: Grace Davison, FCC technology

Table 2: Comparison of yield for FCC of waxy gas oil over commercial equilibrium zeolite and amorphous catalysts, source: (Sadeghbeigi, 2000)

Yields, at 80 vol% Conversion	Amorphous, High Alumina	Zeolite, XZ-25	Change from Amorphous
Hydrogen (wt %)	0.08	0.04	-0.04
C_1's 1 C_2's (wt %)	3.8	2.1	-1.7
Propylene (vol %)	16.1	11.8	-4.3
Propane (vol %)	1.5	1.3	-0.02
Total C_3's	17.6	13.1	-4.5
Butenes (vol %)	12.2	7.8	-4.4
i-Butane (vol%)	7.9	7.2	-0.7
n-Butane (vol%)	0.7	0.4	-0.3
Total C_4's	20.8	15.4	-5.4
C_5-390 at 90% ASTM gasoline (vol	55.5	62.0	+6.5
Light fuel oil (vol %)	4.2	6.1	+1.9
Heavy fuel oil (vol %)	15.8	13.9	-1.9
Coke (wt %)	5.6	4.1	-1.5
Gasoline octane number	94	89.8	-4.2

It can be seen that there is an increase in the production of gasoline when a zeolite catalyst is used, also a significant decrease in the dry gas is noted. The higher activity comes from the active sites of the zeolites (Sadeghbeigi, 2000).

3.4.2 PROCESS OPTIMIZATION

Areas of concern exists to the refiner regarding the optimum operation of the FCC unit. Operators can only make a few changes to maintain system stability during operation but robust engineering studies have to be carried out to find ways of moving the system operation to a more optimized state with ease of predictability of the output products. The ease of predictability also allows for better planning in the factory therefore enabling the refiner to meet market demands. The optimization of the FCC will sometimes conflict with other objectives of the refinery such as yields and profits and work has been done to find a good trade-off between process optimization and production objectives of the FCC.

A number of studies in the field of process development have been conducted by different researchers. These include thermodynamic studies that allow for the system energy losses to be

minimized making the process more efficient. A few scholars have looked at varying the process inputs such as oxygen into the reactor, in a bid to try and minimise carbon monoxide formation which when released into the atmosphere contributes to the high pollution levels in the air, this has negative health effects on the humans and animals around the area.

Catalyst to oil ratio (COR) in the unit is an area where extensive research has been conducted in a bid to find the optimum operating values regions, this however highly depends on the feed characteristics into the unit. A high COR will result in a lower feed rate into the system, the conversion of products is poorly compared to the refiners' expectations.

Process debottlenecking has also been considered with various system hardware changes been implemented, to further improve the operation of the FCC unit.

A number of studies are highlighted below in detail that discuss process developments over the years.

Thermodynamic optimization

Thermodynamics is concerned with how energy is transformed. The first law of thermodynamics observes that energy is conserved, yet it also poses no restriction on the process direction, this can be disputed rather, and this dispute constitutes the second law of thermodynamics. The second law of thermodynamics is a general principle which places constraints upon the direction of heat transfer and the attainable efficiencies of heat engines. This goes beyond the limitations imposed by the first law of thermodynamics. The second law states that in a cyclic process, entropy will either increase or remain the same (Smith, Van Ness, 2005).

In a steady state process there is minimum work that can be used to achieve the desired work, this is referred to as ideal work. The change of state associated with the work, complete reversibility, is the limiting factor. For such a case the entropy generated is zero for uniform surrounding temperature, T_{σ}, (Smith, Van Ness, 2005), and the equation is given below:

Equation 16

$$\dot{W_{ideal}} = \Delta(\dot{Hm})_{fs} - T_{\sigma}\Delta(\dot{Sm})_{fs}$$

Work that is wasted due to irreversibility in a process is called lost work. This can also be defined as the difference between the actual work and the ideal work of the system. Lost work is mathematically represented by the equation below:

Equation 17

$$\dot{W_{lost}} = T_{\sigma}\Delta(S\dot{m})_{fs} - \dot{Q}$$

Thermodynamic optimization is a procedure to quantify and minimize the amount of fluid and chemical losses, also known as lost work. The derivations from the second law of thermodynamics can be used to try and optimise existing systems.

When modelling an existing unit, for thermodynamic optimization, it is important to know the range of the operating conditions. Souza et al conducted a case study to determine the optimum operating conditions for the given unit feed (Souza *et al.*, 2011):

- Catalyst to oil ratio, COR, 2 to 25
- Catalyst input temperature of 680 ºC to 720 ºC
- Gasoil input temperature of 210 ºC to 220 ºC
- Riser height from 10 to 50D where D is the diameter of the riser

The operating conditions were varied within the limits given and the response of the unit was analysed. From the responses, it was realised that the gasoil conversion remains constant achieving a plateau when a COR of 18 was reached(Souza *et al.*, 2011). Figure 9 shows the graphical results of the work done by Souza et al.

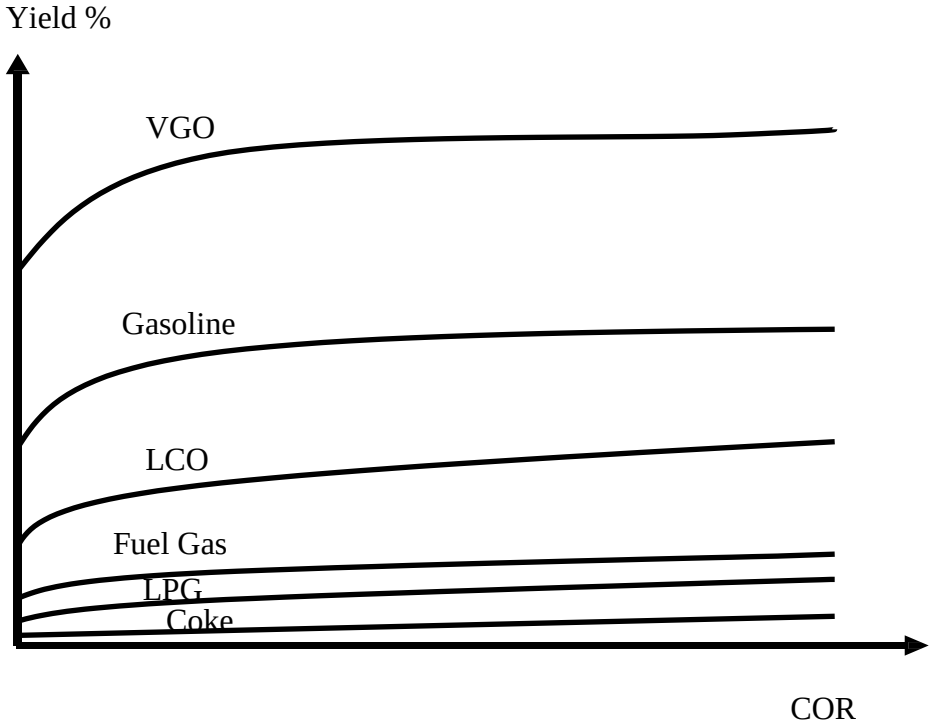


Figure 9: Analysis of COR, source: (Souza *et al.*, 2011)

The optimum operating conditions cannot be generated just from the COR analysis, the other operating conditions have to be fixed as well to obtain the highest desirable yield in the process. Normally the optimization objective function is the output mass flow rate of the desired product with a fixed COR.

Most units are operated at low COR of as little as 3. When the catalyst flow rate is varied and plotted against the flow rate of the gasoline it can be observed that the unit operates optimally at a ratio of 3. Figure 10 shows this relationship.

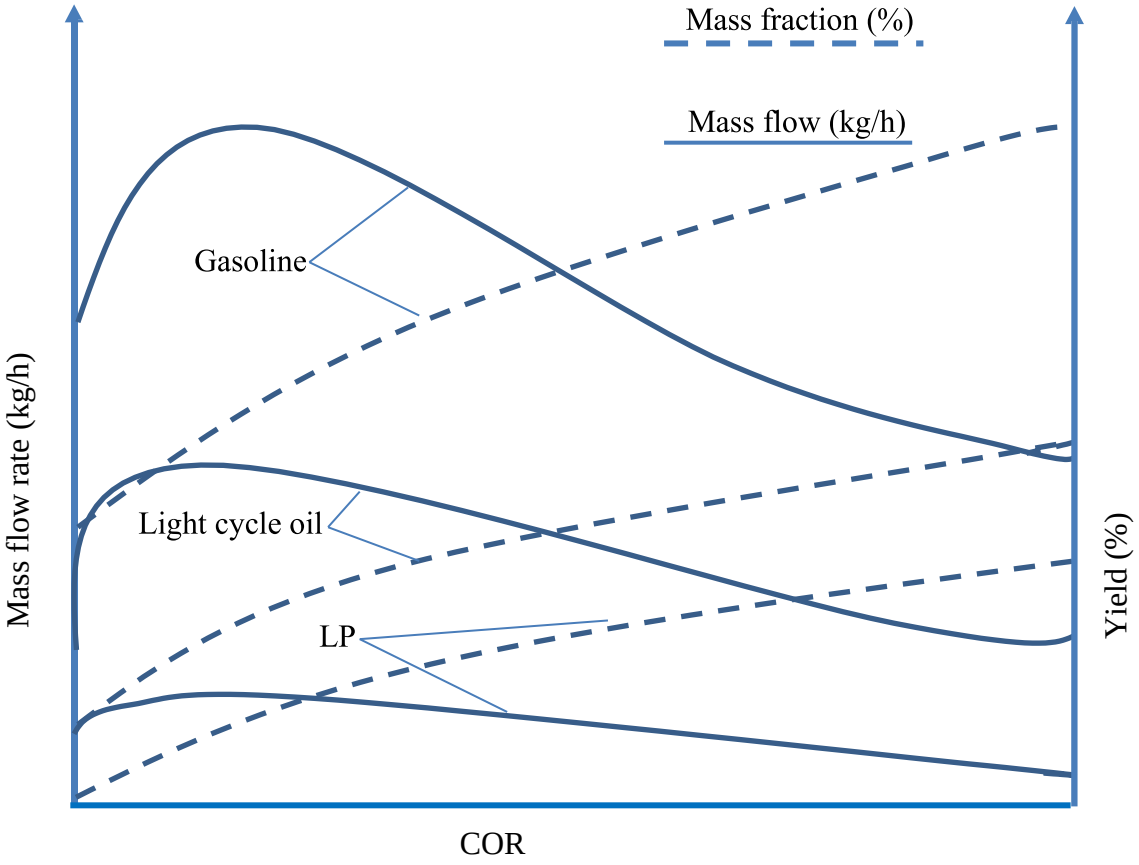


Figure 10: Fixed mass flow of catalyst, source: (Souza *et al.*, 2011)

Looking into the units thermodynamic loses to try and optimise the unit was pivotal as this would prevent the destruction of exergy in any system. The study by Souza et al formulated a methodology for the calculation of the total entropy of the FCC system from the second law of thermodynamics, and it introduced process exergetic analysis. Entropy studies can be conducted

if the following parameters are known; velocities into the unit, product mass fractions of the different components and temperatures.

The entropy in the riser of each domain is given by:

Equation 18

$$\dot{S}_{gen,ve} = \left(\sum_{i=2}^{N+2} \dot{m}_\iota s_i\right)_{inlet} + \left(\sum_{i=2}^{N+2} \dot{m}_\iota s_i\right)_{outlet} - \left(\frac{\dot{Q}}{T}\right)$$

The two extra lumps (N + 1 and N + 2) are used to account for the steam and catalyst contributions. The subscripts *ve* and *gen* mean volume element and generated.

This equation requires that the specific entropies of each lump be calculated. These lumps are not components in isolation hence assumptions have to be made, it will be assumed that:

i. All lumps, except the coke, have ideal gas behaviour
ii. The specific reference entropy of each lump is assumed to be a hydrocarbon with similar molecular weight

For ideal gases entropy is calculated using the following equation:

Equation 19

$$\int_{s_o}^{s} dS = \int_{T_o}^{T} \frac{Cp}{T} dT - \int_{p_o}^{p} \frac{R}{P} dP$$

T_0, P_0, and S_0 are the reference states for the temperature, pressure, and entropy respectively.

The evaluation of equation 4 requires the determination of the specific heat, C_p, as a function of the temperature. For the gas phase lumps ($i = vgo$, light cycle oil, gasoline, fuel gas and LPG) the specific heats are calculated by:

Equation 20

$$C_{pi} = C_1 + C_2 \left[\frac{\frac{C_3}{T}}{\sin\frac{C_3}{T}}\right]^2 + C_4 \left[\frac{\frac{C_3}{T}}{\cosh\frac{C_5}{T}}\right]^2$$

Where the constants C_1, C_2, C_3, C_4, and C_5 were obtained from tabulated data.

For the coke, the specific heat of the graphite carbon curve was obtained from a correlation reported by Perry and Green:

Equation 21

$$Cp_{coke} = 2.673 + 0.002417T - \frac{1169900}{T^2}$$

Specific heat of the catalyst was taken as a constant, the following equation was used for the specific heat of the steam:

Equation 22

$$Cp_{steam} = 0.807 \times 10^{-12}T^4 - 2.964 \times 10^{-9}T^4 + 4.152 \times 10^{-5}T^2 - 1.108 \times 10^{03}T + 4.08$$

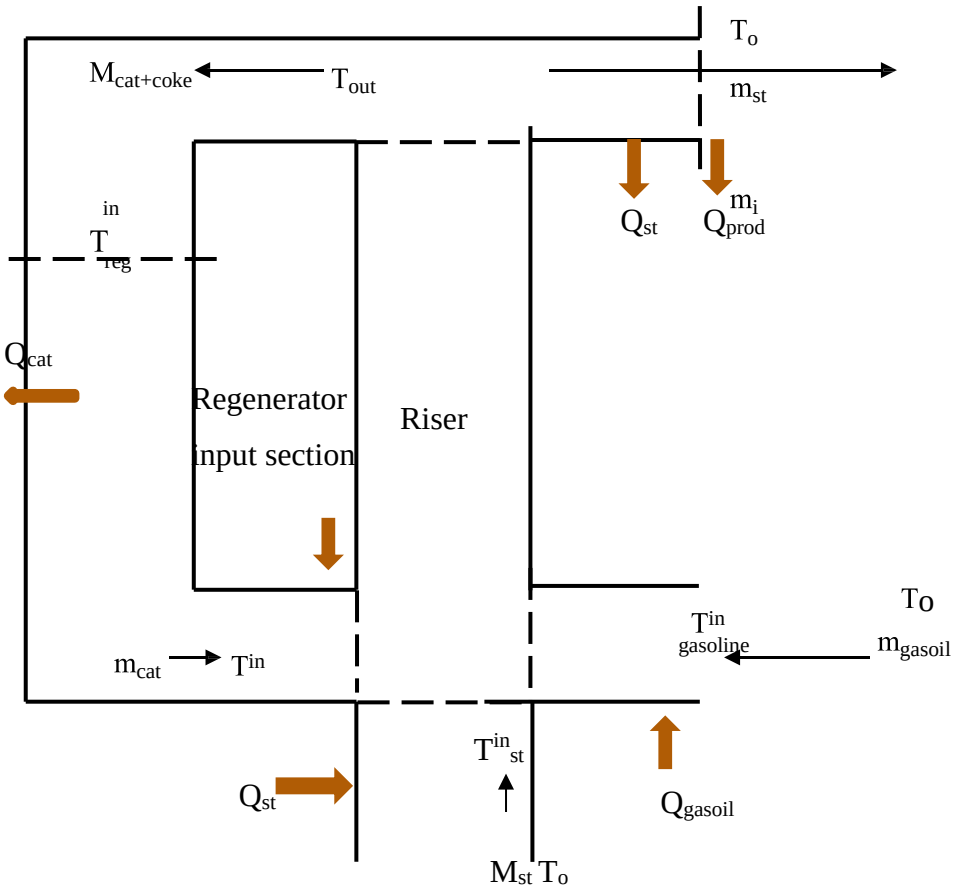


Figure 11: FCC energy interaction and flow rates, source (Souza *et al.*, 2011)

Figure 11 explains the boundaries and the relationship between the different energies in the system. The catalyst leaves the riser at temperature T_{out} and loses heat at the stripper and the pipes before entering the regenerator. This amount of lost energy is represented $\dot{Q}^{c}_{cat}$.

In the regenerator, the catalyst is re-heated up to its riser inlet temperature, T^{in}_{cat}, the catalyst is reheated up to its riser inlet temperature~700ºC.(Souza *et al.*, 2011)

The total exergy is then expressed using the following term:

Equation 23

$$\dot{E}_{net} = \dot{E}_{produced} - \dot{E}_{dest}$$

$$\dot{E}_{net} = \dot{E}_{produced} - \dot{E}_{cat} - \dot{E}_{gasoil} - \dot{E}_{st} - \dot{E}_{cooling} - T_o\dot{S}_{gen}$$

$\dot{E}_{dest}$ accounts for system losses and must be subtracted from the total exergy to give the net exergy.

In conclusion it was observed that for any given catalyst mass flow rate, there exists an optimum value for the COR for maximum mass flow rate production of gasoline or any other desired product. Exergy (thermodynamic) based optimization methodology for FCC units design was introduced based on the second law of thermodynamics. The process net exergy production rate was selected as the objective function for the optimization procedure, which in turn minimizes the system energetic losses. The objective function (net exergy production rate) was maximized through the minimization of the destroyed exergy inside the FCC unit by varying the operating conditions.(Souza *et al.*, 2011)

Optimization of the operating parameters

As we move out of an era where fuel quality is set using vehicle exhaust fumes, and move into an era were 'well to wheels' is becoming a standard. Focus has been shifted to the energy consumption to product ratio and CO_2 emissions that various products give during their process of manufacturing. Various techniques have been suggested in the optimization drive ranging from multi-variable optimization of FCC systems to adjusting the inputs into the FCC.

Multi variable optimization has been researched as an option to find optimum operating conditions for the refinery process and recent studies show that it could possibly be one of the solutions that could optimize the refinery with regards to energy savings and noxious gas emissions (O'Connor, 2007).

The first attempt at multi variable optimization was attempted by Kasat et al, in 2002, the non-dominated sorting algorithm was used to optimize four decision variables in the FCC, these variables were air temperature, feed temperature, air flow rate and riser temperature (Al-mayyahi, Hoadley and Smith, 2012).

The highest concentration of CO_2 emissions around the FCC unit operating envelope is found in the regenerator and utilities section. The utility production of CO_2 is based on the pinch analysis after maximizing the energy of the FCC (Al-mayyahi, Hoadley and Smith, 2012). The feed preheater also contributes significantly to the amount of CO_2 produced through an exothermic reaction of methane during combustion. It has been suggested that operating the FCCU at an energy efficient point will reduce the amount of CO_2 produced (Al-mayyahi, Hoadley and Smith, 2012). If the energy required for the heat of formation, (ΔH_f), of the products in the reactor is known the regenerator can be operated efficiently whilst potentially reducing the amount of CO_2 produced. In the optimization of the energy used in the FCCU, it is important to note that the end riser temperature is important as it will determine the recirculation rate of the catalyst from the regenerator. A low end riser temperature will result in a high catalyst to oil ratio, this could see a low production of profitable products.

A study was carried out by Al-mayyahi et al to minimize CO_2 formed in the FCC using the multivariable method. Air temperature, feed temperature, air flow rate and riser temperature were chosen as the decision variables. Each decision variable was varied one at a time whilst the CO_2 was monitored. The results obtained showed that the air temperature and the air flow rate had minimum impact on the yields as well as the production of CO_2. Figures 12-16 illustrate the results obtained by Al-mayyahi et al.

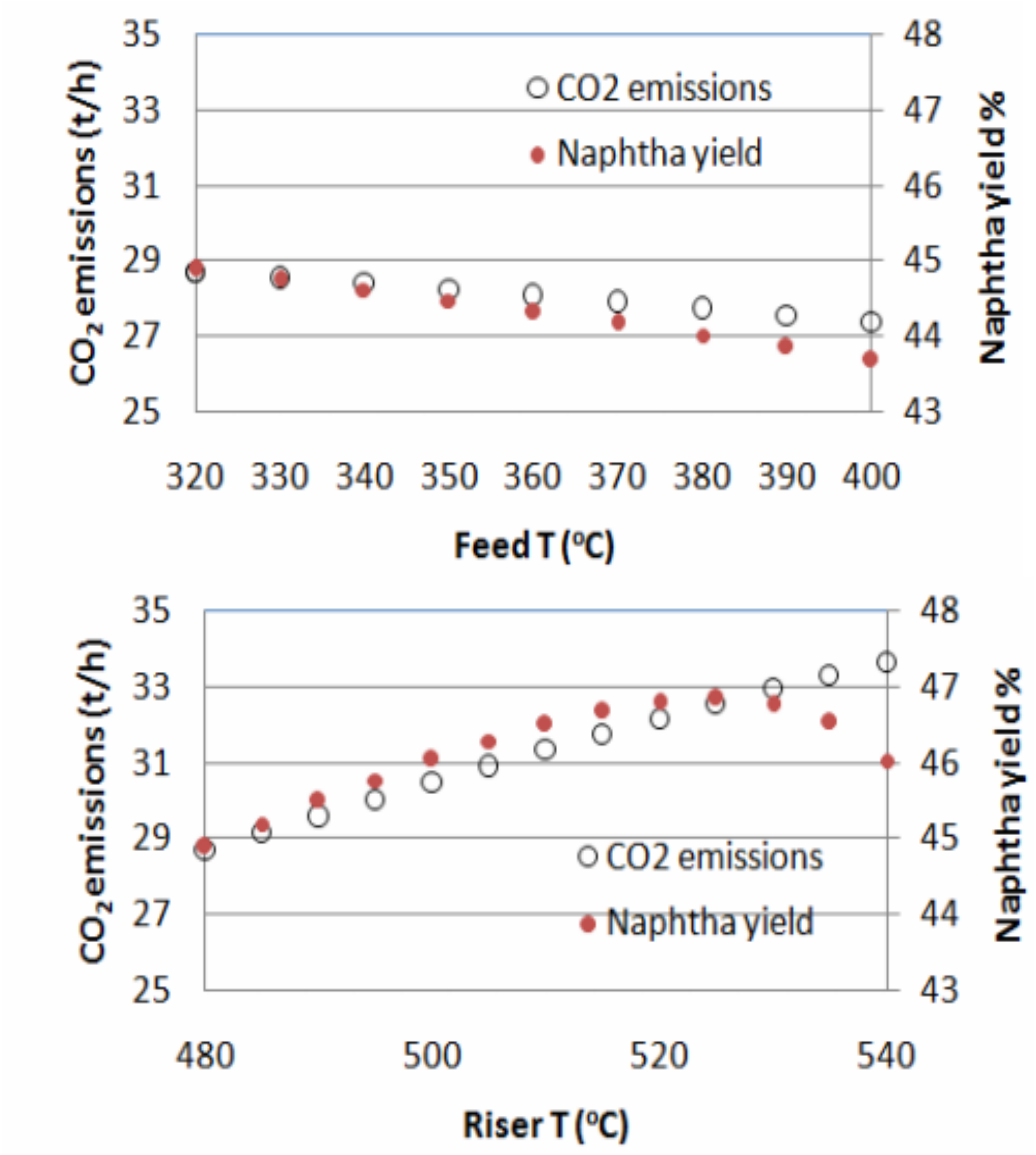


Figure 12: Effect of feed temperature and riser temperature on yields and emissions, source: (Al-mayyahi, Hoadley and Smith, 2012)

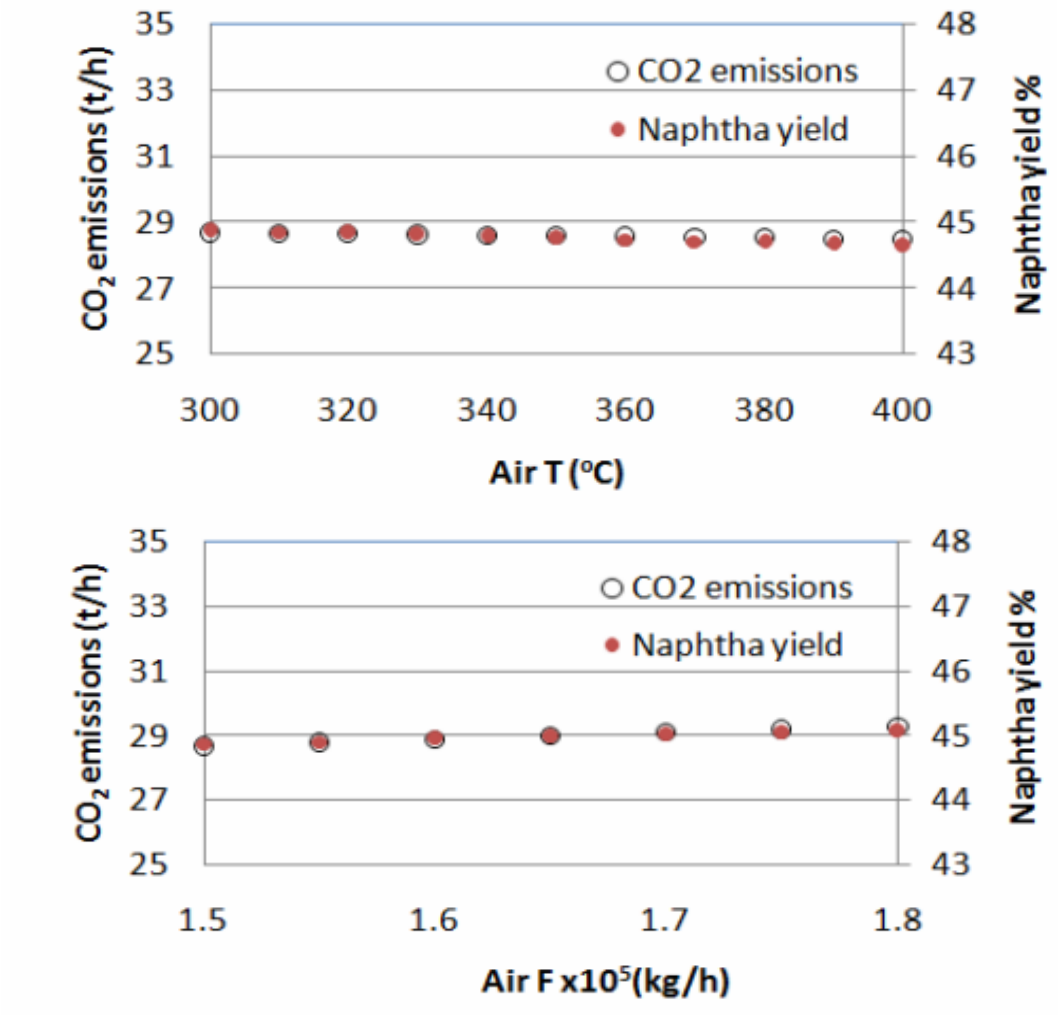


Figure 13: Effect of air temperature and air flow rate, source: (Al-mayyahi, Hoadley and Smith, 2012)

Multi variable analysis showed that an increase in naphtha yield resulted in an increase of CO_2 production as well.

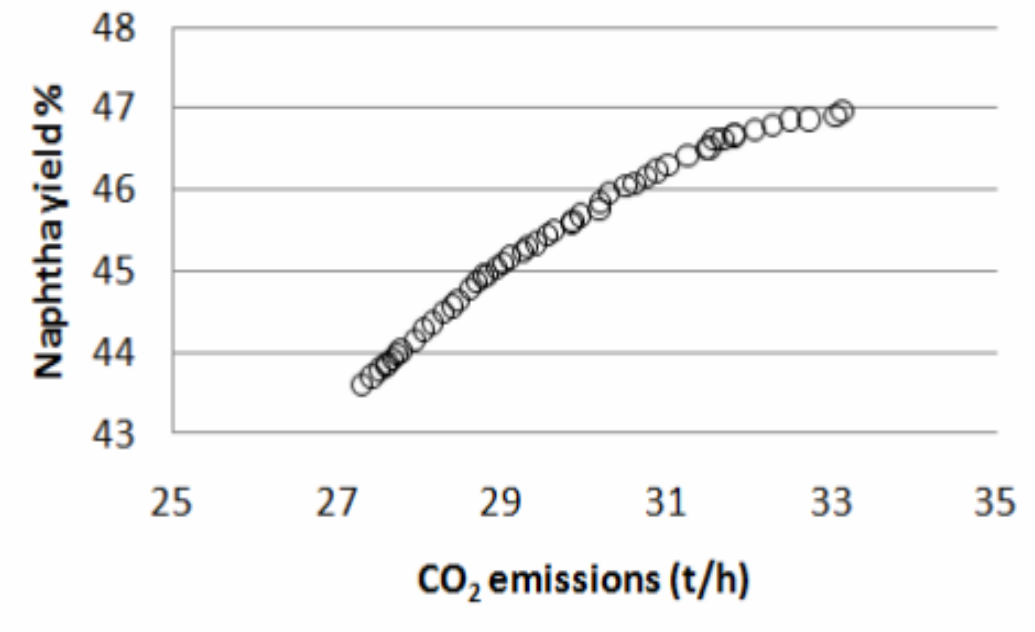


Figure 14: Effect of Naphthalene yield on CO_2 production, source: (Al-mayyahi, Hoadley and Smith, 2012)

The corresponding values of the other decision variables and the optimum operations are shown below.

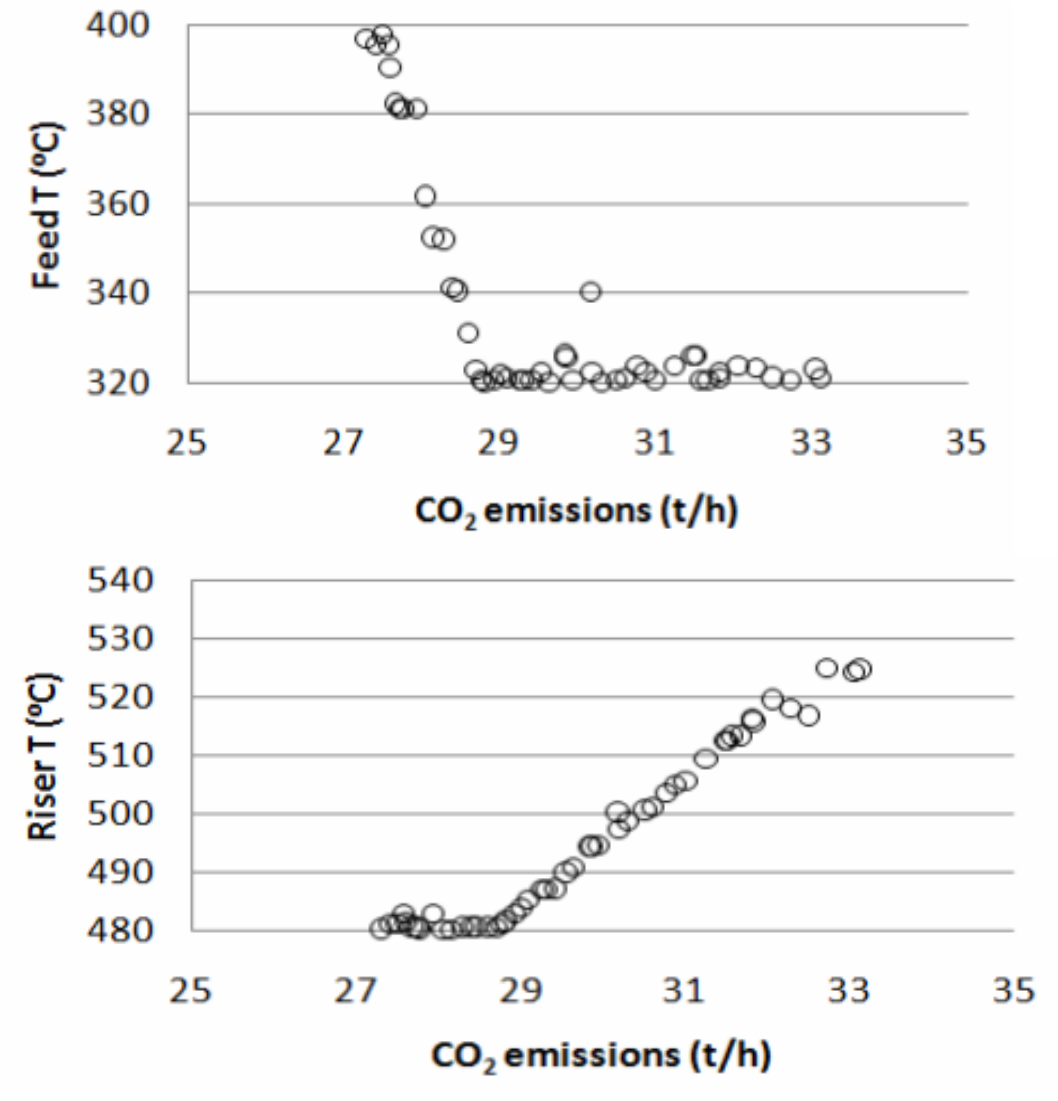


Figure 15: Effect of feed and riser temperature on the CO_2 produced, source: (Al-mayyahi, Hoadley and Smith, 2012)

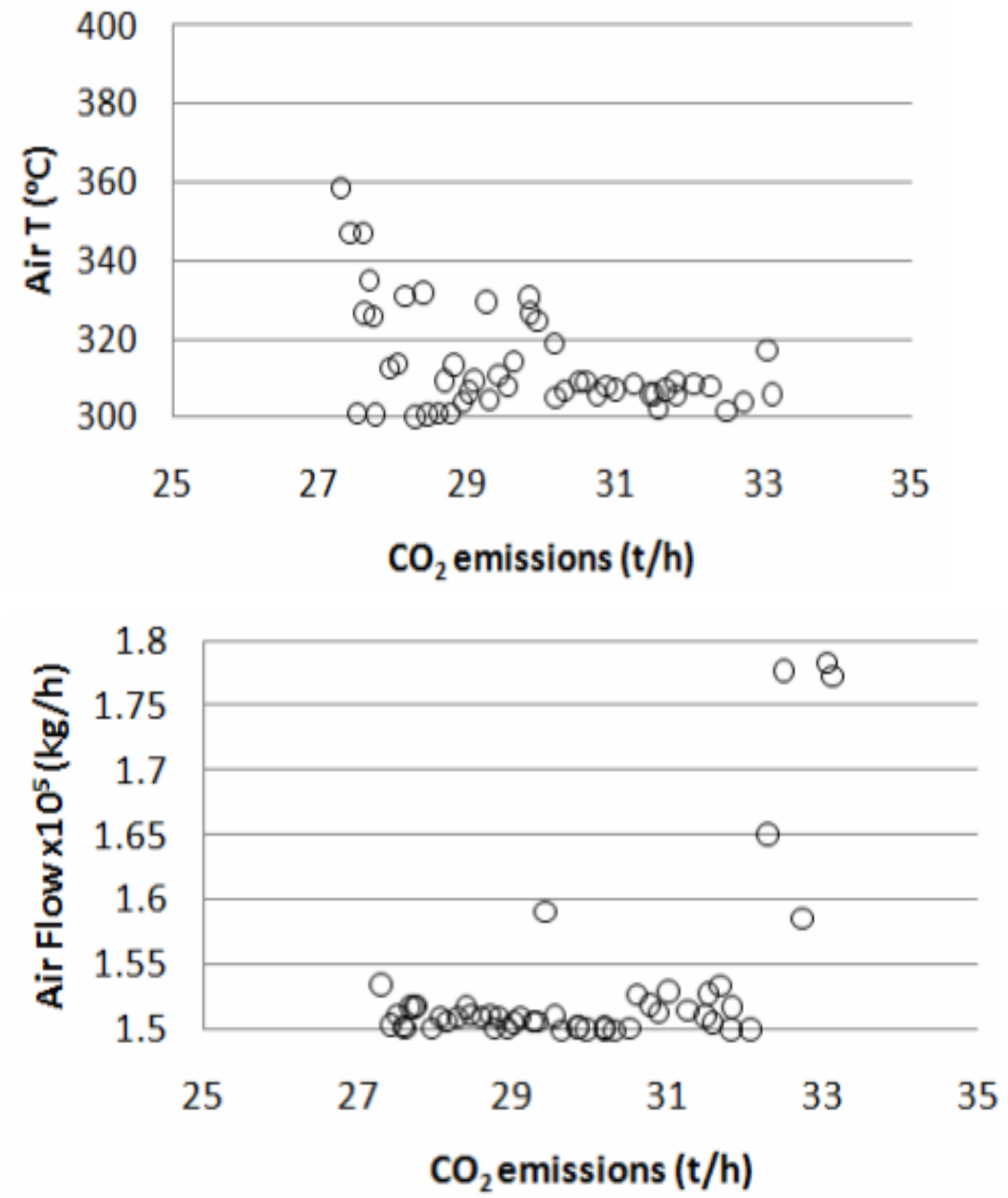


Figure 16: Effect of air temperature and flow on CO_2 emissions, source: (Al-mayyahi, Hoadley and Smith, 2012)

The results showed that decreasing the feed temperature resulted in more CO_2 being produced, this could have been to the fact that a higher COR was needed to supply the energy in the reactor to assist with the reaction, as more catalyst was supplied more carbon was deposited resulting in more CO_2 being released during regeneration (Al-mayyahi, Hoadley and Smith, 2012).

In conclusion, multi variable optimization was successful, two objectives have been optimized considering four decision variables and four constraints, using a binary coded genetic algorithm.(Al-mayyahi, Hoadley and Smith, 2012)

The operating parameters of any given process are vital when considering process optimization. Varying the input rates, pressure and temperatures of the system yields different results in the process outputs. A lot of process improvement studies have varied the inputs into the FCC unit, Yakubu et al varied the air input rate into the regenerator to try and reduce the amount of CO_2 produced as a way of curbing greenhouse emissions. Matlab and HYSYS were used as modelling tools to simulate an existing FCC unit.

From the optimization model, it was concluded that for the reduction of CO_2 it was necessary to increase the amount of air into the regenerator from 66kg/h to approximately 84 kg/h, the yield of CO produced was treated as a constraint (Yakubu, Patel and Mujtaba, 2017).

A study by Macerato et al looked at the benefits of oxygen enrichment in the regenerator as way of increasing the yield of lighter more profitable products. Oxygen enrichment increases the capacity of a given unit by overcoming air blower capacity or the regenerator superficial velocity. This is done by increasing the oxygen content in the air being blown into the regenerator thereby making more oxygen available for the combustion reaction. The excess oxygen ensures that the coke that is deposited on the catalyst is completely burnt off and a cleaner catalyst, with high surface activity is sent to the regenerator, and lighter compounds are produced in the reaction.

The investigation by Macerato et al revealed that a 27 mole % increase resulted in the capacity of the unit increasing by 27% (Macerato and Anderson, 1988). As the regenerator is enriched with oxygen the nitrogen content in the feed decreases. This decrease results in an increase in energy in the regenerator and less energy being taken out with the flue gas. An increase in the oxygen will however eventually affect the COR, by increasing it, and the production is reduced. An increase of 1-3% is recommended as this will ensure that the COR is not compromised and the production is maintained at an optimal rate (Macerato and Anderson, 1988).

Process debottlenecking

Debottlenecking refers to hardware changes on the system after process optimization has been completed. This could be changing valve size to help control better pressure in the riser system or changing the internals of the system. Increasing line sizes to alleviate effects of pressure is also a

way off debottlenecking to make the system more efficient as well as reduce on the downtimes caused by equipment failure.

In a study by the UOP Company a number of FCC internals were looked at and alternatives to the existing internals were made.

Traditionally the feed distributors are made from metal, however due to the harsh environment in the FCCU, it was suggested that a trial run be conducted in which ceramic distributors would be used. This was a successful run and this led to the commercialisation of ceramic distributors in 2007. The following graphic illustrates the results of the trial run. Both the distributors were put into the same FCC and were in operation for 18 months. The results showed that the ceramic distributor did not go through any corrosion.(Couch and Wolschlag, 2010). Figure 17 shows the pictorial evidence of the distributors after the 18 month trial run.



Figure 17: Metal vs ceramic tip, source: (Couch and Wolschlag, 2010)

A lot of other developments have been made with the disengager arms in the regenerator being modified as well as the catalyst distributors being modified(Couch and Wolschlag, 2010).

3.4.3 PROCESS MODELLING

Unit processes can be classified as being either kinetic or unit models. In kinetic models the different chemical reactions that take place are used to estimate the products that are produced. Kinetic modelling looks at the rates of reaction of all the reactions taking place within a certain boundary. Unlike kinetic models, unit models deal with separation or phase changes such as distillation and condensation and are easier to generalize in terms of the products produced. Products resulting from chemical reactions, in unit models, can be predicted using simple unit

operation solving methods (Franks, 1972). In kinetic modelling every reaction is unique, this is represented by a distinct chemical model, which takes into cognisance the phases involved for the reaction to occur as well as the various unit configurations. The process geometrics and reaction mechanisms also change vastly when catalysts are introduced in kinetic modelling.

Kinetic models

In FCC reactions the chemical components are grouped into lumps based on the chemical species with similar behaviors of their "pseudo" species, on the assumed yields of the reactions taking place, the mechanistic reactions taking place or the pathway of the reactions. The reason for the lumps is due to a high number of components being present in the feed and the products, mapping the chemical reactions of all the single components in the feed is a near impossible exercise. A number of lumped models exist in literature, ranging from two lumps to as many as fifty lumps. A comparative study by Yousuo et al showed that the more lumps in a model, the greater the accuracy. The figure below illustrates a typical six lump model that groups the lumps according to their similarities in chemical behaviours.

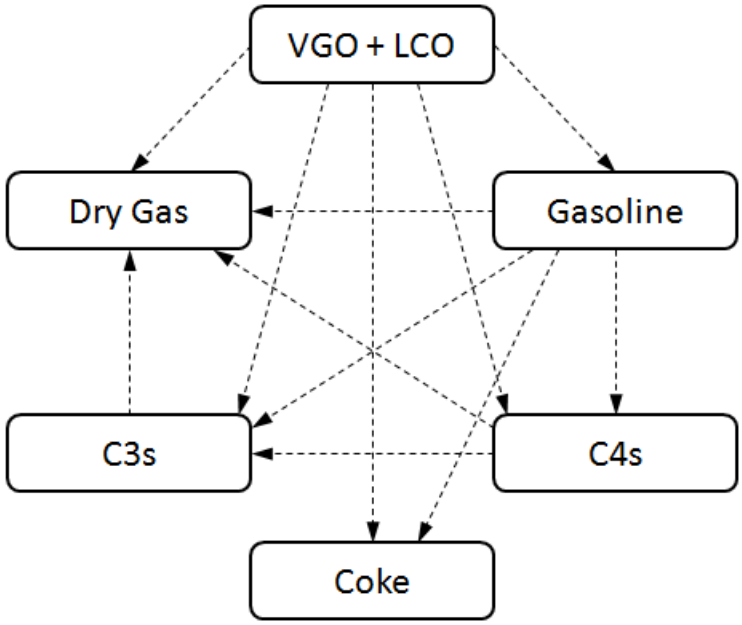


Figure 18: Six lump model, source: (Yousuo and Ogbeide, 2014)

***Yield lumps*.** These lumps were the first to be used when it came to kinetic modelling of the FCC. The lumps were grouped according to the yields that the refiner collected from the fractionation section of the products of the FCC, figure 18 shows a typical example of the lumping method.

***Pseudo chemical lumps*.** These lumps are grouped together on the basis of the chemical likeness as well as the boiling points of the components present. This type of lumping groups components as being either light or heavy. Figure 19 shows a ten lump model by Jacob et al that demonstrates this type of lumping.

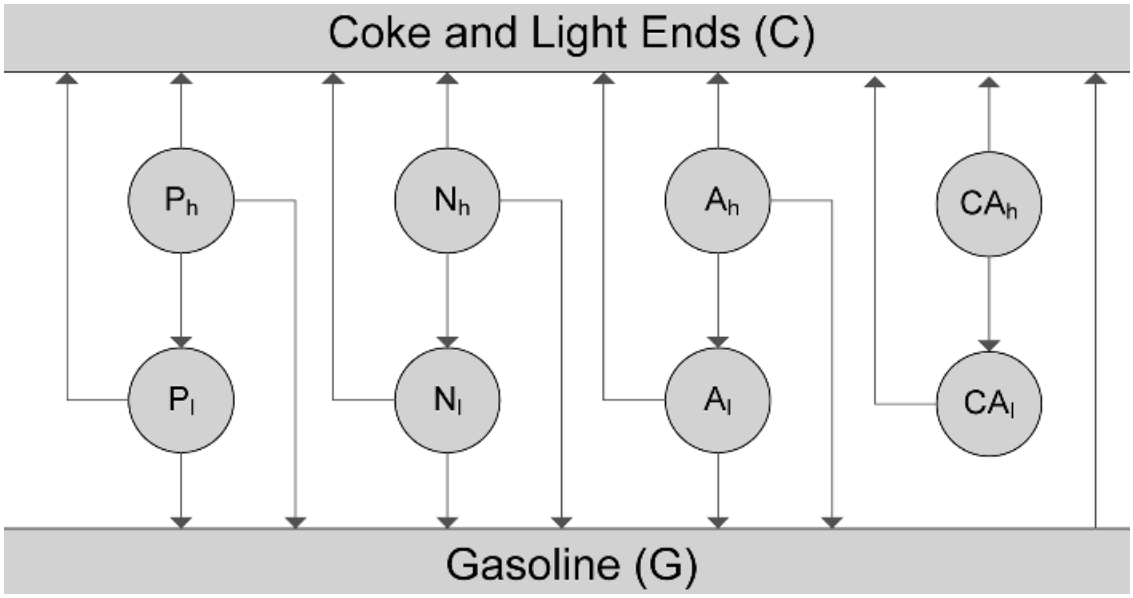


Figure 19: Ten lump model, source : (Jacob *et al*., 2014)

The subscripts, l and h, mean light component and heavy component. P, are parrafins, N, represents naphthene's, A represents aromatics and CA represent chained aromatics. This clearly shows that the pseudo chemical lumping method.

***Mechanistic reactions*.** Mechanistic models track the intermediate chemicals such as ions and free radicals that occur in the catalytic reactions. The transition state theory helps in quantifying the rate constants involved in adsorption, reaction and desorption of reactant and product species from the catalyst surface.

***Pathway models*.** Structure oriented modelling (SOL) is a method for describing the composition, reactions, and properties of complex hydrocarbon mixtures. The individual hydrocarbon molecules are represented as a vector of incremental structural features. The mixture of hydrocarbons is

represented as a set of vectors, each with an associated weight percent. The vector representation of molecules provides a convenient framework for constructing reaction networks of arbitrary size and complexity, for developing molecular-based property correlations, and for incorporating existing group contribution methods for the estimation of molecular thermodynamic properties (Quann and Jaffe, 1992).



A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0



A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO
1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure 20: SOL lumps, source : (Quann and Jaffe, 1992)

Unit level models

These models assume the behaviour of the different equipment found in the FCC and compare them to existing equipment available in literature to enable the simulation of the behaviour of the process under study. The FCC unit can be sub divided into a unit models.

Riser reactor. A plug flow reactor is normally used to simulate the reactor. The gas and the liquid are assumed to be fluid and the catalyst deactivation is due to the solid coke deposited on the surface of the catalyst.

Stripper section. The stripper section is modelled similarly to a constantly stirred tank reactor (CSTR) that is well mixed.

Regenerator. A bubbling bed reactor is used to model the regenerator's dense as well as lean section.

Disengager. The disengager section contains cyclones that separate the product gas from the deactivated catalyst. The cyclones are modelled to remove up to 99.9% of the catalyst in the product gas.

In this project ASPEN HYSYS will be used for the simulation, the software uses the 21 lump kinetic method to predict results. The unit level models described above are incorporated into ASPEN HYSYS tool.

4. MATERIALS AND METHODS

A number of optimization tools are available to be used by refiners, these tools aid in providing a guide for the refiner to operate the plant at its most optimum within specified constraints. Aspen PIMS is a linear programming (LP) tool that is often used for refinery optimization, it is made up of a number of sub models that represent the different units in a refinery. The FCC unit is quite unique in every refinery, hence a specific model has to be built and optimized for each refinery, in order for it to produce reliable results during LP optimizations. The optimized FCC sub model is then built into Aspen PIMS together with other sub models and used to predict the optimum volumes that the refinery should run to meet the customer demand subject to constraints provided. These constraints may include feed rates, emissions as well as product quality.

In the following chapter optimization of FCC simulation will be done in Aspen HYSYS. A number of steps and assumptions will be made during the simulation, the inbuilt model of an FCC in Aspen HYSYS will be used.

4.1 MODEL STRUCTURE

In Aspen HYSYS the inbuilt FCC model is made up of a number of sub models that behave in the same way that the regenerator and the reactor do in satisfying the heat balance.

The table below explains the different sub models that the FCC unit has.

Table 3: FCC sub models (adapted from (Pashikanti and Liu, 2012))

Sub model	Purpose	Unit operation	Consideration
Riser	Convert feed to product species using 21-lump kinetics	Plug flow reactor (PFR) allows any angle of inclination	Pressure drop is a combination of pressure drop due to solid and vapour phases Catalyst activity decay due to kinetic

			and metal coke on catalyst Slip factor correlations (difference between vapour and solid velocities) to estimate specie density
Reactor/Stripper	Complete feed conversion and remove adsorbed hydrocarbons	Bubbling bed reactor with two phases	Switches to fluidized-bed reactor model for units with low catalyst holdup
Regenerator	Combust coke present on catalyst	Bubbling bed reactor with two phases	Kinetic models for coke combustion with air and enriching oxygen
Regenerator freeboard	Complete combustion of coke	Simple plug-flow reactor	Additional kinetics to match behaviour of industrial units
Cyclones	Separate solids from hydrocarbon and effluent vapours	Two-phase, pressure drop calculation	Pressure drop is a combination of pressure drop due to solid and vapour phases
Delumper	Converts lumped composition into set of pseudo components based on true boiling point (TBP) suitable for fractionation	–	Carries chemical information about the kinetic lumps as an attribute of the pseudo component Additional delumping of light gas into C1–C4 components using known kinetics

Slip factor and voidage

In the FCC model it is imperative that the slip factor, φ, which is the ratio between the gas velocity and the catalyst particle velocity is known so as to calculate the residence time of the gases and the particles in the reactor. The residence time assists in estimating the reaction time in the reactor and preventing over cracking that produces dry gases. Correlations are mostly used to calculate

slip factors, the Aspen HYSYS model uses a correlation similar to the Bolan-Kenny et al which uses dimensionless Froude (Fr) numbers,

Equation 24

$$\varphi = 1 + \frac{5.6}{Fr} + 0.47 {Fr_t}^{0.47}$$

$$Fr = \frac{u_o}{\sqrt{gD}}$$

$$Fr_t = \frac{u_t}{\sqrt{gD}}$$

The voidage, ε, assists greatly in the calculation of the pressure drop in the reactor. Once the reactor is over loaded with catalyst the pressure drop decreases enabling the operator to make the right changes so as to maintain the required product slate.

21 lump model

The 21 lump model which is similar to the 10 lump model, runs in the background of the model during simulation. The 21 lump model groups the chemical structure as well as the boiling points of the lumps similarly to the 10 lump model, the 21 lump model however includes a boiling point range for heavier lumps (boiling point 510°C). The 21 lump model also splits the coke lumps into two, one of the coke lumps is assumed to be coke deposited by the hydrocarbons during the reaction and the other lump is assumed to be from metal activity.

Catalyst deactivation

As the catalyst moves in the FCC unit deactivation occurs. Deactivation, ϕ, is the aging of the catalyst and in this process it loses its activity. A number of equations can be used to calculate the deactivation so as to replace the old catalyst with new catalyst. Deactivation also allows the model to predict the correct yields as a function of the age of the catalyst.

Equation 25

$$\emptyset_{coke} = \emptyset_{kcoke} \emptyset_{mcoke}$$

$$= \exp[-a_{kcoke} c_{kcoke} f(c_{metal})]$$

4.2 METHODOLOGY

In order for the simulation to be conducted plant data was collected for an average of 6 months. The data was comprised of lab routine analysis' and Distributed Control System (DCS) data. This data was taken from a plant that is currently operational in southern Africa, which uses feed that resembles that of vacuum gas oil. A base model was built using the data and the objective of the project was conducted to optimize the energy as well as the emissions during production.

4.2.1 BASE MODEL CONSTRUCTION

In the base model construction the inputs from the plant were used. These include the dimensions of the specific unit and the operating conditions. The catalyst properties were assumed to be similar to one that is found in the model library, the properties were slightly adjusted to match the yield on the plant.

The distillation data from the running plant could not be obtained hence data obtained from literature was used.

4.2.2 OPTIMIZATION

The optimization process allowed for the different inputs to be varied whilst monitoring the response of the system with attention being paid to the energy and the emissions being produced. This optimization was conducted in order for the objective of the report to be met.

4.3 MODEL

Aspen HYSYS v8.8 was used to build the model. The following operating conditions were used to build the model.

Table 4: Operating conditions

Condition	Operation
Feed	400^{o}C
End of rise temperature	625.1^{o}C
Riser inlet steam	200^{o}C
Stripping steam	5000kg/h
Regenerator dense bed temperature	680^{o}C

Table 5: Catalyst Properties

Metal content (V/Ni/Na/Fe/Cu) (ppm wt)	5000/4044/3103/5553/57
Equilibrium activity (%)	66
Inventory (kg)	170000

In Aspen HYSYS, properties environment, a component from the component list library was chosen which had similar components to that of the feed in the refinery being modelled. Other components could be added to the component list, these additional components are however not considered in the reactions taking place in the reactor.

When the component list has been chosen a thermodynamic package is chosen for the simulation. The Peng-Robinson method is used as it best calculates thermodynamic properties of both liquids and gases. The Colstad correlation is used to calculate the density of the fluid. Figure 21 shows the Aspen HYSYS user interface for the initial set up.

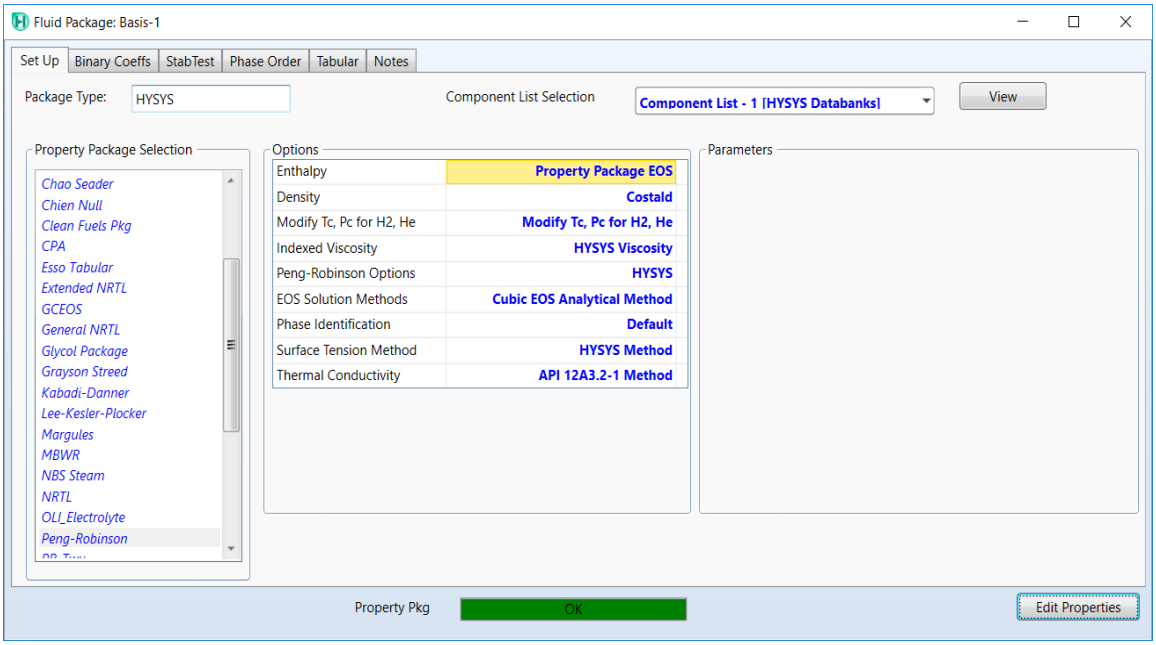


Figure 21: Thermodynamic properties

Once the components and the thermodynamic package were chosen in the properties environment, the basic flow diagram of the FCC was constructed in the simulation environment.

In the simulation environment the object palate was brought up and the FCC model was chosen for the simulation. The configuration background appears, and the different properties and the

dimensions were selected as shown from figure 22-30. The solver in the simulation environment must be held, this will prevent the model from constantly running in the background.

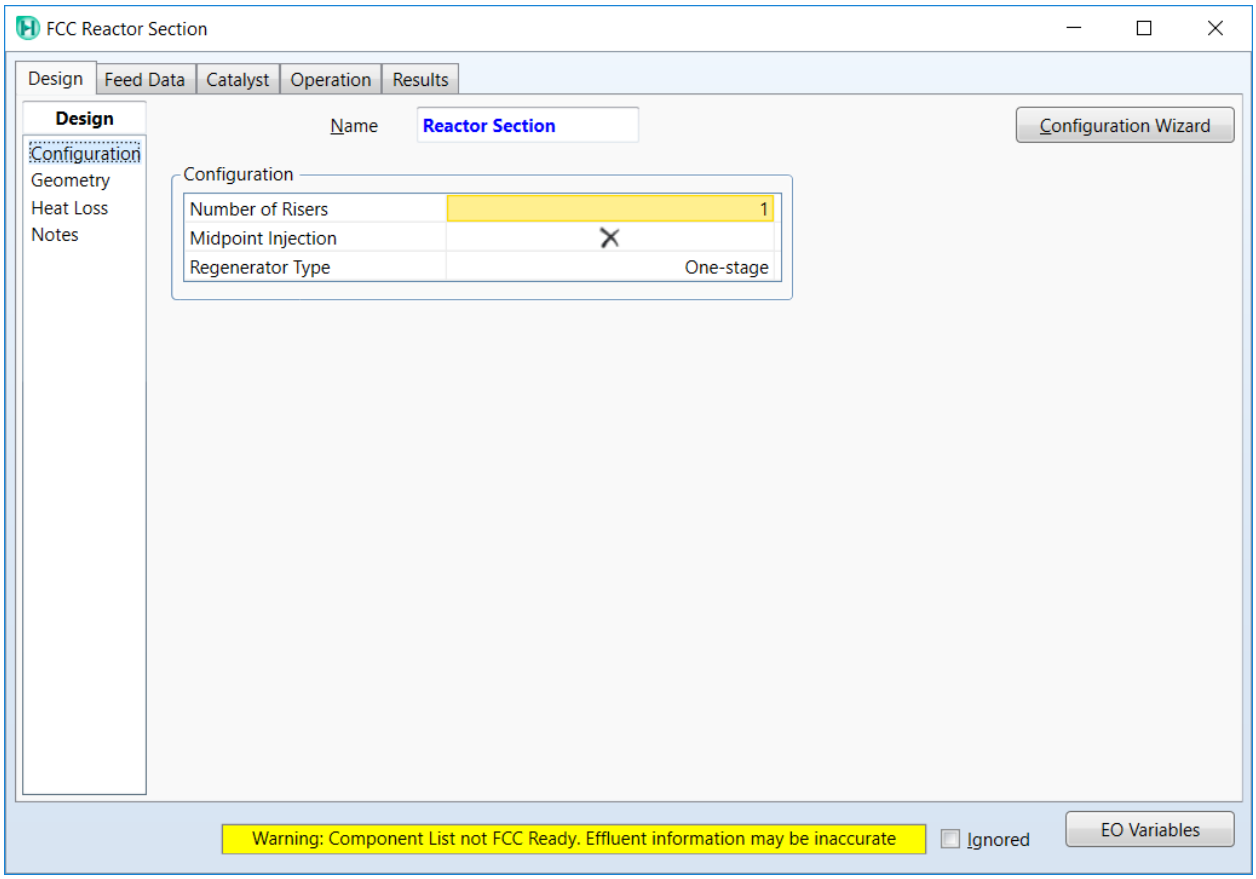


Figure 22: FCC Configuration

In the configuration one riser was selected, the feed point of the riser was selected to be at the bottom of the riser.

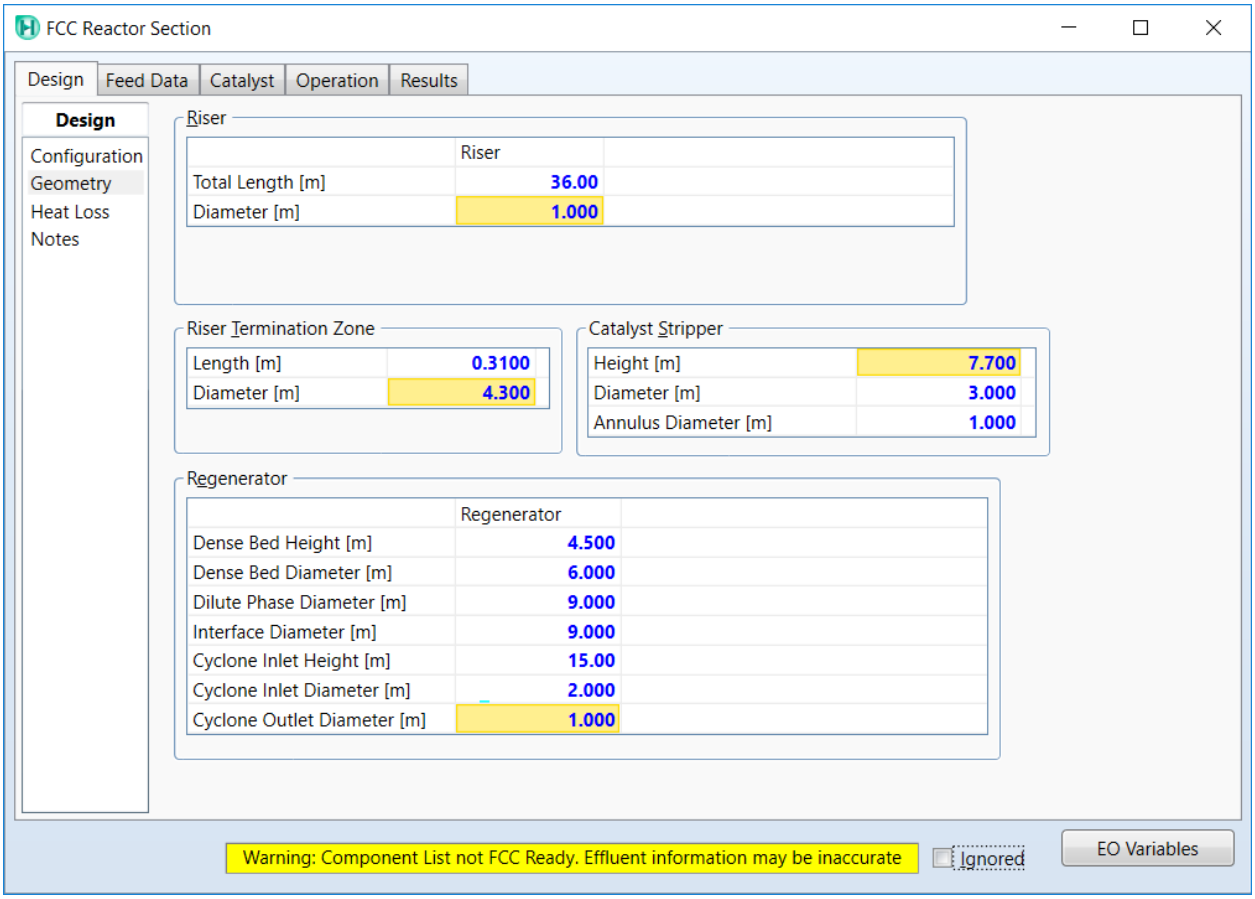


Figure 23: FCC Geometry

The geometry of the riser and the regenerator were specified into the model. Care must be taken to put in the correct dimensions as the model is sensitive to dimension changes.

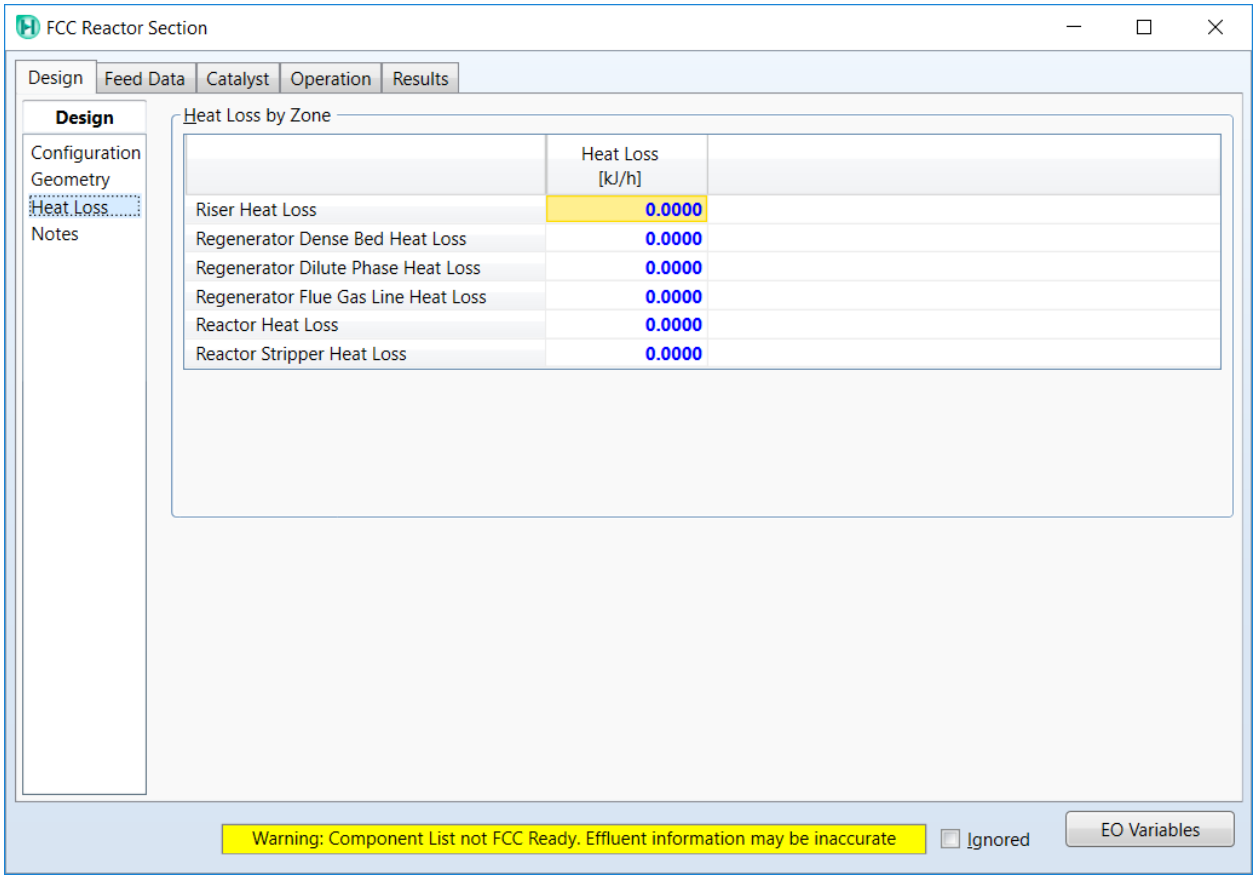


Figure 24: Heat losses

It is assumed that there are no heat losses to the environment as the reactor is insulated.

After the design section of the model is completed the feed data is put in. The feed is assumed to be similar to vacuum gas oil, the different feed types exist in the model directory and were selected from there. The feed properties are shown below.

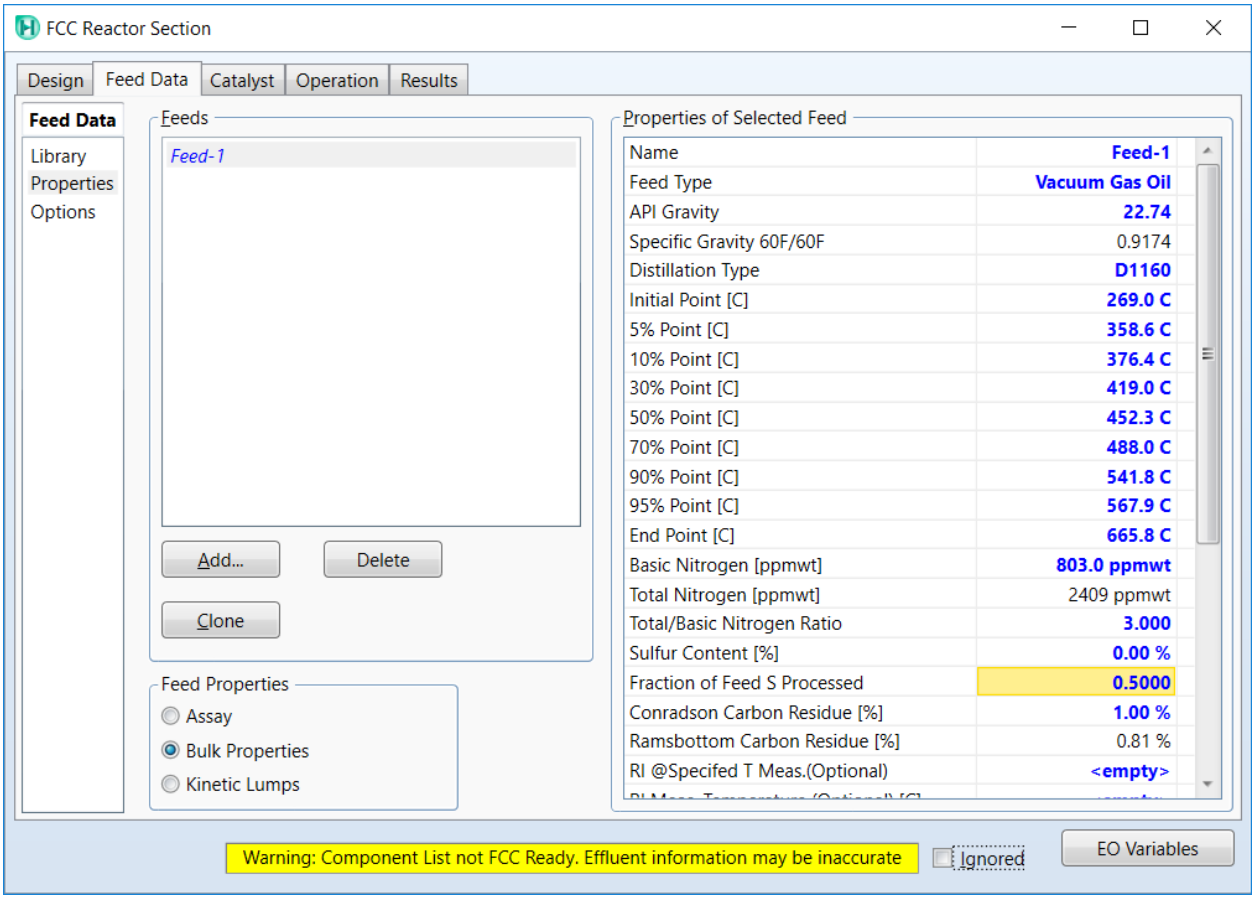


Figure 25: Vacuum gas oil properties

The catalyst was selected from the model directory as well. The catalyst used in the FCC unit is a ZSM-5 catalyst, the af-3 catalyst in the library was assumed to behave in a similar way to the catalyst in the refinery does.

The catalyst was not blended.

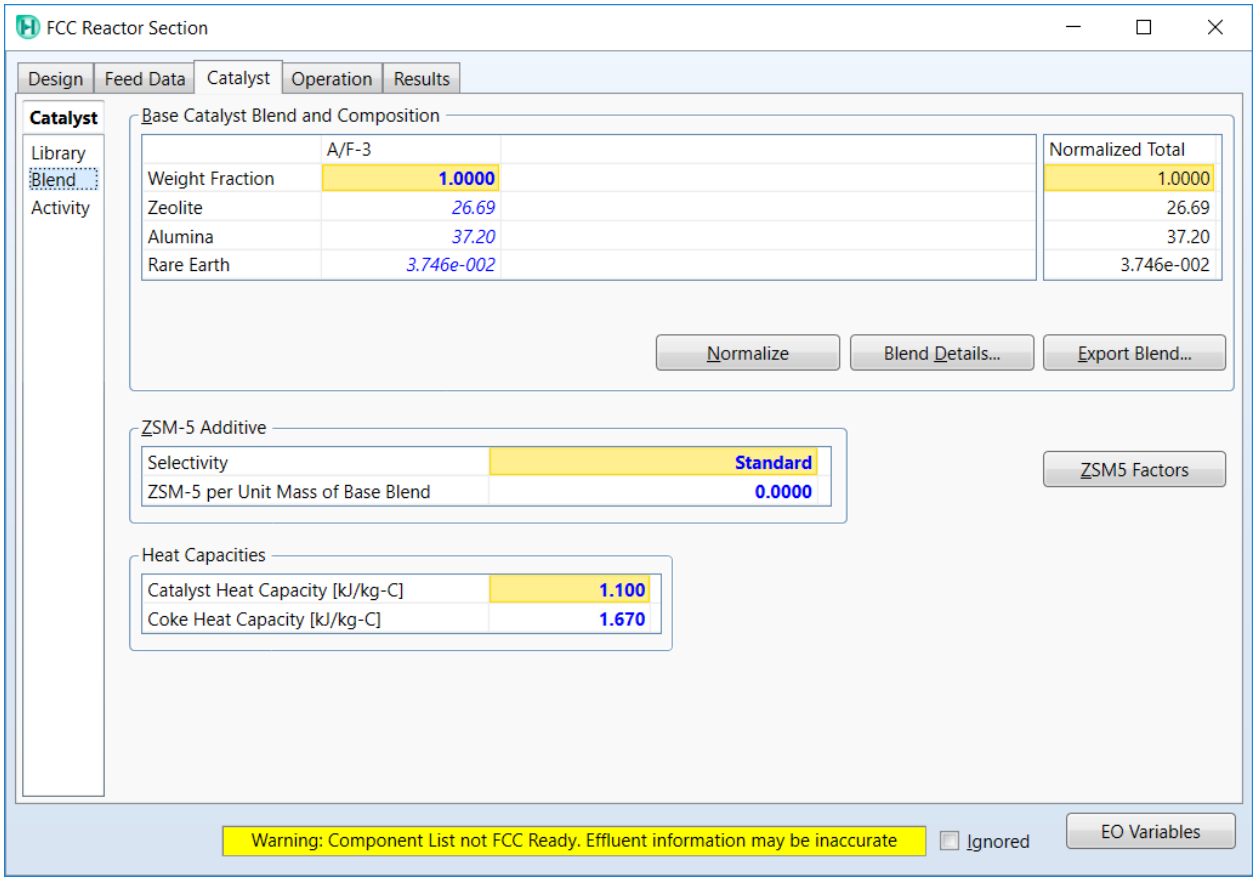


Figure 26: Catalyst blend

The catalyst activity is normally obtained from the manufacturer as plant tests for the activity are not part of routine analysis.

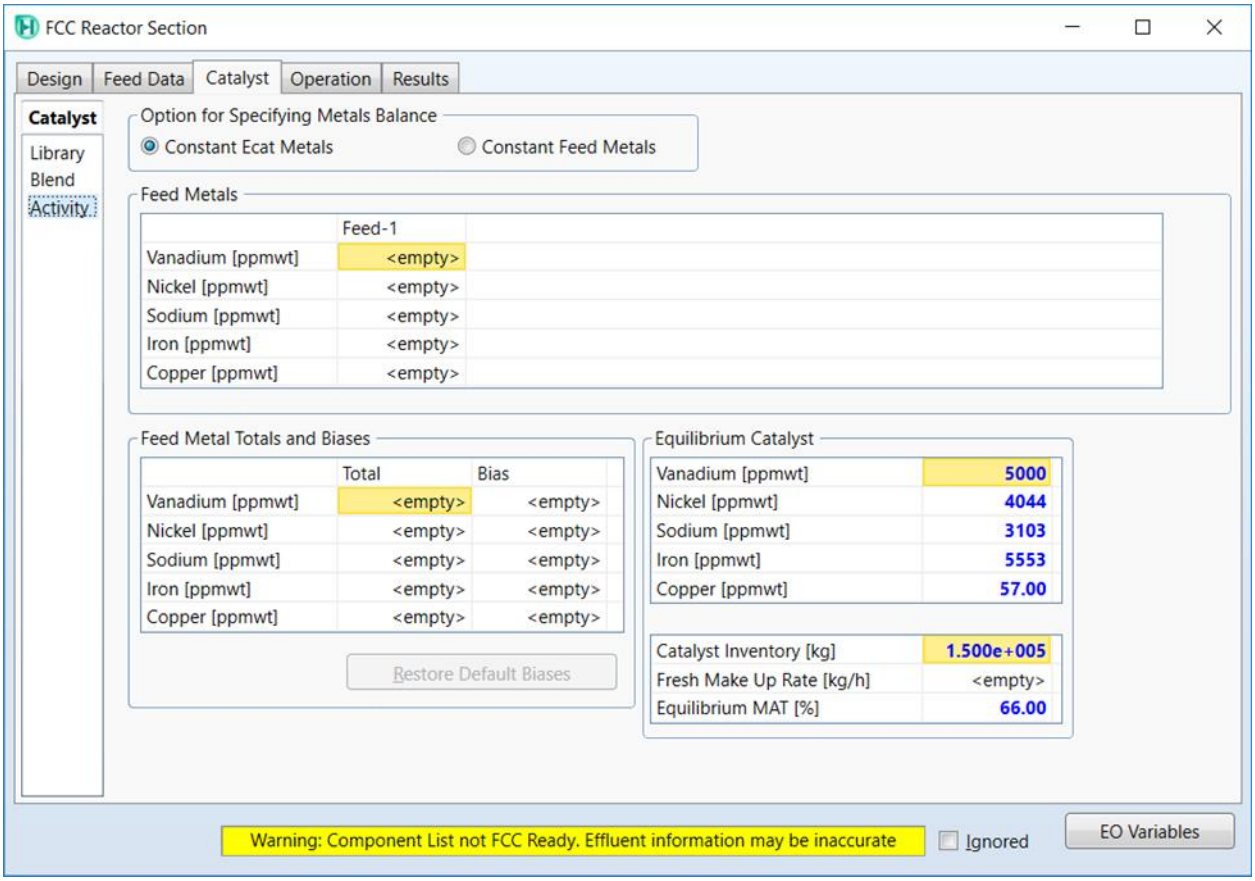


Figure 27: Catalyst activity and properties

When the catalyst properties had been added the operating properties were added to the model. The feed, riser, regenerator, and pressure control properties were added in the different windows as shown from figures 28-31.

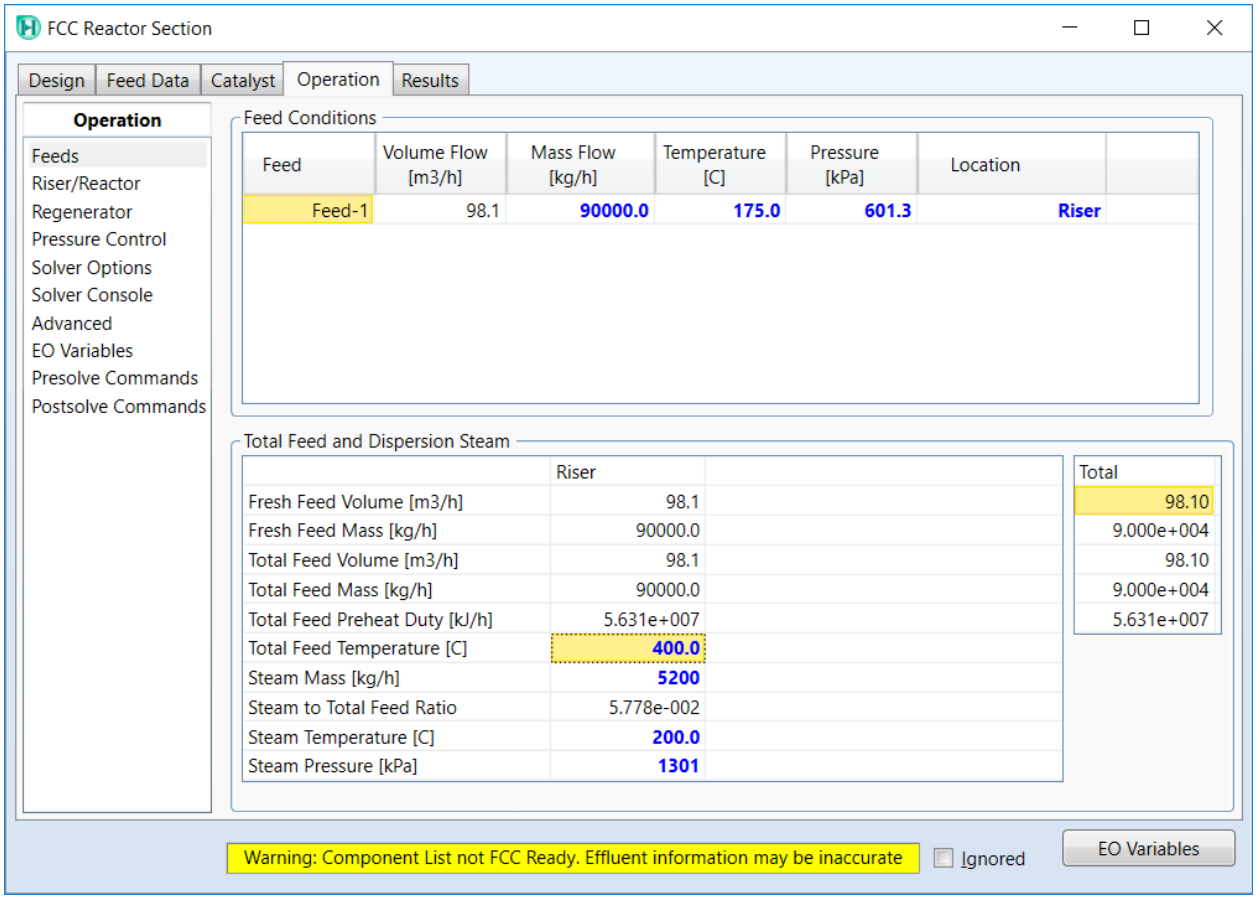


Figure 28: Feed properties

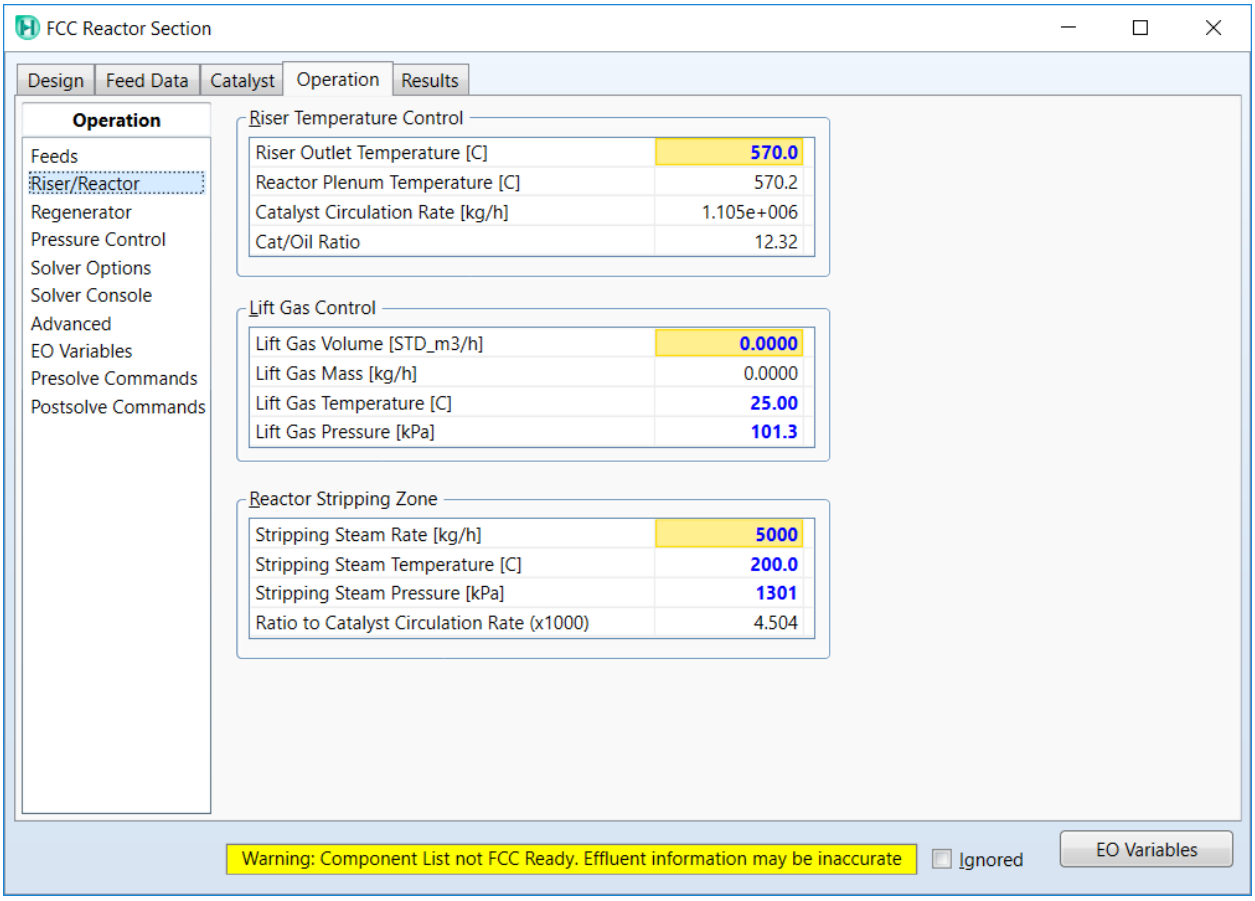


Figure 29: Riser conditions

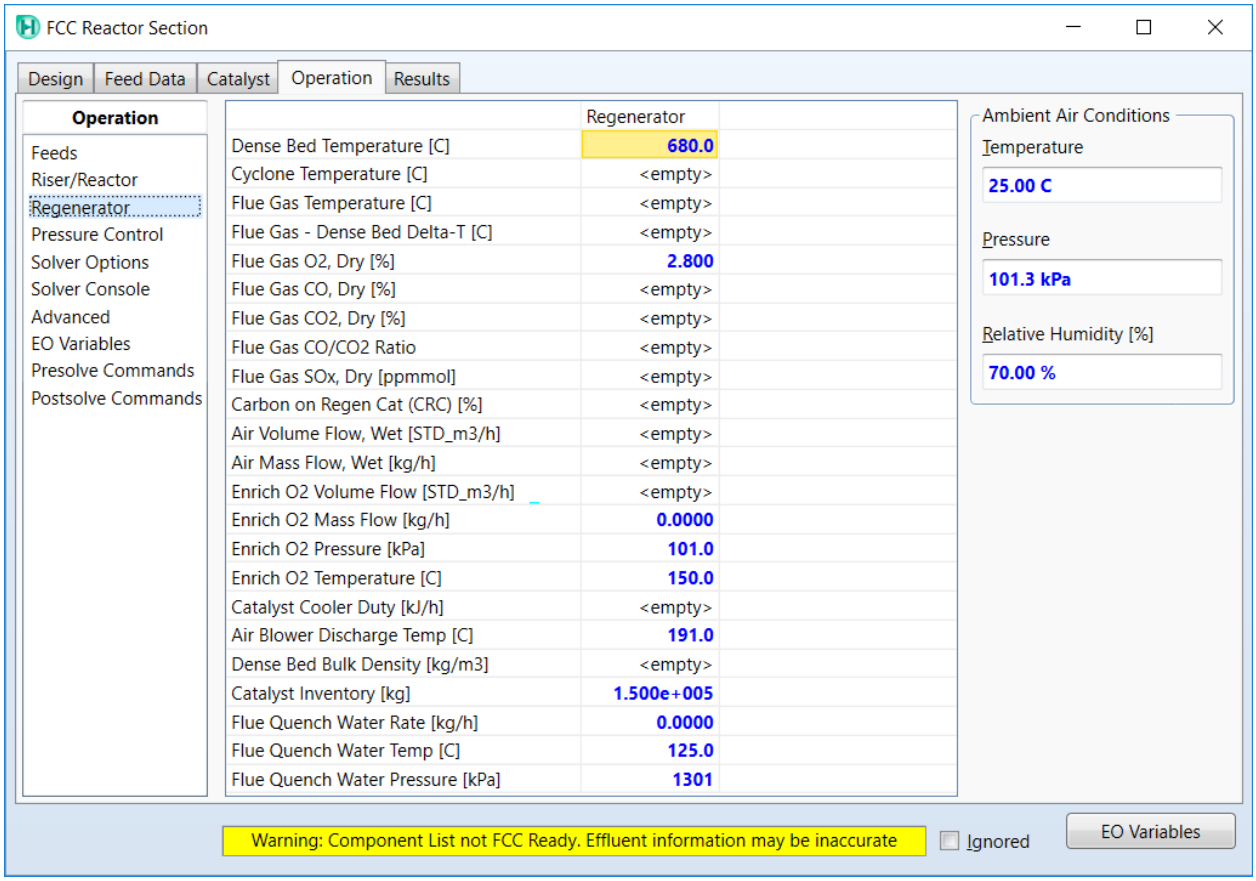


Figure 30: Regenerator conditions

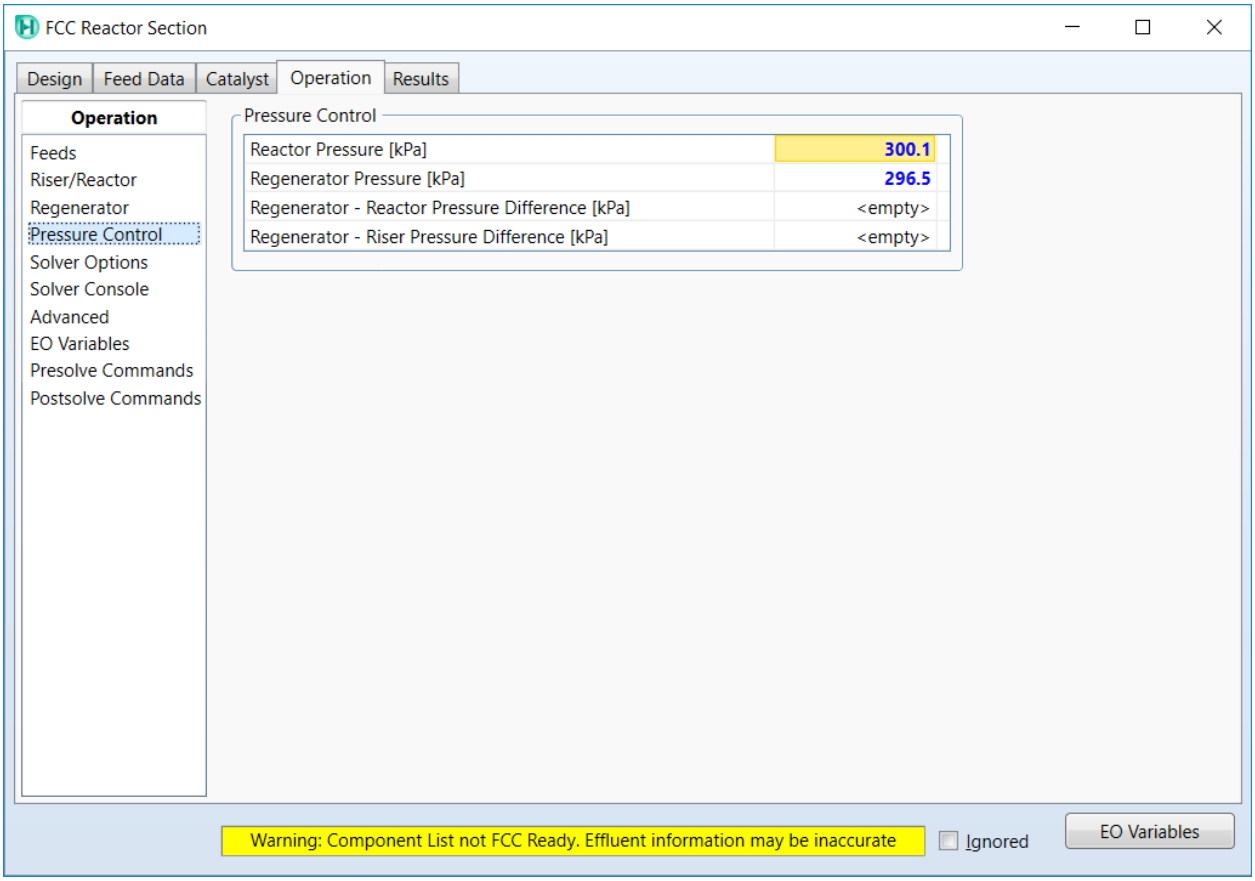


Figure 31: Pressure control

When the different conditions in the model have been added the solver is left to run. The model is set to converge at to the nearest 0.00001 in the simulation result. The results of the simulation are shown in figure 32. The results show that the data used from the plant is reliable and can be used for further optimization activities.

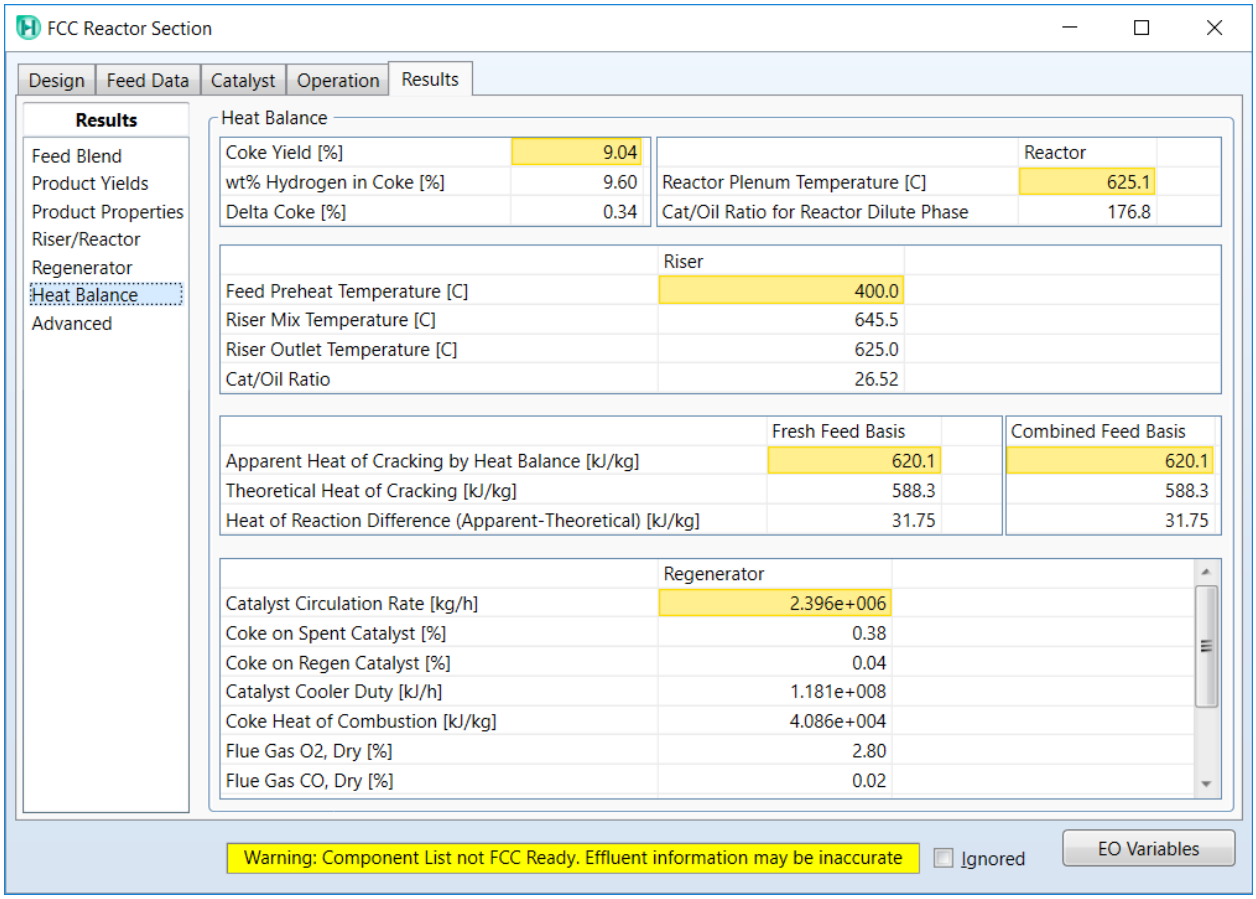


Figure 32: Simulation results

4.4 CONCLUSION

The converged model is used for the optimization process. The end of riser temperature will be set as the independent variable. As the end of riser temperature is varied over a temperature range, the production of propylene, the energy consumed as well as the CO_2 produced will be observed. Recommendations after the analysis of the results will be given. The steps for the optimization process are outlined below:

- A case study was carried out and on the variable object window, the variables are chosen, figure 33.
- In the case study window the independent variable is chosen and range is selected. In this case, the end of riser temperature is varied in the range of 580-650^{o}C with increments of 5^{o}C.

After running the simulation, the results and the plots of the case study can be viewed. The next chapter will discuss the results of the optimization case study.

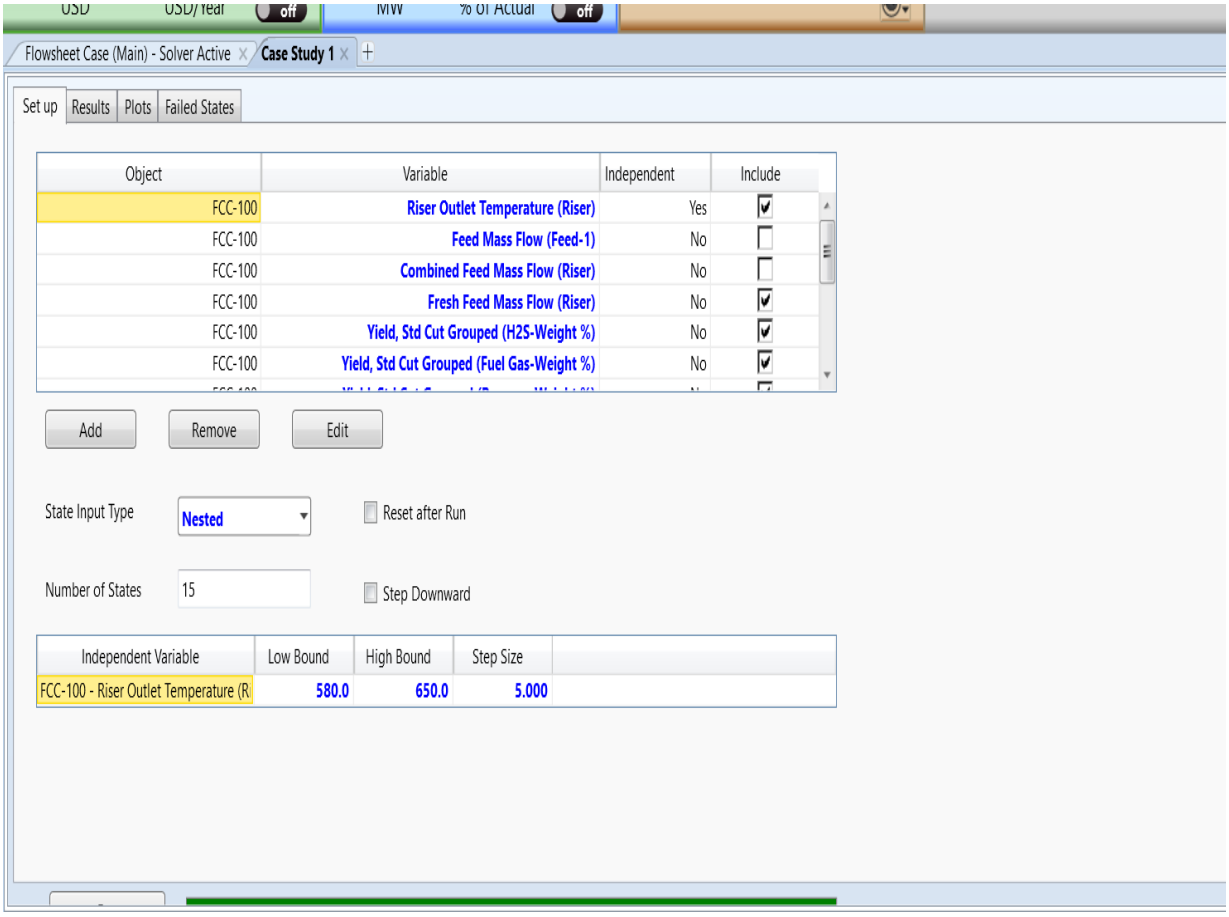


Figure 33: Case study window

5. RESULTS AND DISCUSSION

The objective of this project was to optimize the energy used in the FCCU and to try and decrease the amount of CO_2 emitted in the process, this would in turn give the optimum operating point for the refiner. The yields of different products are observed as presented by the simulation with special attention being paid to propylene as it is the most profitable product in the product stream. The results from the optimization will be discussed in this chapter.

5.1 OPTIMIZATION RESULTS

The results from the case study are given in the following table. Graphs representing the various relationships in the variables are presented.

Table 6: Simulation results

	End of riser (ºC)	Propylene weight %	nButane weight %	Heat of cracking (kJ/kg)	CO_2 weight %
State 1	580	15.01	2.01	647.48	0.135
State 2	585	15.11	1.99	645.42	0.129
State 3	590	16.42	1.93	638.84	0.118
State 4	595	17.35	1.89	633.18	0.112+
State 5	600	17.87	1.87	629.60	0.111
State 6	605	18.10	1.86	626.69	0.113
State 7	610	18.19	1.85	623.38	0.117
State 8	615	18.23	1.85	619.01	0.122
State 9	620	18.25	1.85	613.17	0.129
State 10	625	18.24	1.85	605.46	0.138
State 11	630	18.22	1.84	595.31	0.148
State 12	635	18.17	1.84	581.72	0.161
State 13	640	18.10	1.83	563.00	0.177
State 14	645	17.98	1.82	536.05	0.199
State 15	650	17.80	1.80	495.28	0.229

The results show that the propylene produced increases as the end of riser temperature increases, from 585ºC to 620ºC, there after a constant volume is produced. As the temperature is increased a dip in the production of propylene is noticed and this could be due to over cracking.

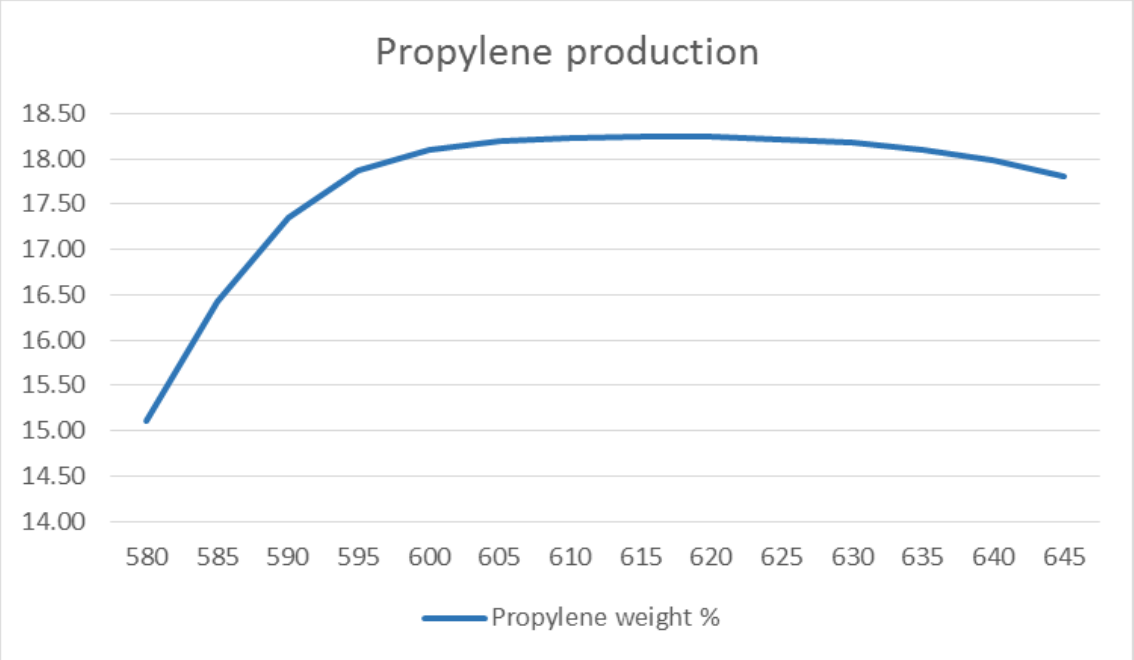


Figure 34: Propylene production

The amount of CO_2 produced is very high at higher temperatures. This could be contributed by the fact that the valuable products under go combustion at higher temperatures producing more CO_2. At a temperature of 600°C the least amount of carbon dioxide is produced, thereafter a rapid increase of CO_2 gases is observed, this could be due to the fact that as temperatures are increased over cracking of lighter components occurs, which leads to the formation of the CO_2. Butane is one component that could be converted to CO_2 as the end of riser temperature is increased.

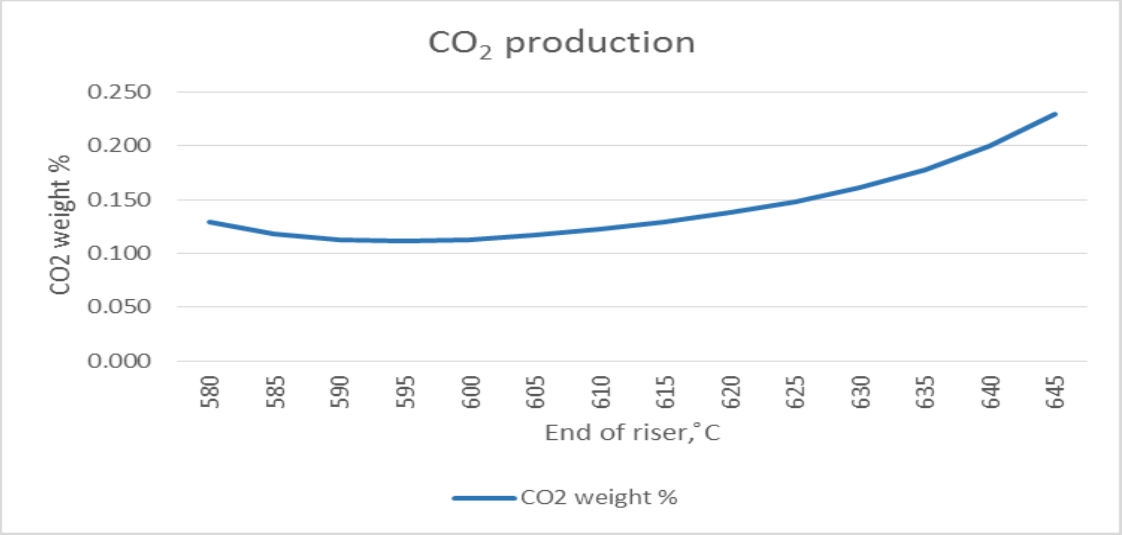


Figure 35: CO_2 formation

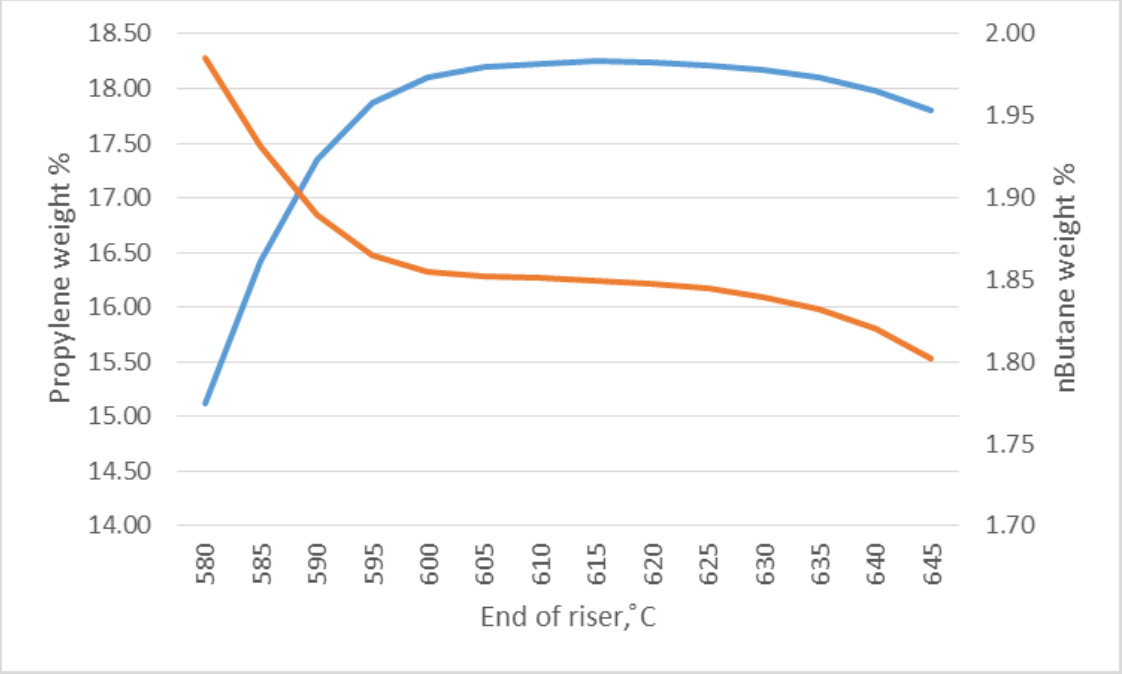


Figure 36: Consumption of nButane

The energy that is required for the cracking reaction to occur decreases as the end of riser temperature is increased. The cracking reaction is endothermic and the heat is provided by the regenerated catalyst. At lower temperatures, end of riser, more energy is required as the end of riser temperature gradually increases the amount of energy required decreases.

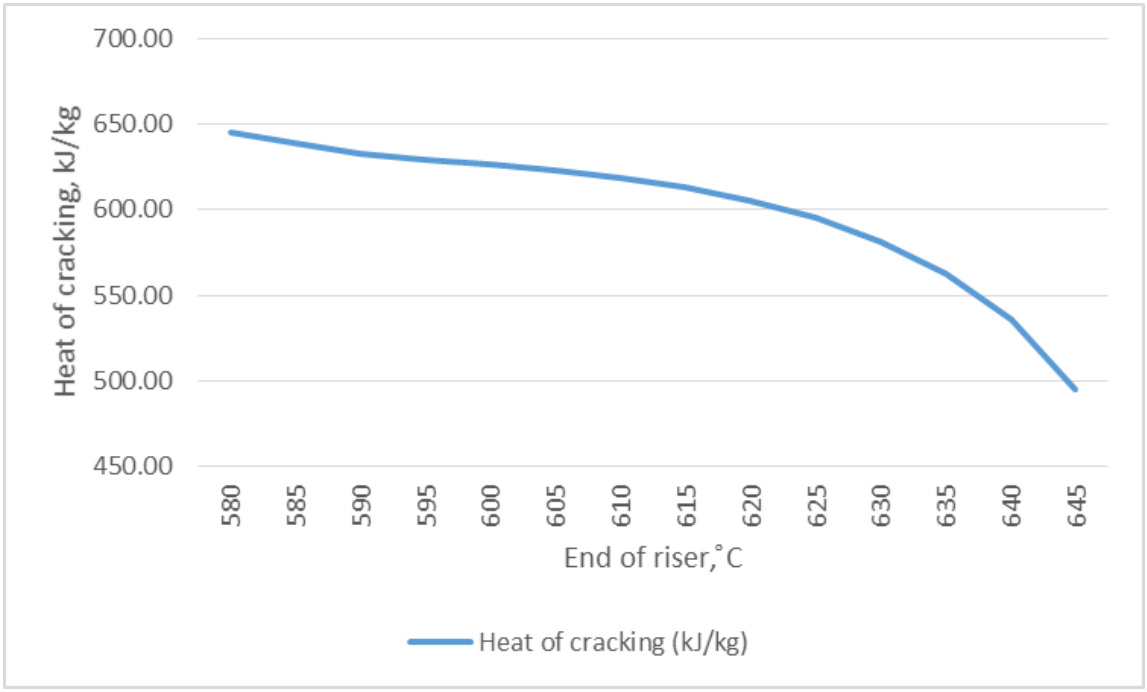


Figure 37: Energy requirements for cracking

An observation to note is that as the heat of reaction decreases the propylene production increases, 613.17kJ/kg is required for the production of propylene at 620ºC.

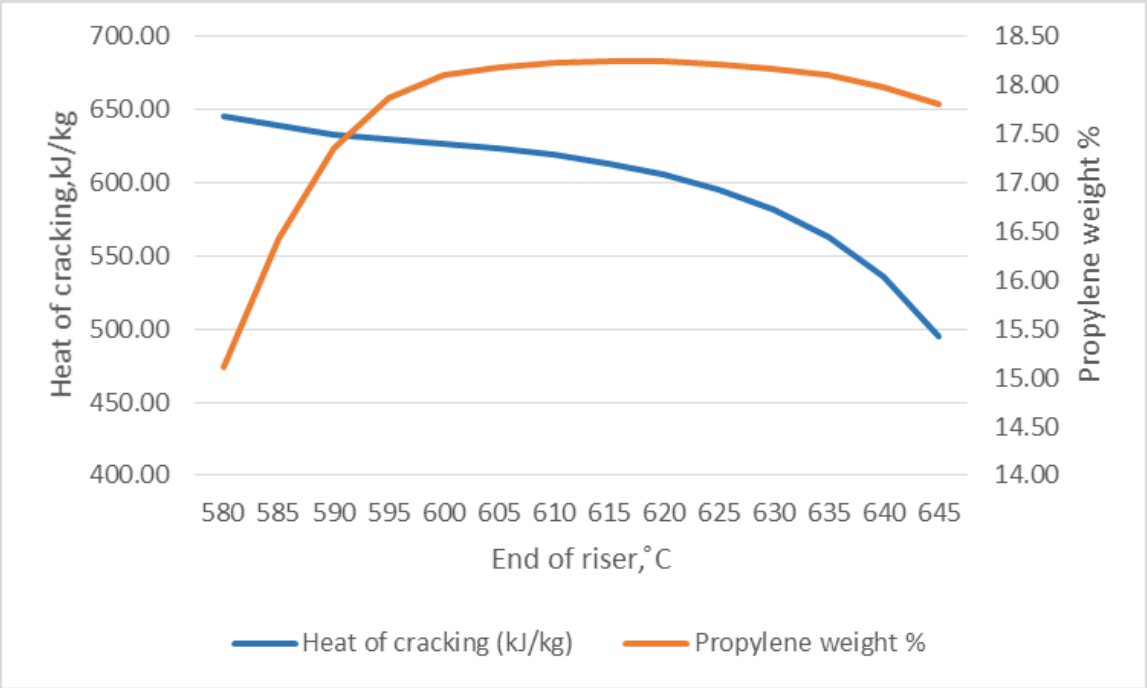


Figure 38: Energy required for propylene production

5.2 RECOMMENDATION AND CONCLUSION

The project was aimed to find the optimum operating condition of a currently full scale operating FCCU. The optimum operating conditions would be those that fulfil the objective of the production of an environmentally friendly light products. As the world moves towards less emissions and less energy consumption, it is crucial that the whole production process is optimized.

A simulation of the FCCU was built in Aspen HYSYS and a case study that focused on the end of riser temperature as the independent variable was conducted.

From the previous section the various reactions of the dependent variables to the independent variable were made and conclusions can be drawn from the results. These results together with knowledge gained from various literature could be used as a recommendation to the FCCU.

5.2.1 RECOMMENDATION

The optimum production of propylene was found to be at 620^{o}C, at a feed rate that was kept constant at 108253.37kg/h during the simulation. The production of CO_2 gases is also observed to be at its minimum at that temperature. The refinery is currently operated at 625^{o}C, which produces significantly more CO_2. The pressure conditions should be maintained at the current rate.

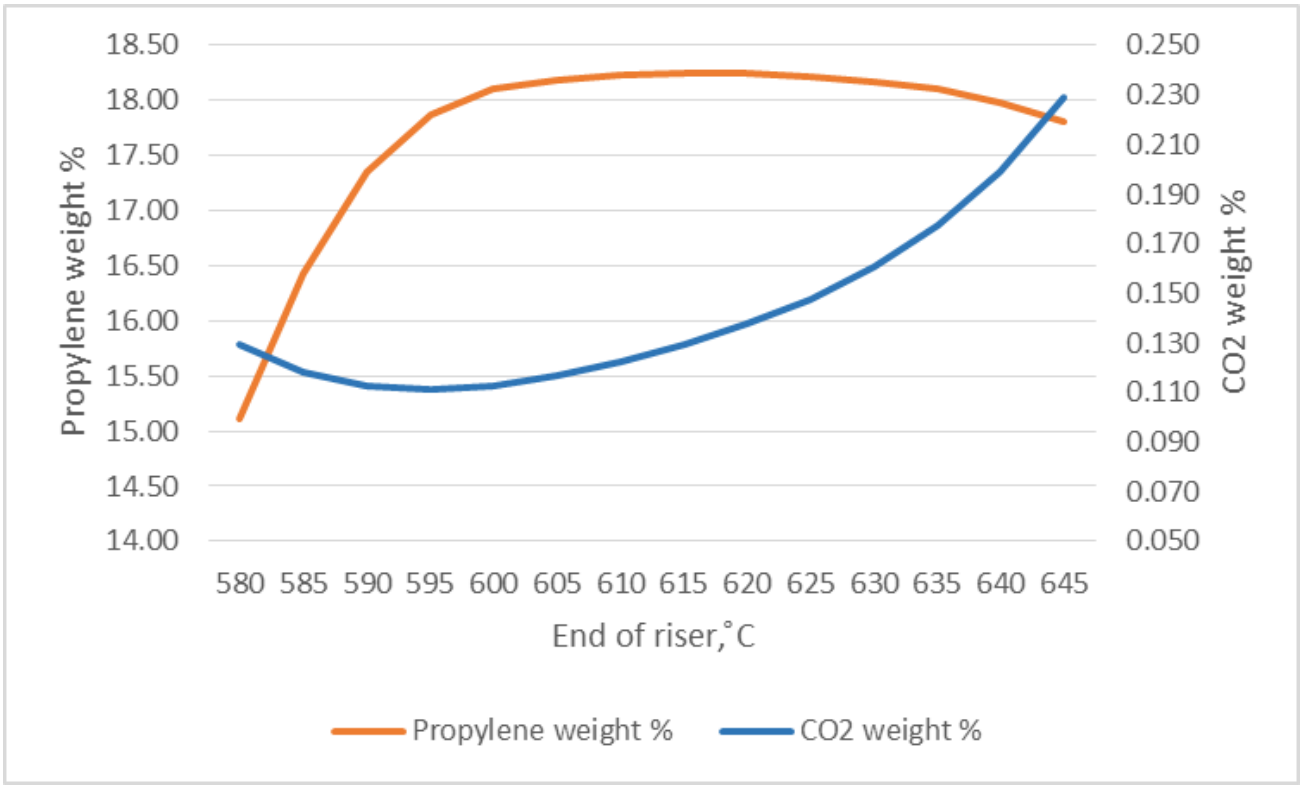


Figure 39: Propylene to CO_2 production

Design Expert® was used to further analyse the results for the research objectives.

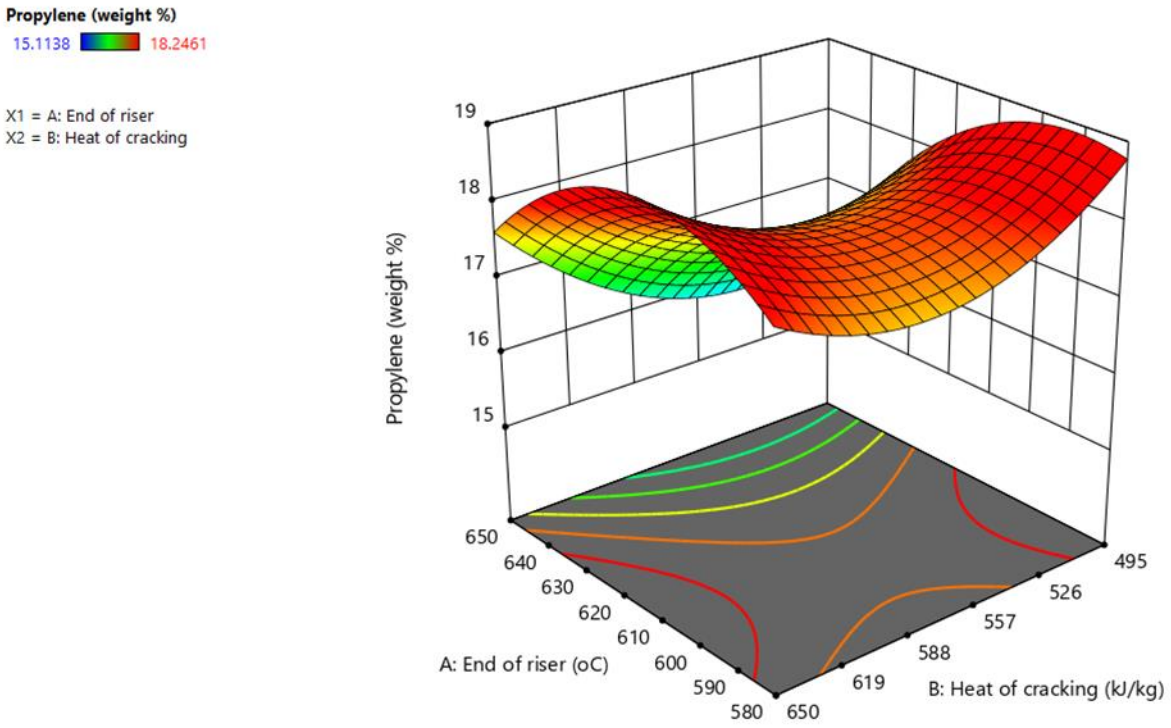


Figure 40: Propylene production

From the analysis in figure 40, it can be observed that at temperatures between 580-650℃ and heats of cracking of 495-645kJ/kg the amount of propylene being produced is optimized. The current operating conditions of 625℃ produce an average of 16weight% of propylene in the products. The current conditions are not well optimized as a lot of energy is used whilst producing 2 weight % less propylene.

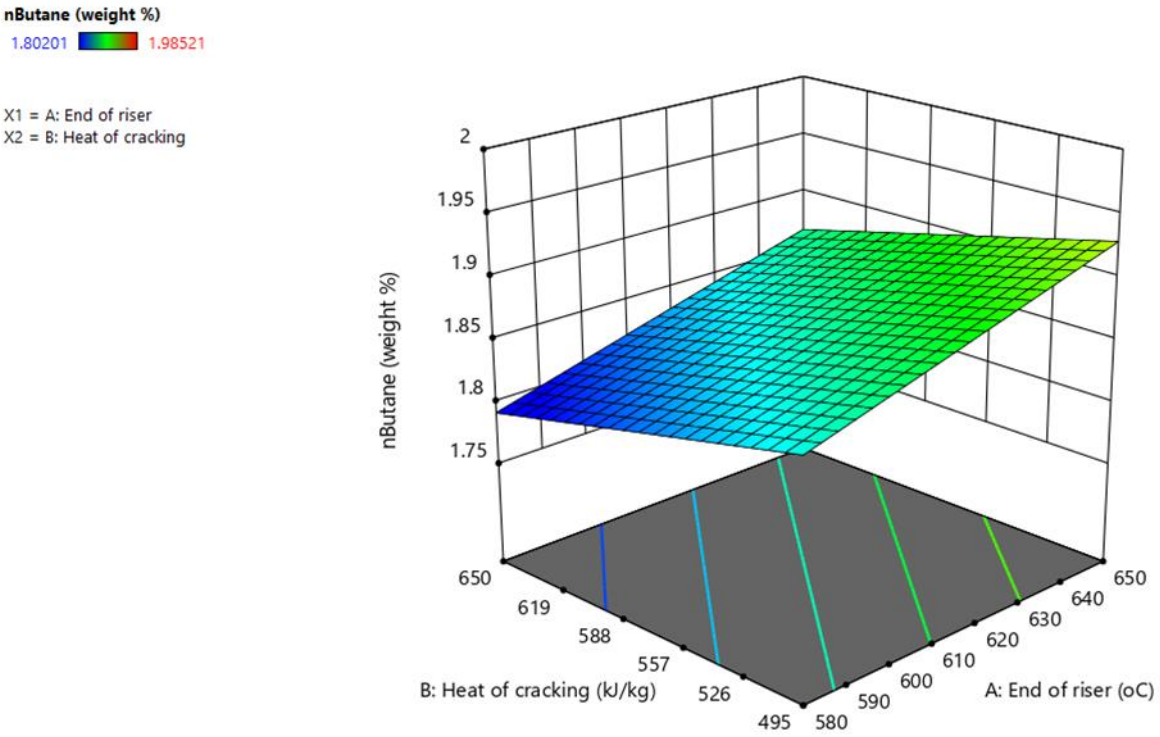


Figure 41: nButane production

Figure 41 shows that higher temperatures the production of nButane is favoured. In light of the favourable production of butane at these temperatures it is however not the most desirable product. It is eventually blended into gasoline to increase the product value.

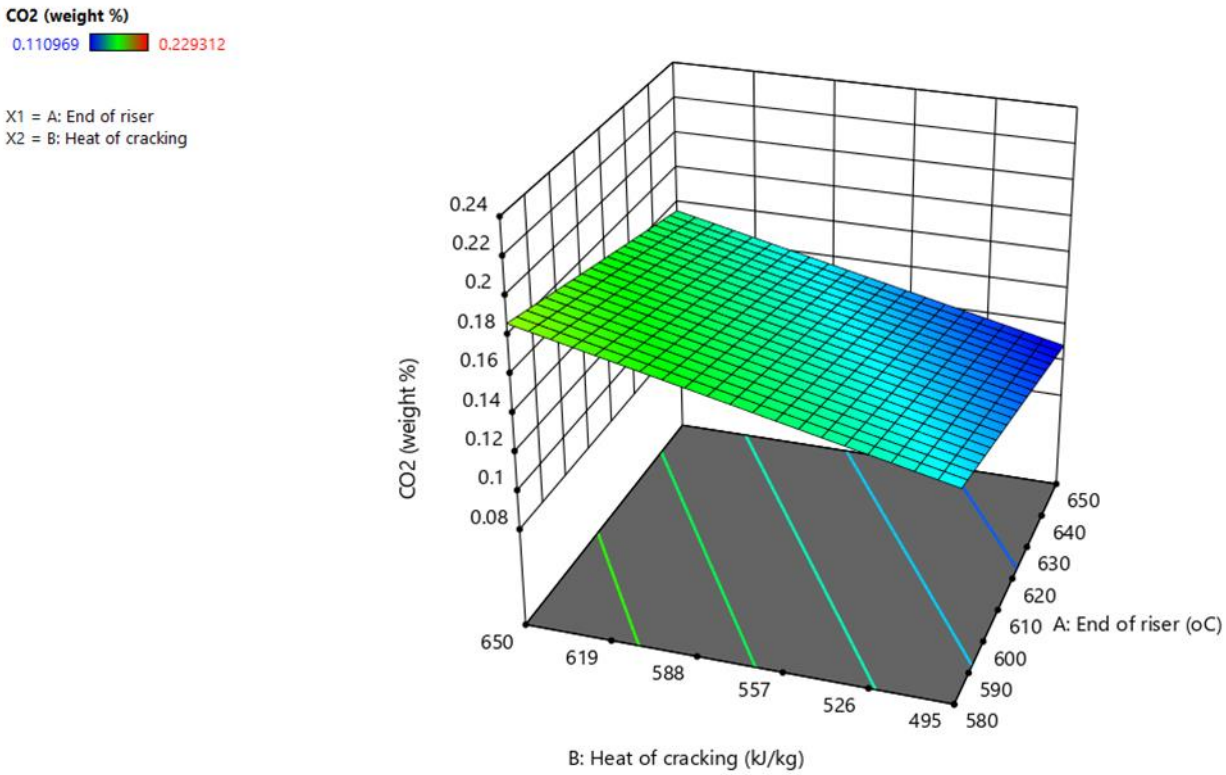


Figure 42: CO_2 production

Figure 42 clearly illustrates the trend of CO_2 production in relation to energy and temperature. From the analysis it can be seen that the CO_2 production is heavily dependent on the energy consumption of the system. It is highly recommended to operate the system at lower energy consumption to produce less CO_2 in the emissions.

5.2.2 CONCLUSION

In conclusion the current operating conditions do not offer the most environmentally safe conditions. If the end of riser temperature is reduced to 620^{o}C the amount of CO_2 produced is reduced by at least 6.98%. As stated in the recommendation it can be concluded that a better operating point for the FCC under study exists.

6. REFERENCES

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