



Sudan University of Science and Technology
Collage of Petroleum Engineering
Department Of Transport And Refining



*Project Submitted to College of Petroleum Engineering in Partial Fulfillment for the
Degree of B.Sc in Refining Engineering*

Research Titled:

Investigation on Alkylation process

التحقق من عملية الإلكلة

Prepared By:

1. Ahmed Mohammed Osman Mohammed
2. Abdulhafeez Ahmed AbdulhafeezAwadalla
3. Mazin Salah AbdallateefSharef
4. Abobaker Mohammed Musa Abdalla
5. Omer AbdulazizDafallahAlshreef

Supervised by:

Eng. Mohammed Edris Osman

October, 2017

الآية

قال تعالى:

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

{ . . . وَأَنْزَلَ اللَّهُ عَلَيْكَ الْكِتَابَ وَالْحِكْمَةَ وَعَلَّمَكَ مَا لَمْ تَكُنْ تَعْلَمُ

وَكَانَ فَضْلُ اللَّهِ عَلَيْكَ عَظِيمًا }

Dedication

We would be honor to dedicate this project to our parents, the two persons that gave the toolsand values necessary to be where we are standing today.

To all brothers,sisters, friends, teachers, colleague, relatives, & anyone who assisted, advised, &supported us and our, project.

AKNOWLEDGMENT

In the beginning, we would like to thank Allah for his grace & blessings on us to achieve this work successfully, Also we would like to thank the consortium of Sudan University for science & technology, without excluding anyone from teachers, assistant teachers, colleagues, to personnel of university's libraries.

We would like to take this opportunity to express our deepest gratitude to our supervisor, Eng. Mohammed Edris Osman who has given us his constant encouragement constructive advices & his patience in monitoring our progress in this project.

Our appreciation & special thanks go for Miss. Isra Osman Mohammed for supplying us with the valuable information & for her cooperation with us which meant a lot to us. Last but not least to our families, all my lecturers, friends & colleagues for their encouragement & kind support when we need it most.

ABSTRACT

This project study the implantation of alkylation unit in order to increase amount of gasoline produced in Khartoum refinery using LPG produced from RFCC as a feed. In this thesis simulation of unit has been done using HYSYS simulator also conducting material balance, reactor design and cost estimation.

It was found that alkylation unit product 214 ton/dayof gasoline, which equivalent 6% of the gasoline produced from Khartoum refinery. correlation calculation of material balance was conducted, the results was compared with simulation results and it was found that results show some variation also reactor design and calculation were conducted.

Keywords: alkylation unit, simulation, gasoline, Khartoum refinery, reactor design, cost estimation, HYSYS.

التجريد

من اجل زيادة كمية الجازولين المنتجة في مصفاة الخرطوم م؛ يدرس هذا المشروع اقامة وحدة الكلة في مصفاة الخرطوم باستخدام ال LPGالمنتج من وحدة الRFCC.في هذا البحث تم عمل محاكاة لوحدة الالكله باستخدام برنامج ال هابيسيس بالاضافة الى معادلة المادة وتصميم للمفاعل وتقدير للتكاليف ووجد ان وحدة الالكله تنتج 214 طن في اليوم من الجازولين اى ما يعادل 6% من انتاج مصفاة الخرطوم من الجازولين في اليوم. تم عمل حسابات لموازنة المادة باستخدام لمعادلات وقورنت بنتائج المحاكاة ووجد ان النتائج تظهر بعض الاختلاف وتم عمل تصميم للمفاعل الخاص بالوحدة.

LIST OF CONTENTS

الآية	i
Dedication	ii
AKNOWLEDGMENT	iii
ABSTRACT	iv
التجريد	v
LIST OF CONTENTS.....	vi
LIST OF FIGURES.....	viii
LIST OF TABLE.....	ix
Chapter 1 Introduction.....	1
1.1 Introduction:	1
1.2 Problem Statement:	2
1.3 Objectives:.....	2
1.4 Scope of study:	2
Chapter 2 Literature Review	3
2.1 Introduction	3
2.2 History of Alkylation unit :	3
2.3 Alkylation Processes:	5
2.4 Hydrofluoric Acid Alkylation:	5
2.5 Solid Catalyst Alkylation:	6
2.6 Alkyclean Process:	7
2.7 Sulfuric acid alkylation :	8
2.7.1 The cascade alkylation process:	8
2.7.1.1 Feed pretreatment:	8
2.7.1.2 Reaction:.....	8
2.7.1.3 Refrigeration:.....	9
2.7.2 Stratco effluent refrigerated alkylation process :	10
2.8 Effect of Operating Conditions:	11
2.8.1 Olefin Type:.....	12
2.8.2 Iso-butane Concentration:	12
2.8.3 Acid Strength:.....	13
2.8.4 Degree of Agitation:	13
2.8.5 Space Velocity:.....	14

2.8.6 Reaction Temperature:	15
Chapter 3 Methodology	17
3.1 Selection of case study:	18
3.2 Process Description:	18
3.2.1 Hysys process simulator:	18
3.2.2 Simulation steps:	20
3.3 Material Balance :	26
3.3.1 Material Balance equation :	27
3.4 Design.....	27
3.5 Cost estimation:	27
3.5.1 Types of Capital Cost Estimates:.....	28
3.5.2 COST INDEXES:.....	28
3.5.3 Methodpower factor applied to plant – capacity ratio:.....	28
3.5.4 Capital cost data for processing plant (1990):	30
3.5.5 Relative labor rate and productivity indexes in the chemical and allied products industries for the United States (1989) :	30
Chapter 4 Results and Discussions	31
4.1 Material Balance:	31
4.1.1 Results:	31
4.1.2 Material Balance Discussion:	33
4.2 Design:.....	33
4.2.1 Results:	33
4.2.2 Design Discussion:	35
4.3 Cost estimation results:.....	35
Chapter 5 Conclusion and Recommendation.....	36
5.1 Conclusions:	36
5.2 Recommendations:	36
5.3 References:	37

LIST OF FIGURES

Figure (2.1) Simplified diagram of the Phillip's HF alkylation process.....	6
Figure (2. 2) AlkyClean process	8
Figure (2. 3) Cascade auto-refrigerated alkylation process:	10
Figure (2. 4) Stratco effluent refrigerated alkylation process:	11
Figure (2. 5) Emulsion of hydrocarbon in sulphuric acid:	14
Figure (2. 6) Alkylation unit location in refinery	15
Figure (2. 7) Block diagram of alkylation process	16
Figure (2. 8) Role of alkylation and polymerization units in the refinery:	16

LIST OF TABLE

Table (1.1) Solid acid alkylation processes	7
Table (1.2) Effect of type of olefin on alkylate octane number	12
Table (3.1) 1Volume and mass factors for alkylation conversions	26
Table (3. 2) Type of Capital Cost Estimates.....	28
Table (3.3) Cost index.....	29
Table (4.1) overall Material balance	31
Table (4.2) Material Balance around the reactor	31
Table (4. 3) component material balance by factor	33
Table (4.4) VOLUME DESIGN	34

Chapter 1 Introduction

1.1 Introduction:

Today gasoline is the most important product of a typical oil refinery, The entire refinery process is designed to maximize its production.

Gasoline is a complex mixture of molecules with a boiling range of 85-195°C including reformat, alkylate, aliphatic naphtha (light straight-run naphtha), aromatic naphtha (thermal and catalytic cracked naphtha) and additives.

The important qualities for gasoline are octane number (antiknock), volatility (starting and vapor lock), and vapor pressure (environmental control.) Additives are often used to enhance performance and provide protection against oxidation and rust formation.

In general, gasoline are blended from several petroleum refinery process streams that are derived by the following methods, direct distillation of crude oil, catalytic and thermal cracking, hydrocracking, catalytic reforming, alkylation, and polymerization.

One of the importance unit to produce high octane gasoline is Alkylation unit

Alkylation now produces the most important gasoline component in the refinery. Alkylation units make high-octane gasoline blending components that contain little or no benzene and other undesirable constituents, making the process ideally suited for producing reformulated gasoline..

Alkylation is a secondary refinery unit operation that many refineries have this unit because it adds high octane hydrocarbons to motor and aviation gasoline. High octane hydrocarbons are needed to help prevent autoignition of gasoline (knocking) in an engine and to meet recommended engine octane ratings.

The process combines an unsaturated light hydrocarbon (propylene, also known as propene or butylenes, also known as butene) with iso-butane to produce alkylate. Either sulfuric or hydrofluoric acid is used as the catalyst for the alkylation reaction. (U.S Energy information administration).

1.2 Problem Statement:

There are amounts of gases in Khartoum refinery company that may have an economic feasibility, Some of these important gases are iso-butane & olifenes. If it's processed by alkylation unit, it would increase the gasoline production and enhance its octane number.

1.3 Objectives:

Increase the gasoline production in Khartoum refinery company and enhance its octane number using sulfuric acid alkylation unit.

1.4 Scope of study:

The scope of this project is to give a comprehensive study for an alkylation unit. The project will cover the following:

- 1-material balance
- 2-simulation
- 3-design unit
- 4-cost estimation

Chapter 2 Literature Review

2.1 Introduction

Alkylation is the process of producing gasoline range material (alkylates) from olefins such as propylene (C₃=), butylenes (C₄=) and amylene (C₅=), and iso-butane. Butylene is the most widely used olefin because of the high quality of the alkylate produced.

The current trend toward elimination of methyl tertiary butyl ether (MTBE) has resulted in increased attention to alkylation technology. An alternative process is the polymerization process in which polymeric materials from unreacted olefins are formed. Reformulated gasoline requires a low olefin content. This makes polymer gasoline undesirable as a blending stock. The motor octane number of a polymer gasoline is much lower than the corresponding values obtained from alkylation. This has resulted in the shutdown of the polymerization units in refineries using alkylation. (Fahim 2010).

Motor fuel alkylation in the petroleum refining industry refers to the acid catalyzed conversion of C₃-C₅ olefins with iso-butane into highly branched C₅-C₁₂ iso-paraffins collectively called alkylate, a valuable gasoline blending component. A major constituent of alkylate is 2,2,4-trimethyl pentane which is defined as 100 on the octane scale.

Alkylation reactions are catalyzed by liquid and solid acids, including H₂SO₄, AlCl₃-HCl, HF, HF-BF₃, H₂SO₄-HSO₃F (Fluorosulfuric acid), Trifluoromethane sulfonic acid chloride Pt alumina, BF₃ on alumina, zeolites, and ion exchange resins.

However, the catalysts and associated processes commercialized during WWII for aviation gasoline, HF alkylation, and sulfuric acid alkylation, are the focus of this section as these remain the primary commercial motor fuel alkylation processes. A solid catalyst alkylation process (UOP Alkylene™) has been developed and is being offered to the industry. (Jones 2015)

2.2 History of Alkylation unit :

In 1932–6, alkylation was independently discovered by UOP, 1 Shell, the Anglo Iranian Oil Company (AIOC), and Texaco whose first publications issue in that order. Herman Pines told the story of UOP's discovery of the alkylation of ethylene by

pentanes in 1932.2 At that time leading universities taught that iso-paraffins were inert except at high temperatures and pressures. After finding anomalies in an olefin assay based upon H₂SO₄ extraction Pines and his mentor V. I. Ipatieff hypothesized that paraffins may not be inert to acids. Despite ridicule, they tested that hypothesis by bubbling ethylene into chilled pentanes over AlCl₃. All the ethylene was converted into saturated hydrocarbons. Over the next few years they tested AlCl₃-HCl, H₂SO₄, HF, and HFBF₃ as alkylation catalysts. (Jones 2015)

Alkylate was found to have excellent aviation gasoline properties. It was the highest octane fuel component then known, with high motor octane and excellent lead response. All of the properties derive from the highly-branched paraffins that form its composition. (Jones 2015)

Humble Oil built the first commercial H₂SO₄ alkylation unit in 1938 at Baytown, Texas. Alkylation for aviation gasoline grew rapidly with the Allies war effort. In 1939, six petroleum companies formed a consortium to pool their alkylation technology and develop both sulfuric acid and HF acid processes for 100 octane aviation fuel. The first commercial HF alkylation unit started up in 1942. During the war 60 alkylation units were built for the Allies' war effort. Half were built with sulfuric acid as the catalyst and half with HF. (Jones 2015)

Following World War II, most alkylation operations were discontinued although a few refiners continued to use the process for aviation and premium automobile gasolines. (Jones 2015)

In the mid-1950s, use of higher performance automotive engines required the refining industry to both increase gasoline production and quality. The development of catalytic reforming, such as UOP Platforming™, provided refiners with an important refining tool for production of high octane gasolines. However, the motor fuel produced in such operations, called reformate, is highly aromatic with a higher sensitivity (the spread between research and motor octane) and a lower lead response than alkylate. Many refiners expanded their alkylation operations and began to broaden the range of olefin feeds to both existing and new alkylation units to include propylene and occasionally even some pentenes along with the butenes. (Jones 2015)

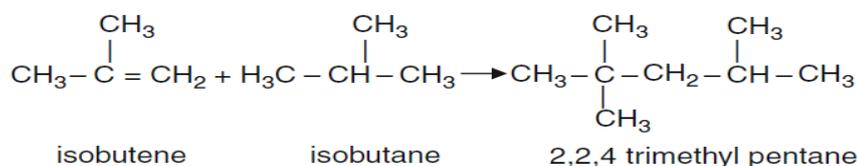
With the phase-out of leaded gasolines and the advent of environmental gasolines the lead response of alkylate is no longer valued, but the importance of alkylate and its production have both grown because of its other properties. Its high unleaded motor octane, low volatility, low-sulfur, and nearly zero olefins and aromatics make alkylate

critical to the production of quality environmental gasolines. Alkylate can reach 60% of low-sulfur reformulated premium Licensors of motor fuel HF Alkylation processes are UOP LLC and Phillips. Licensors of H₂SO₄ alkylation processes are Exxon Mobil and Stratco Engineering. (Jones 2015).

2.3 Alkylation Processes:

Alkylation is catalysed by a strong acid, either sulphuric (H₂SO₄) or hydrofluoric (HF). In the absence of catalysts, alkylation between isobutene and olefin must be run under severe conditions such as T = 500 C (932 F) and P = 200–400 bars (2940–7080 psia). In the presence of an acid catalyst, the reaction temperature will be lower than 50 C (122 F), and the pressure will be lower than 30 bars (441 psia). The major difference in using either acid is that iso-butane is quite insoluble in H₂SO₄ but reasonably soluble in HF. This requires the use of high isobutene /olefin ratios to compensate for low solubility in H₂SO₄. Furthermore, the reaction must occur at low temperature. (Fahim 2010).

The alkylation process consists of running the hydrocarbons in liquid form (enough pressure is used to ensure that) and at low temperature and with a high iso-butane (iC₄) to olefin (such as C₄=) ratio. The reaction products are sent to an acid settler where the acid is recycled back to the reactor. Products are then separated into gaseous LPG propane and n-butane and the desired product of alkylate. (Fahim 2010). An overview of different types of alkylation processes is given the sections underneath.



2.4 Hydrofluoric Acid Alkylation:

Two hydrofluoric acid (HF) alkylation processes are commonly available. These are the Phillip process and the UOP process. The HF processes have no mechanical stirring as in the sulphuric acid processes. The low viscosity of HF and the high solubility of iso-butane in the acid allow for a simpler design. The emulsion was obtained by injecting the hydrocarbon feed into the continuous HF phase through

nozzles at the bottom of a tubular reactor. Reaction temperature is about 30C (86 F), allowing for the use of water as a coolant to the reactor. (Fahim 2010).

The two processes are quite similar. The residence time in the reactor is 20–40s.

The hydrocarbon phase is sent to the main fractionation column to obtain stabilized alkylate. H₂SO₄ alkylation processes are favour over the HF processes because of the recent concern about the mitigation of HF vapour. HF is a very hazardous material for humans because it can penetrate and damage tissue and bone. (Fahim 2010).

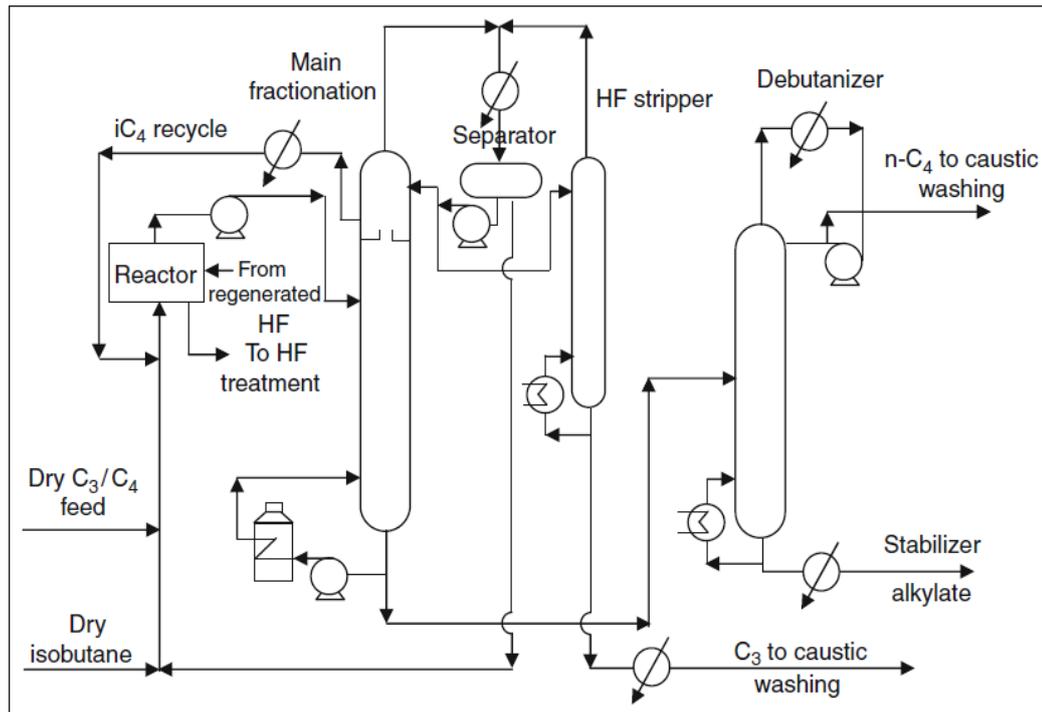


Figure (2.) Simplified diagram of the Phillip's HF alkylation process

2.5 Solid Catalyst Alkylation:

Alkylation processes based on solid acids are not yet operated on an industrial scale. However, several companies have developed processes or already offer technology for licensing. The overall process scheme is similar to the liquid acid base process scheme, except for the regeneration section, which is necessary for solid acid catalysts because of rapid deactivation. Hydrogen has proven to be very effective for the regeneration of the catalysts. Examples of solid acid alkylation technologies are shown in Table. (Fahim 2010).

Table (1.) Solid acid alkylation processes

Process	Reaction temperature (°C)	iC ₄ /olefin	Catalyst
UOP alkylene	10–40	6–15	HAL-100
Lurgi Eurofuel	50–100	6–12	Faujasite-derived
Haldor Topsoes FBA	0–20		CF ₃ SO ₃ H/SiO ₂
ABB Lummus AlkyClean	50–90	8–15	Zeolite-derived (SAC)

2.6 Alkyclean Process:

Lummus technology has developed a solid acid catalyst gasoline alkylation technology (Amico et al. 2006).

The Alkyclean process employs a zeolite catalyst coupled with a novel reactor processing to yield a high quality alkylate product. The process shown in Figure 2.2 consists of four main sections: feedstock pretreatment, reaction, catalyst regeneration and product distillation. An olefin feed is preheated and fed with the iso-butane recycle to the reactor. The reactor operates at 50–90 C (122–194 F) with liquid phase conditions. Multiple reactors are used to allow for the catalyst regeneration cycle. During regeneration, olefin addition is stopped and hydrogen is added to achieve a low reactor concentration of dissolved hydrogen while maintaining liquid phase alkylation reaction conditions. This minimizes energy consumption during the switching of the operation. The swing reactor coupled with long catalyst life allows the refiner to work without the need of taking the reactor off-line for moderate temperature regeneration that restores the catalyst activity completely. (Fahim 2010).

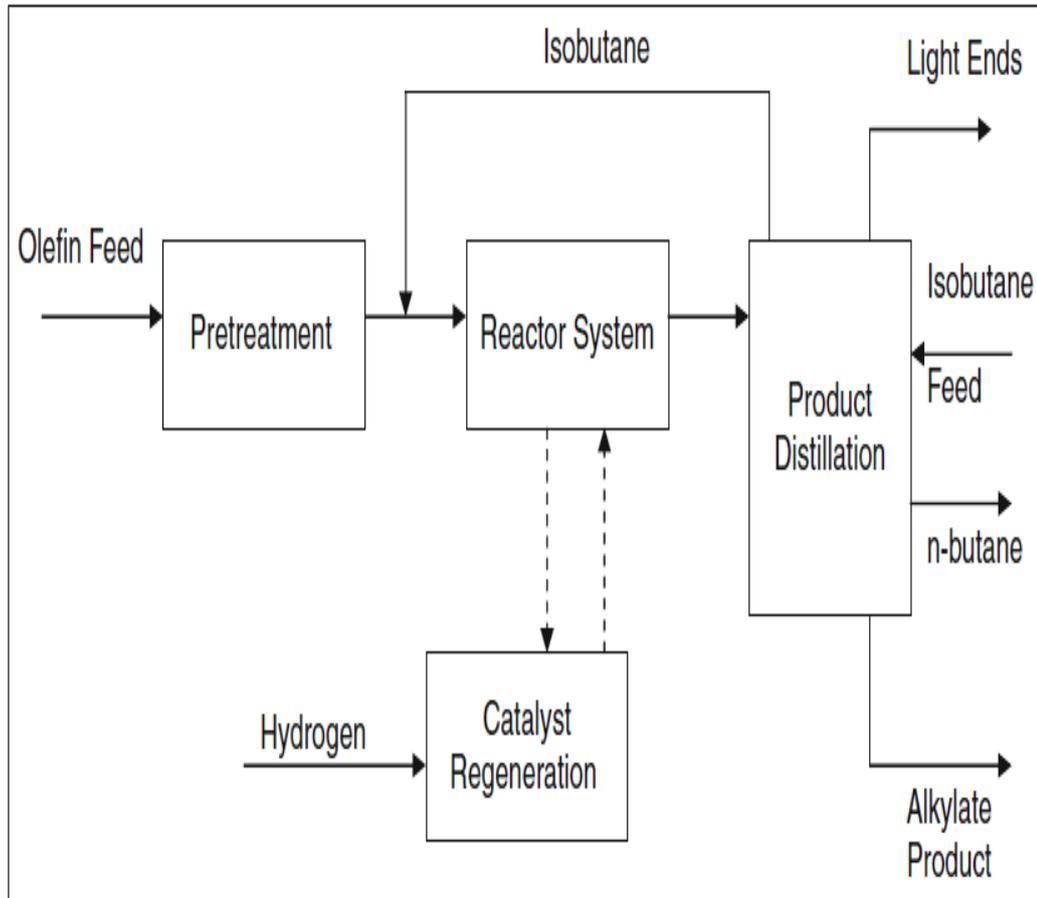


Figure (2. 1) Alkylclean process

2.7 Sulfuric acid alkylation :

Today there are two processes for H₂SO₄ alkylation the Cascade process licensed by Exxon Mobil and MW Kellogg and the Stratco effluent refrigerated process. (Jones 2015)

2.7.1 The cascade alkylation process:

2.7.1.1 Feed pretreatment:

It usually consists of deethanizing and Merox-treating of FCC olefin. Some refiners have added selective hydrogenation units (SHP) to saturate dienes and reduce acid consumption. Feeds are generally not dried. (Jones 2015)

2.7.1.2 Reaction:

The FCC olefins are chilled and coalesced to remove water and injected through sparge rings to 3–6 agitated reaction zones in a large horizontal reactor/settler vessel.

Recycle iso-butane from the deiso-butanizer and the refrigeration system and recycle acid from the settler are fed to a pre-flash zone and “cascade” from one zone through specially designed weirs from which the process name derives. Typical iso-butene olefin ratios are 8–12 for the process. (Jones 2015)

The first zone in the cascade reactor has the lowest operating temperature and the highest iso-butane concentration and produces the highest octane alkylate. As additional olefin is injected in subsequent zones the temperature increases and iso-butane concentration decreases and successively lower octanes are produced. Because iso-butane and H₂SO₄ are highly immiscible, each zone requires a mixer with high power inputs to produce a tight emulsion. (Jones 2015)

After the final reaction zone the emulsion is allowed to settle. The settler acid phase is pumped back to the lead zone and the hydrocarbon phase effluent is pumped to effluent treating. (Jones 2015)

2.7.1.3 Refrigeration:

The heat of reaction is removed by “auto-refrigeration” at reaction temperatures of 35–65F. While refrigeration is often viewed as costly, in this process it conserves the heat of reaction to distill 4–5 moles of iso-butane recycle per mole of olefin alkylated and concentrates propane. Iso-butane and propane vaporized from the reactor are compressed, and condensed with cooling water and recycled as “refrigerant” to the reactors. A fraction of the refrigerant is charged to the depropanizer to remove propane contained in the feeds from the unit. (Jones 2015)

2.7.1.4 Effluent treating:

The hydrocarbon effluent containing alkylate and excess iso-butane is warmed by chilling recycle iso-butane and feed and treated to remove traces of entrained acid and ester reaction intermediates. Treating systems include washing with fresh acid and aqueous caustic (as shown). Caustic and water washes, bauxite, and KOH pellets have also been used. (Jones 2015)

2.7.1.5 Fractionation:

After effluent treating the balance of reactor iso-butane requirement is distilled from the Alkylate and n-butane deiso-butanizer tower (DIB). Most refiners charge saturated butanes from other units to the DIB for Iso-butene/n-butane splitting. N-butane is distilled from the Alkylate for control of product RVP in a debutanizer, and

in some cases an n-butane vapor draw from the DIB. Finally, in a few units, aviation alkylate is produced by removing heavy ends in a Rerun column.(Jones 2015).

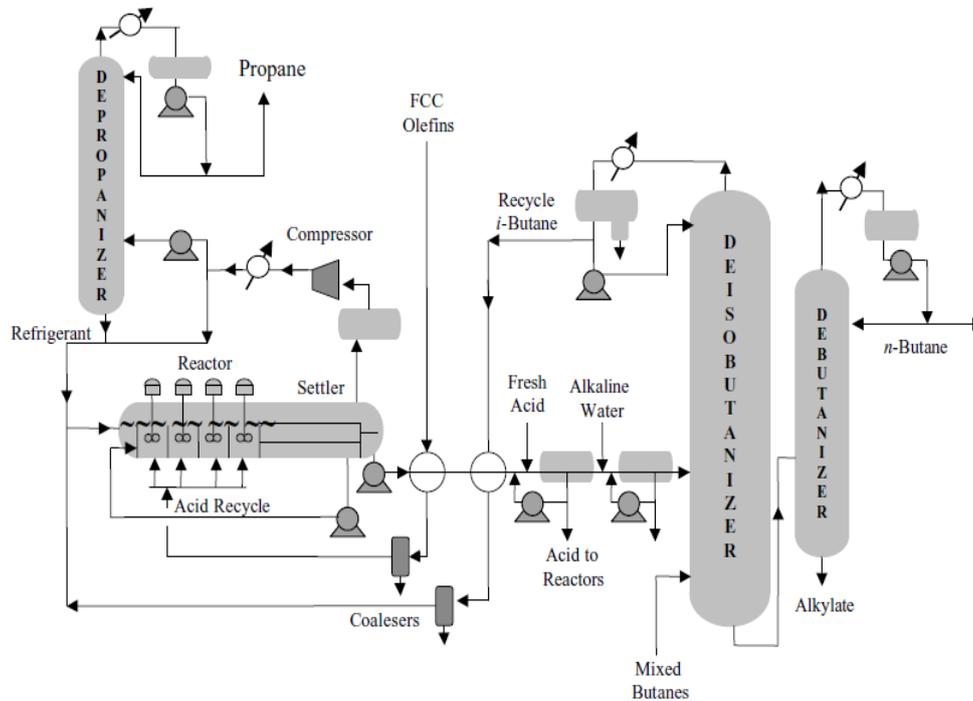


Figure (2. 2) Cascade auto-refrigerated alkylation process:

2.7.2 Stratco effluent refrigerated alkylation process :

In the Stratco process, the principal differences from the Cascade process are in the reactor and refrigeration design and that the reaction is carried out without vaporization.(Jones 2015)

2.7.2.1 Reaction:

Treated feeds and recycle iso-butane are first chilled and coalesced to remove water and charged to several Stratco contactors. Feed and iso-butane from the DIB and refrigeration and recycle acid from the settler are emulsified together by the high power impeller of the Stratco Contactor. After reaction and chilling the emulsion passes to the settler located above the contactors for acid separation. The acid phase is recycled by gravity to the contactor impeller and the hydrocarbon phase (effluent) routed in the tube-side of the contactor heat exchanger.(Jones 2015)

2.7.2.2 Refrigeration:

The heat of reaction is removed by chilling the emulsion in shell side of the contactor heat exchanger by partially vaporizing settler effluent on the tube side. Refrigerant vapor is separated from the effluent liquid in a flash drum, compressed, and condensed. A portion of the condensed refrigerant is routed to a depropanizer. The balance of the refrigeration and depropanizer bottoms are flash cooled and returned to the reactors. (Jones 2015).

2.7.2.3 Effluent treating and fractionation:

These steps are essentially the same as in the Cascade process.

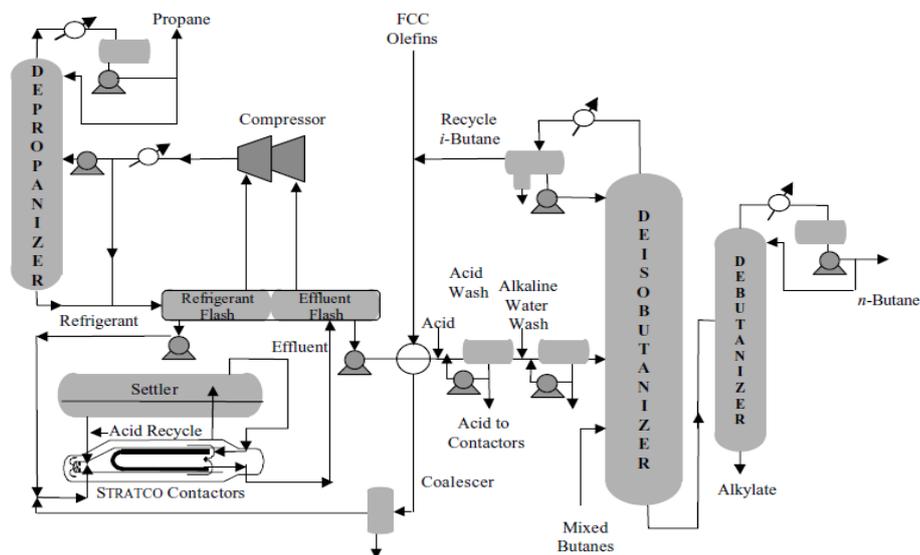


Figure (2. 3) Stratco effluent refrigerated alkylation process:

2.8 Effect of Operating Conditions:

The process conditions that influence the quality of alkylate product and acid consumption rate are the olefin type, dilution ratio d ($iC_4/iC_4=$), mixing temperature, impeller speed, space velocity (or residence time) and acid strength. (Fahim 2010).

2.8.1 Olefin Type:

The presence of propylene or pentene with butane will lower the octane number and increase the acid consumption. The octane number of alkylates produced from light olefins is given Table 2.1.

Butene in sulphuric acid as a catalyst gives the best octane numbers as shown in Table 2.1.

The presence of propylene with butene increases acid consumption and lowers the alkylate octane number. In the case of a (C₃=/iC₅=) feed mixture, the trend is interesting since sulphuric acid consumption decreases up to 82 vol% of the (C₃=/iC₅=) mixture. However, the octane number also decreases. This might suggest that at lower acid consumption, it is better to separate the (C₃=/iC₅=) mixture from C₄= and let it react with iC₄ in a separate reactor (Kranz (1988)).

Table (1.) Effect of type of olefin on alkylate octane number

Types of Olefin	RON		MON	
	HF	H ₂ SO ₄	HF	H ₂ SO ₄
Propylene	91-93	91-92	89-91	90-92
Butene-1	90-91	97-98	88-89	93-94
Butene-2	96-97	97-98	92-93	93-94
Isobutene	94-95	90-91	91-92	88-89
Amylene	90-92	91-92	88-89	89-91

2.8.2 Iso-butane Concentration:

The iC₄/C₄= ratio has an important role regarding the quality of alkylate produced and the amount of sulphuric acid consumption. The following reasons explain the behavior.

- High iso-butene concentration (iC₄) prevents olefin polymerization which results in low quality alkylate and high sulphuric acid consumption.

- Solubility of iC_4 is lower than C_4 . Thus high a concentration of iC_4 is required in the mixed hydrocarbons to compensate for its low solubility.
- The conversion to alkylate (y) increases as (iC_4/C_4) is increased.
- The rate of alkylate formation increases while the rate of formation of undesirable heavy alkylates decreases as iC_4 increases, as will be discussed later.
- As iso-butane increases, alkylate MON increases and sulphuric acid consumption decreases.

For all these reasons, the iC_4/C_4 ratio is kept in industrial operation between 5:1 and 15:1 as the external iso-butane to olefin (I/O) ratio. Inside a reactor with high circulation, this ratio becomes 100–1000:1. (Fahim 2010)

2.8.3 Acid Strength:

An optimum value of acid strength of 90 wt% H_2SO_4 is maintained by adding fresh concentrated acid (98–99 wt%). The spent acid is purged out of the system and usually regenerated outside the refinery. As the strength of the acid decreases, the acid consumption increases with the octane number decreases.

The minimum acid strength required to operate the system should not be lower than 85 wt%. At lower strength, polymerization occurs and a “runaway” condition prevails. To provide a sufficient margin of safety, acid strength is kept around 90 wt%. Although water lowers the acid activity, 1–2 wt% water is added to ionize the acid. The acid strength decreases because of the formation of gums and other products resulting from the reaction with other impurities. Thus, acid make-up has to be added. (Fahim 2010)

2.8.4 Degree of Agitation:

When the hydrocarbons (iC_4 and C_4) are dispersed in sulphuric acid, as shown in Figure, the speed of the impeller determines the dispersed phase size (droplet diameter) and hence, the interfacial contact area. The reaction rate of iC_4 and C_4 is quite fast, and the reaction is controlled by mass transfer. Side reactions cause the formation of heavy alkylates as given by the following equation. (Rase (1977)

$$\frac{R_{iC_8}}{R_{\text{heavy alkylate}}} = \frac{(\text{Const})[iC_4]_h N^{0.75} (1 - H_a)}{(SV)_o}$$

where $[iC_4]_h$ is the concentration of iC_4 in hydrocarbon phase, N is the impeller speed (rpm), H_a is the fractional acid hold-up, $(SV)_o$ is the space olefin velocity (1/h), $R_{\text{Heavy alkylate}}$ is the rate of formation of the undesirable heavy alkylate, and R_{iC_8} is the rate of formation of the target alkylate iC_8 . This equation shows that the quality of alkylate produced can be improved by increasing impeller velocity and iC_4 concentration. The rate ratio on the left side of the equation can be maximized by using a low acid hold-up and low olefin space velocity $(SV)_o$. Since the solubility of iC_4 in the sulphuric acid is lower than that of $C_4=$, the reaction is controlled by the rate of mass transfer and the dissolution rate of the iC_4 in the acid. (Fahim 2010).

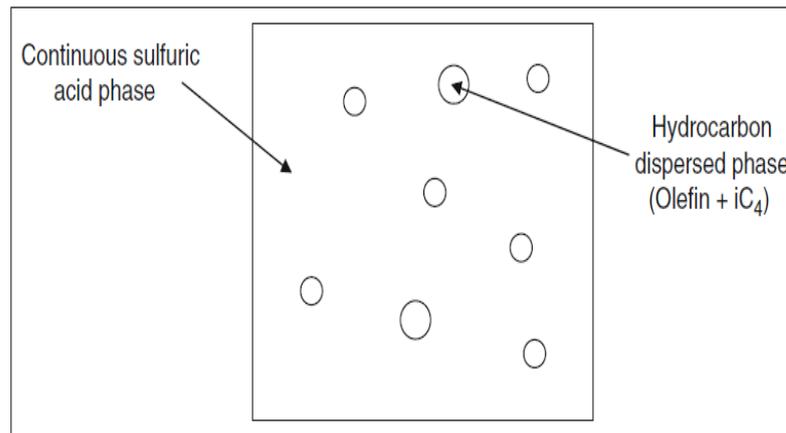


Figure (2. 4) Emulsion of hydrocarbon in sulphuric acid.

2.8.5 Space Velocity:

The olefin space velocity is defined as:

$$(SV)_o = \frac{\text{Olefin volumetric rate (bbl/h)}}{\text{Acid volume in contactor (bbl)}}$$

The residence time in the reactor is $(1/(SV)_o)$ and is defined as the residence time of the fresh feed and externally recycled iso-butane in the reaction mixture. Since the alkylation reaction is very fast, the residence time is not a limiting parameter. However, as the space velocity increases, the octane number tends to decrease while acid consumption tends to increase. Residence time for sulphuric acid is usually from 5 to 40 min, and for hydrofluoric acid, it is 5–25 min. (Fahim 2010)

2.8.6 Reaction Temperature:

The reaction thermodynamics and kinetics are favoured at low temperatures, as shown before. Sulphuric acid alkylation units are operated at 5–10 C (40–50 F). Above 10 C, oxidation and side reactions are promoted, and the deteriorate-alkylate yield and quality while acid consumption increases.(Fahim 2010)

It is impossible to run the reaction below 0 C (32 F) because acid viscosity will be too high and agitation becomes difficult. Above 21 C (70 F), the polymerization of olefin will occur, and the octane number of alkylate decrease, For HF alkylation the reaction temperature is less significant and is between 21 and 38 C (70 and 100 F). (Fahim 2010).

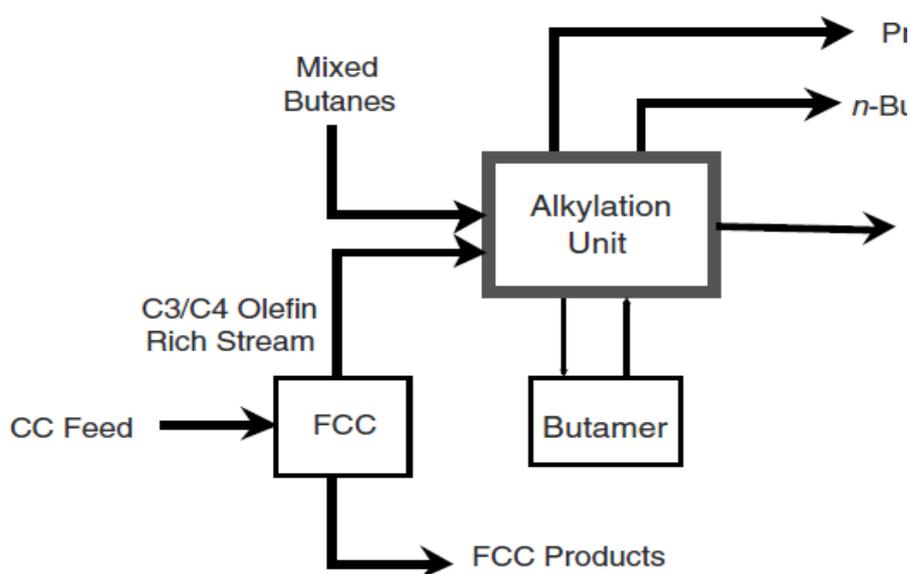


Figure (2. 5) Alkylation unit location in refinery

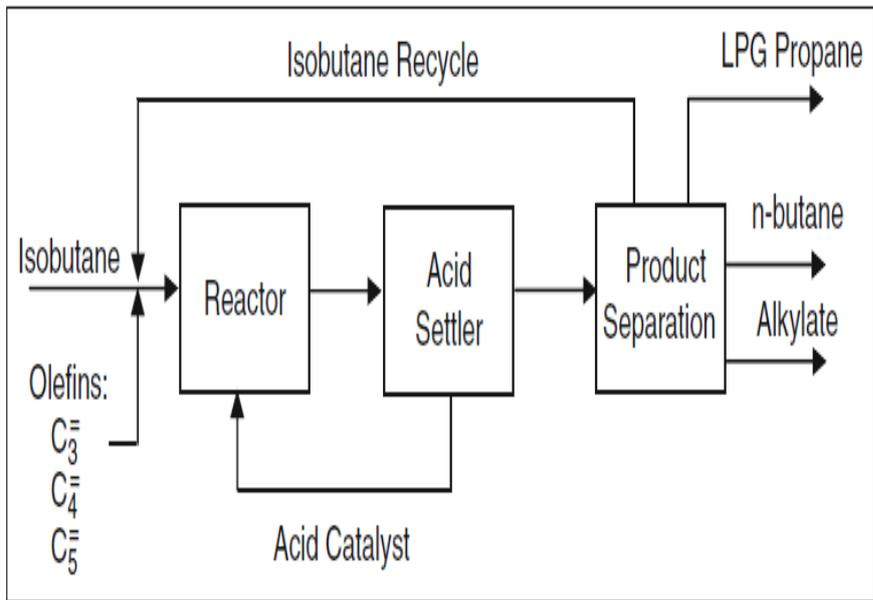


Figure (2. 6) Block diagram of alkylation process

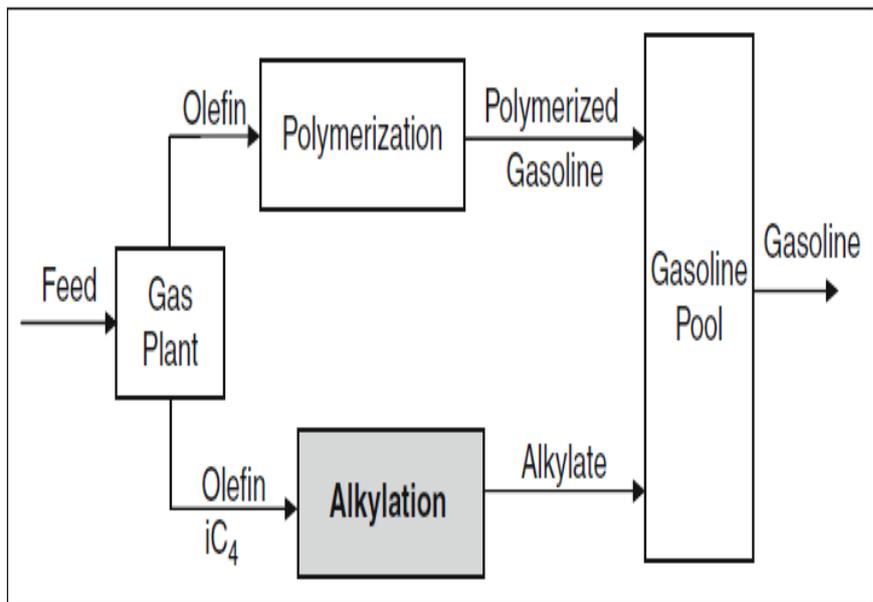
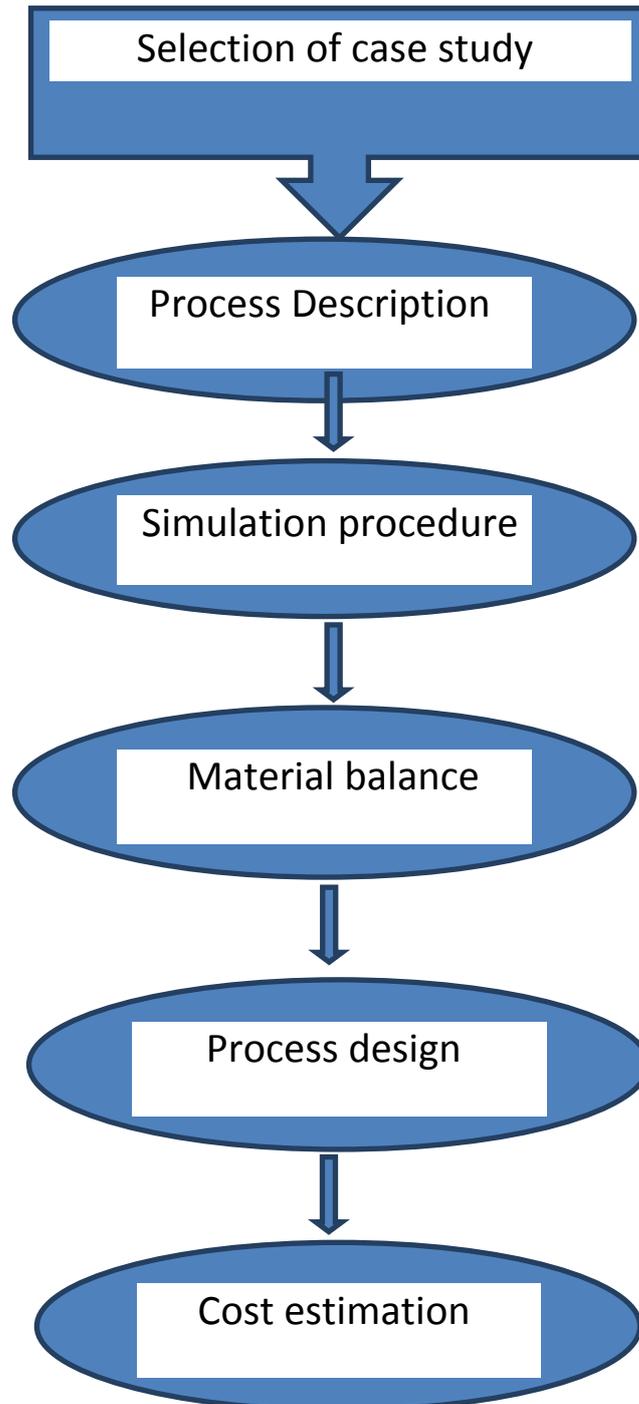


Figure (2. 7) Role of alkylation and polymerization units in the refinery:

Chapter 3 Methodology

In this chapter we will focus on the procedure by which the simulation process will take place and also we will get into the detailed design procedure for add the alkylation unit.



3.1 Selection of case study:

Our case study is to attach an alkylation unit to Khartoum refinery to increase the gasoline yield and to produce gasoline with high octane number.

3.2 Process Description:

A simplified process flow diagram for alkylation unit is shown in figure 3.1 . the olefins and iso-butane that produced from RFCC unit of Khartoum refinery are mixed and feed to H₂SO₄ alkylation reactor, the reactor operates at 15°C and 98 acid strength, the reactor effluent is distilled in distillation column, with alkylate as the bottom product, and light gases as top product.

3.2.1 Hysys process simulator:

Hysys is a process simulation environment designed to serve many processing industries especially oil and gas refining, rigorous steady state and dynamic models for plant design, performance monitoring, troubleshooting, operational improvement business planning and asset management can be created using HYSYS. The built-in property packages in HYSYS provide accurate thermodynamic, physical and transport property predictions for hydrocarbon, nonhydrocarbon, petrochemical and chemical fluids. .

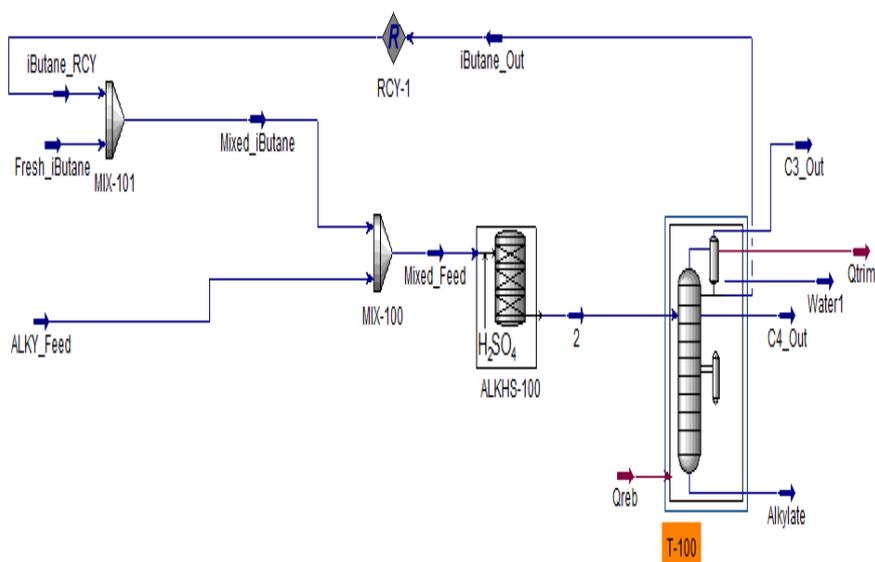
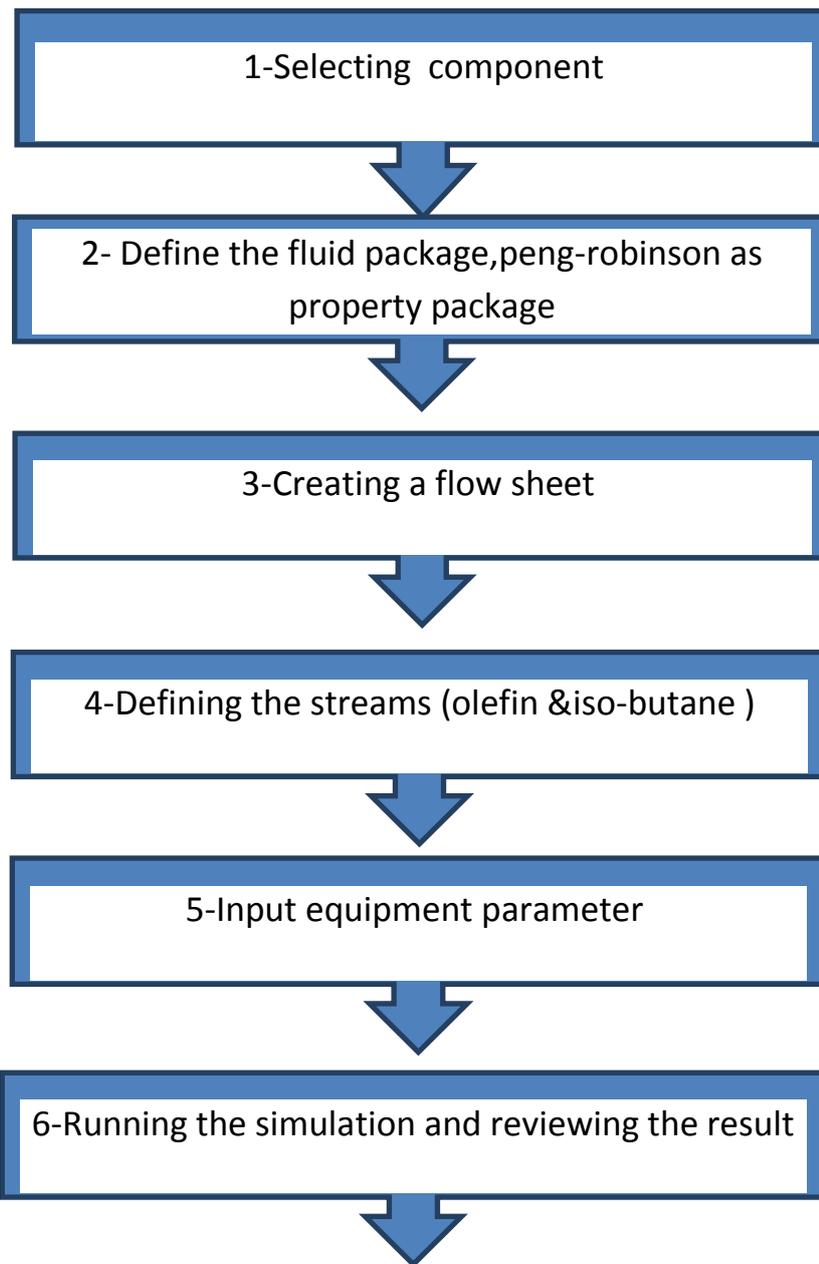
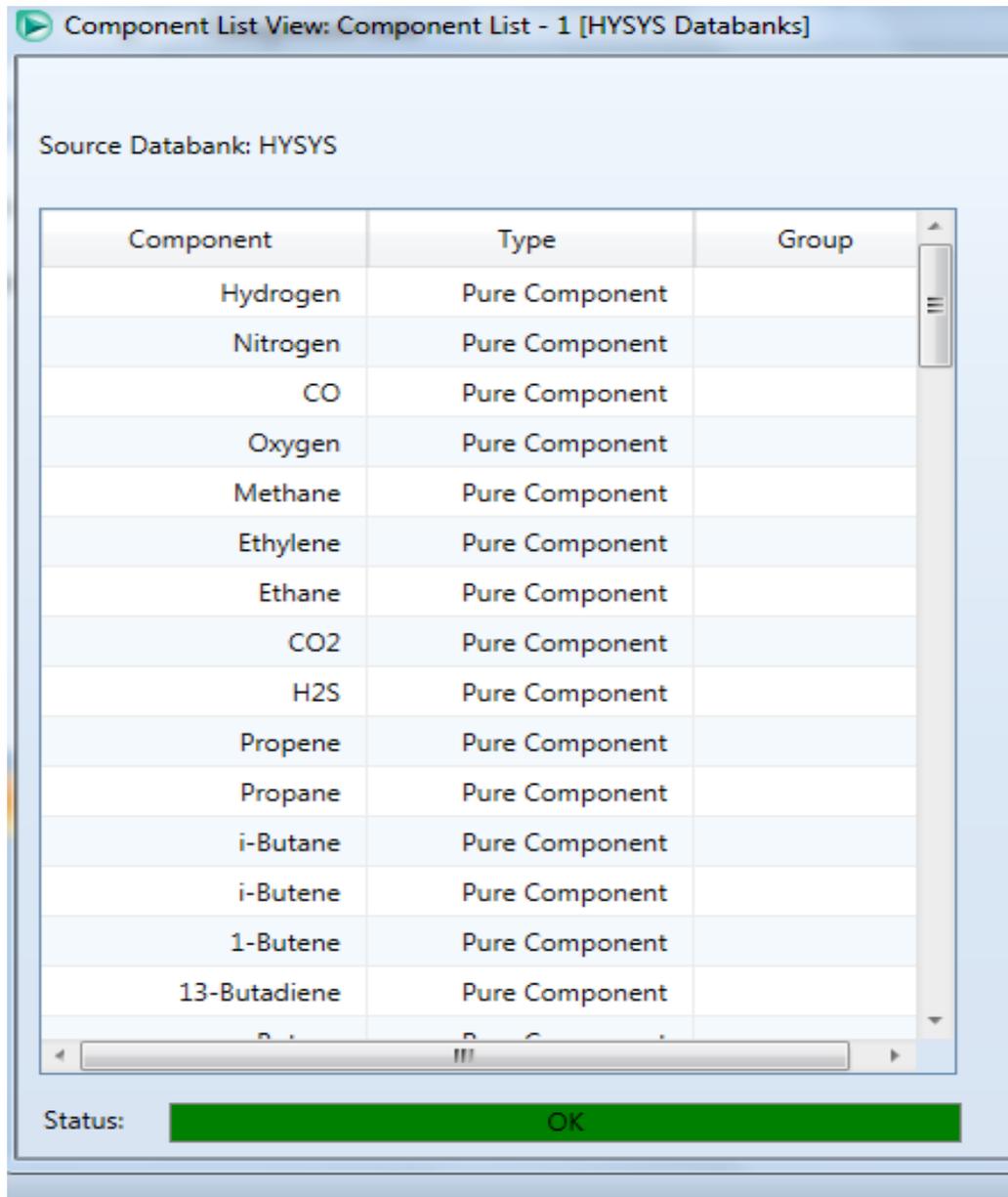


Figure (3.1) Sulfuric acid alkylation flowsheet

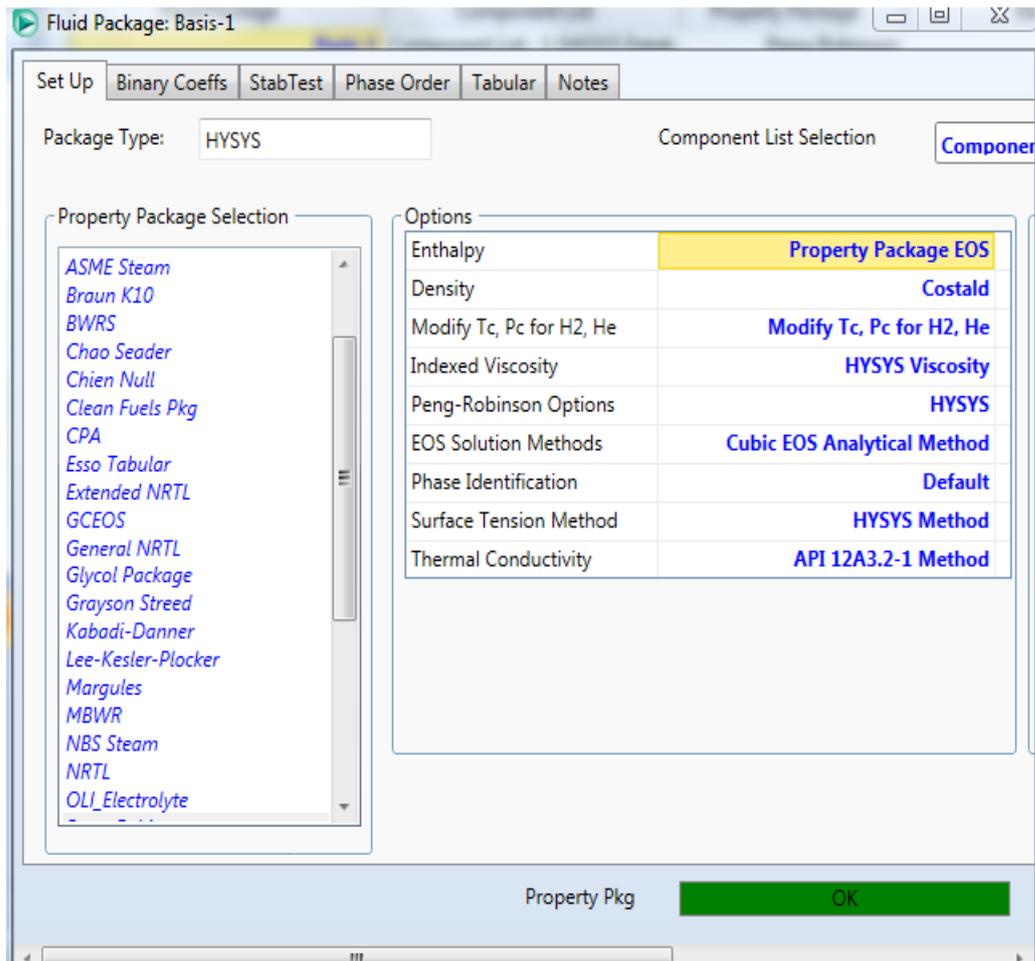


3.2.2 Simulation steps:

First of all we have to select the component



Selecting the fluid package :



Adding the olefin stream condition and composition :

Material Stream: ALKY_Feed

Worksheet Attachments Dynamics

Worksheet	Stream Name	ALKY_Feed	Liquid Phase
Conditions	Vapour / Phase Fraction	0.0000	1.0000
Properties	Temperature [C]	30.00	30.00
Composition	Pressure [kPa]	799.0	799.0
Oil & Gas Feed	Molar Flow [kgmole/h]	2129	2129
Petroleum Assay	Mass Flow [kg/h]	1.194e+005	1.194e+005
K Value	Std Ideal Liq Vol Flow [m3/h]	201.1	201.1
User Variables	Molar Enthalpy [kJ/kgmole]	-2.034e-004	-2.034e-004
Notes	Molar Entropy [kJ/kgmole-C]	21.20	21.20
Cost Parameters	Heat Flow [kJ/h]	-4.329e+007	-4.329e+007
Normalized Yields	Liq Vol Flow @Std Cond [m3/h]	199.7	199.7
	Fluid Package	Basis-1	
	Utility Type		

OK

Delete Define from Stream... View Assay

Material Stream: ALKY_Feed

Worksheet Attachments Dynamics

Worksheet		LiqVol Flows	Liquid Phase
Conditions	Methane	0.0000	0.0000
Properties	Ethylene	0.0000	0.0000
Composition	Ethane	0.0000	0.0000
Oil & Gas Feed	CO2	0.0000	0.0000
Petroleum Assay	H2S	0.0000	0.0000
K Value	Propene	0.0000	0.0000
User Variables	Propane	0.0000	0.0000
Notes	i-Butane	0.0000	0.0000
Cost Parameters	i-Butene	0.0000	0.0000
Normalized Yields	1-Butene	201.1494	201.1494
	1,3-Butadiene	0.0000	0.0000
	n-Butane	0.0000	0.0000
	tr2-Butene	0.0000	0.0000
	cis2-Butene	0.0000	0.0000
	i-Pentane	0.0000	0.0000
	1-Pentene	0.0000	0.0000

Total 201.14940 m3/h

Edit... View Properties... Basis...

OK

Delete Define from Stream... View Assay

Adding the iso-butane:

Material Stream: Fresh_iButane

Worksheet Attachments Dynamics

Worksheet	Stream Name	Fresh_iButane	Liquid Phase
Conditions	Vapour / Phase Fraction	0.0000	1.0000
Properties	Temperature [C]	29.92	29.92
Composition	Pressure [kPa]	1172	1172
Oil & Gas Feed	Molar Flow [kgmole/h]	9724	9724
Petroleum Assay	Mass Flow [kg/h]	5.652e+005	5.652e+005
K Value	Std Ideal Liq Vol Flow [m3/h]	1006	1006
User Variables	Molar Enthalpy [kJ/kgmole]	-1.538e+005	-1.538e+005
Notes	Molar Entropy [kJ/kgmole-C]	86.89	86.89
Cost Parameters	Heat Flow [kJ/h]	-1.495e+009	-1.495e+009
Normalized Yields	Liq Vol Flow @Std Cond [m3/h]	1004	1004
	Fluid Package	Basis-1	
	Utility Type		

OK

Delete Define from Stream... View Assay

Material Stream: Fresh_iButane

Worksheet Attachments Dynamics

Worksheet		LiqVol Flows	Liquid Phase
Conditions	Methane	0.0000	0.0000
Properties	Ethylene	0.0000	0.0000
Composition	Ethane	0.0000	0.0000
Oil & Gas Feed	CO2	0.0000	0.0000
Petroleum Assay	H2S	0.0000	0.0000
K Value	Propene	0.0000	0.0000
User Variables	Propane	0.0000	0.0000
Notes	i-Butane	1005.7470	1005.7470
Cost Parameters	i-Butene	0.0000	0.0000
Normalized Yields	1-Butene	0.0000	0.0000
	13-Butadiene	0.0000	0.0000
	n-Butane	0.0000	0.0000
	tr2-Butene	0.0000	0.0000
	cis2-Butene	0.0000	0.0000
	i-Pentane	0.0000	0.0000
	1-Pentene	0.0000	0.0000

Total 1005.74700 m3/h

Edit... View Properties... Basis...

OK

Delete Define from Stream... View Assay

Now the Feed is ready for reactor :

H2SO4 Alkylation Unit: ALKHS-100

Simulation | Calibration | Worksheet | Solver

Simulation

Name: **ALKHS-100** Fluid Package: **Basis-1**

Feed: **Mixed_Feed**

Reactor Specifications

Volume [m3]	60.00
Temperature [C]	15.00

Effluent: **2**

H2SO4 Acid Feed

Mass Flow [kg/h]	1.171e+006
Std Ideal Liq Vol Flow [m3/h]	650.0
H2SO4 Concentration [wt %]	98.00

Buttons: Delete, OK

Results the reactor :

H2SO4 Alkylation Unit: ALKHS-100

Simulation | Calibration | Worksheet | Solver

Simulation

Yields

Propane [wt %]	3.047e-017
Butane [wt %]	1.003e-003
Isobutane [wt %]	99.28
Alkylate (C5+) [wt %]	0.4844

Alkylate Properties

Std. Liquid Density [kg/m3]	714.4
RON (Clear)	97.53
MON (Clear)	92.11
D86 0% [C]	103.0
D86 5% [C]	103.0
D86 10% [C]	103.0
D86 30% [C]	103.0
D86 50% [C]	103.0
D86 70% [C]	111.1
D86 90% [C]	112.9
D86 95% [C]	113.3
D86 100% [C]	165.5

Buttons: Delete, OK

Alkylateproduct:

Material Stream: Alkylate

Worksheet Attachments Dynamics

Worksheet	Stream Name	Alkylate	Vapour Phase	Liquid Phase
Conditions	Vapour / Phase Fraction	0.0000	0.0000	1.0000
Properties	Temperature [C]	77.79	77.79	77.79
Composition	Pressure [kPa]	101.3	101.3	101.3
Oil & Gas Feed	Molar Flow [kgmole/h]	1960	2.021e-002	1960
Petroleum Assay	Mass Flow [kg/h]	2.075e+005	1.499	2.075e+005
K Value	Std Ideal Liq Vol Flow [m3/h]	293.1	2.400e-003	293.1
User Variables	Molar Enthalpy [kJ/kgmole]	-2.189e+005	-1.464e+005	-2.189e+005
Notes	Molar Entropy [kJ/kgmole-C]	254.2	238.5	254.2
Cost Parameters	Heat Flow [kJ/h]	-4.291e+008	-2959	-4.291e+008
Normalized Yields	Liq Vol Flow @Std Cond [m3/h]	287.5	2.351e-003	287.5
	Fluid Package	Basis-1		
	Utility Type			

OK

Delete Define from Stream... View Assay

Material Stream: Alkylate

Worksheet Attachments Dynamics

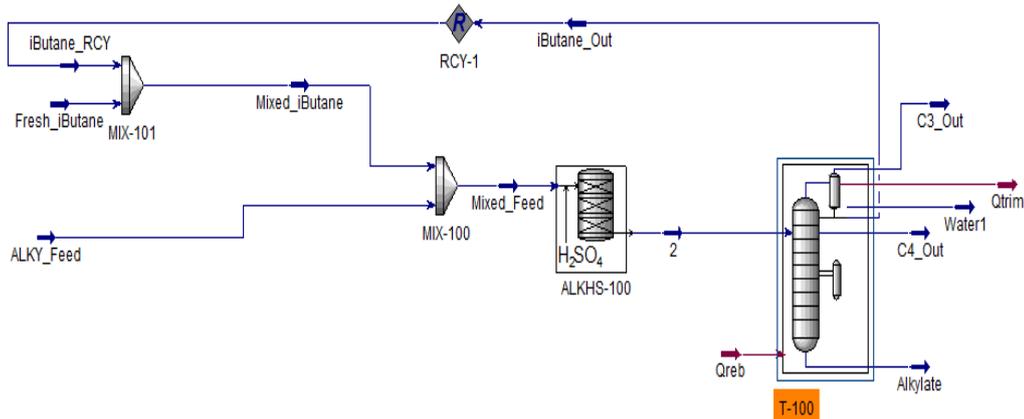
Worksheet		LiqVol Fractions	Vapour Phase	Liquid Phase
Conditions	Ethane	0.0000	0.0000	0.0000
Properties	CO2	0.0000	0.0000	0.0000
Composition	H2S	0.0000	0.0000	0.0000
Oil & Gas Feed	Propene	0.0000	0.0000	0.0000
Petroleum Assay	Propane	0.0000	0.0000	0.0000
K Value	i-Butane	0.0418	0.5779	0.0418
User Variables	i-Butene	0.0000	0.0000	0.0000
Notes	1-Butene	0.0008	0.0101	0.0008
Cost Parameters	13-Butadiene	0.0000	0.0000	0.0000
Normalized Yields	n-Butane	0.0000	0.0004	0.0000
	tr2-Butene	0.0000	0.0000	0.0000
	cis2-Butene	0.0000	0.0000	0.0000
	i-Pentane	0.0000	0.0000	0.0000
	1-Pentane	0.0000	0.0000	0.0000
	n-Pentane	0.0000	0.0000	0.0000
	Mono40*	0.0000	0.0000	0.0000

Total 1.00000

Edit... View Properties... Basis...

OK

Delete Define from Stream... View Assay



3.3 Material Balance :

Detailed material balance is difficult to perform for industrial alkylation processes. A number of side reactions occur, and it is difficult to determine the volume reduction accurately. Alkane hydrocarbons such as C₃, C₄ and C₅, can be produced from the reaction of iso-C₄ with the corresponding olefin.

Alternatively, material balances for the alkylation processes are carried out using empirical factors (Gary and Handwerk, 1994). In Table 3.1 mass factors are given for the consumption of iso-butane with olefins: propylene, butylenes and Citation (Fahim, Al-Sahhaf et al. 2009)

Table (3.) 1 Volume and mass factors for alkylation conversions

	C ₃		C ₄		C ₅	
lb iC ₄ consumed/lb olefin consumed	1.7132		1.1256		1.2025	
bbl iC ₄ consumed/bbl olefin consumed	1.6		1.2		1.4	
Total volume of feed/total volume product	1.234		1.2		1.158	
Product composition %	vol%	wt%	vol%	wt%	vol%	wt%
C ₃	14.15	10.71	–	–	–	–
nC ₄	–	–	6.93	5.83	–	–
nC ₅	3.40	3.14	3.71	3.33	21.80	19.74
Alkylate	75.66	78.34	82.36	83.06	70.23	71.81
Heavy alkylate	5.98	6.70	6.48	7.07	6.95	7.98
Tar	0.811	1.11	0.52	0.71	1.02	1.36

3.3.1 Material Balance equation :

Input = output + consumption

consumption = input – output

Using the empirical factor for 1-butene, listed in Table 3.1 on volume basis:

$$\frac{\text{bbl iso-butane consumed}}{\text{bbl olefin consumed}} = \text{mass factors for alkylation conversions}$$

3.4 Design

3.4.1 Space Velocity:

The olefin space velocity defined as:

$$(SV)_o = \frac{\text{Olefin volumetric rate (bbl/h)}}{\text{Acid volume in contactor (bbl)}}$$

The residence time in the reactor is $\frac{1}{(SV)_o}$ and defined as the residence time of the fresh feed and externally recycled iso-butane in the reaction mixture. Since the alkylation reaction is very fast, the residence time is not a limiting parameter. However, as the space velocity increases, the octane number tends to decrease while acid consumption tends to increase. Residence time for sulphuric acid is usually from 5 to 40 min, and for hydrofluoric acid, it is 5–25 min.

$$\tau = \frac{V_r}{v_o} \text{ OR } (SV)_o = \frac{1}{\tau}$$

$$SV = \frac{v_o}{V_R} V_R = \frac{v_o}{SV}$$

3.5 Cost estimation:

The design engineer, by analyses of costs and profits, attempts to predict whether capital should be invested in a particular project. After the investment is made, records must be maintained to check on the actual financial results. These records are kept and interpreted by accountants. The design engineer, of course, hopes

that the original predictions will agree with the facts reported by the accountant. There is little chance for agreement, however, if both parties donot consider the same cost factors, and comparison of the results is simplified ifthe same terminology is used by the engineer and the accountant.

3.5.1 Types of Capital Cost Estimates:

These estimates are called by a variety of names, but the following five categories represent the accuracy range and designation normally used for design purposes.

Table (3. 1) Type of Capital Cost Estimates

Type of Capital cost	Accuray
Order-of-magnitude estimate (ratio estimate)	over± 30 percent.
Study estimate (factored estimate)	up to ± 30 percent.
Preliminary estimate	Within ± 20 percent.
Definitive estimate (project control estimate)	within ± 10 percent.
Detailed estimate (contractor's estimate)	within ± 5 percent.

3.5.2 COST INDEXES:

Most cost data which are available for immediate use in a preliminary or predesign estimate are based on conditions at some time in the past. Because prices may change considerably with time due to changes in economic conditions, some method must be used for updating cost data applicable at a past date to costs that are representative of conditions at a later time.? This can bedone by the use of cost indexes

$$\text{Present cost} = \text{original cost} \left(\frac{\text{index value at present time}}{\text{index value at time original cost was obtained}} \right)$$

3.5.3Methodpower factor applied to plant – capacity ratio:

This method for study or order-of-magnitude estimates relates the fixed-capital investment of a new process plant to the fixed-capital investment of similar previously

constructed plants by an exponential power ratio. That is, for certain similar process plant configurations, the fixed-capital investment of the new facility is equal to the fixed-capital investment of the constructed facility C multiplied by the ratio R , to a power X multiplied by some factor.

Table (3.) Cost index

Year	Marshall and Swift installed equipment indexes, 1926 = 100		Eng. News-Record construction index			Nelson-Farrar refinery construction index, 1946 = 100	Chemical engineering plant cost index 1957-1959 = 100
	All- industry	Process- industry	1913 = 100	1949 = 100	1967 = 100		
1975	444	452	2412	464	207	576	182
1976	472	479	2401	503	224	616	192
1977	505	514	2576	540	241	653	204
1978	545	552	2776	582	259	701	219
1979	599	607	3003	630	281	757	239
1980	560	675	3237	679	303	823	261
1981	721	745	3535	741	330	904	297
1982	746	774	3825	802	357	977	314
1983	761	786	4066	852	380	1026	317
1984	780	806	4146	869	387	1061	323
1985	790	813	4195	879	392	1074	325
1986	798	817	4295	900	401	1090	318
1987	814	830	4406	924	412	1122	324
1988	852	870	4519	947	422	1165	343
1989	895	914	4606	965	429	1194	355
1990 (Jan.)	904†	924	4673	979	435	1203	356

† All costs presented in this text are based on this value of the Marshall and Swift index unless otherwise indicated.

Cost index and annual average Marshallswift index:

Years	All industry
2016	1611.1
2017	1637.1

3.5.4 Capital cost data for processing plant (1990):

process	Process remark	Typical plant size (bbl/day)	Power factor (X)
Alkylation h2so4	calatyic	10000	0.6

3.5.5 Relative labor rate and productivity indexes in the chemical and allied products industries for the United States (1989) :

Geographical area	Relative labor rate	Relative productivity factor
New England	1.14	0.95
Middle Atlantic	1.06	0.96
South Atlantic	0.84	0.91
Midwest	1.03	1.06
Gulf	0.95	1.22
Southwest	0.88	1.04
Mountain	0.88	0.97
Pacific Coast	1.22	0.89

Chapter 4 Results and Discussions

4.1 Material Balance:

4.1.1 Results:

4.1.1.1 Calculation by hysys:

4.1.1.1.1 Over all material balances:

Table (4.) overall Material balance

Component	Feed (<i>bbbl/day</i>)	Products (<i>bbbl/day</i>)
Butene	301.9104	0
Fresh iso-butane	1518	0
RCY iso-butane	1.377×10^7	1.376×10^7
C3 out	0	2.826
C4 out	0	1.682×10^4
Alkylate	0	2379
Total	13771819.91	13779211.83

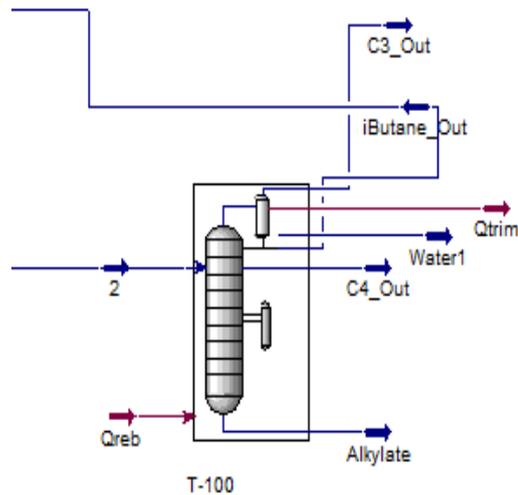
4.1.1.1.2 Material balance around reactor:

Input – output = consumption

Table (4.) Material Balance around the reactor

Comp	Input	Output	Consumption
Iso-butane	1.410300816×10^7 *	1.407787218×10^7 *	25135.98
1-butene	51636.3618	28323.2500	23313.1118

4.1.1.1.3 Material balance around Distillation:



Iso-butane balance:

Iso-butane*stream 2 = iso-butane*alkylate stream + iso-butane*C4out stream +
 iso-butane *C3out stream + iso-butane*i butane stream + iso-butane*water stream

$$0.995*7.095*10^5 = 1960*0.0605 + 1225*0.6872 + 7.063 *10^5*0.9981 +$$

$$0.3748*0.0219 + 0$$

$$705952.5 = 118.58 + 841.82 + 704958.03 + 8.20812*10^{-3} + 0$$

$$705952.5 = 705918.43$$

1-Butene balance:

1-butene*stream 2 = 1-butene*alkylate stream + 1-butene*C4out stream +
 1-butene *C3out stream + 1-butene*ibutane stream + 1-butene*water stream

$$0.0024*7.095*10^5 = 0.0013*1960 + 0.3070*1225 + 0 + 0.0019*7.063*10^5 + 0$$

$$1702.8 = 2.548 + 376.075 + 0 + 1341.97 + 0$$

$$1702.8 = 1720.59$$

4.1.1.2 Calculation by factors:

$$\frac{\text{bbl iso-butane consumed}}{\text{bbl olefin consumed}} = \text{mass factors for alkylation conversion}$$

For 1-butene:

$$\frac{25135.98}{1.2} = 20946.65 (\text{bbl/day})$$

Table4.3 component material balance by factor :

Table (4. 1) component material balance by factor

Feed	BPD
iC4	1.410300816*10 ⁷
C4=	51636.3618
Total	14154644.52
Products	
Remaining C4=	30689.7118
Alkylate	31628.04506
nC4	266127.1883
nC5	142472.1311
Heavy alkylate	248846.202
Tar	19969.13967
Total	739732.4179

4.1.2 Material Balance Discussion:

The amount of (iso-butane and 1-butene) consumed have been calculate by using the input and output of this component from hysys.

This amount were recalculated by using another method (empirical factor) and results were compared between hysys and empirical factor, and we found there is a little different between them.10%

4.2Design:

4.2.1Results:

$$V_R = \frac{v_0}{SV}$$

Where :

V_R =reactor volume

v_0 =olifenvolummitric flow rate

SV = space velocity

Table (4.) VOLUME DESIGN

Residence time (τ) (min)	$S V = \left(\frac{1}{\tau}\right) \frac{1}{hr}$	$v_o \left(\frac{m^3}{hr}\right)$	$V_R (m^3)$
5	12	2	0.166
10	6	2	0.333
20	3	2	0.666
30	2	2	1
40	1.5	2	1.333

We choose 40 min as a residence time there for our reactor volume is $1.333m^3$

$$S V = \frac{60}{40} = 1.5$$

volume reactor =

Table (4.5) Effect of Volume on Alkylate Flow rate & Octane number:

Reactor Volume (m^3)	Alkylate flow rate ($\frac{m^3}{hr}$)	RON	MON
0.1666	15.43	97.53	92.11
0.333	15.48	97.53	92.11
0.666	15.57	97.53	92.11
1	15.66	97.53	92.11
1.333	15.76	97.53	92.11

4.2.2 Design Discussion:

The volume of alkylation unit was calculated using the residence time or space velocity and we found the volume of reactor increasing as the residence time increased and decreasing with increasing of space velocity

4.3 Cost estimation results:

Correlation plant:

The capacity of similar constructed plant in Gulf country is 10,000 (bbl/day), and its estimated cost is \$35 million.

The capacity of new plant from simulation result :

$$\text{Capacity} = 15.76 (\text{m}^3/\text{hr})$$

$$= 2379 \text{ bbl/day}$$

$$R = \left(\frac{\text{Capacity of new plant}}{\text{capacity of constructed plant}} \right)^X$$

$$R = \left(\frac{2379}{10000} \right)^{0.6} = 0.422$$

(FE) from marshallswift index

$$FE = \left(\frac{1637.9}{1611.1} \right)$$

$$C_n = C \cdot FE(R)^X$$

$$C_n = 35 * \left(\frac{1637.9}{1611.1} \right) \left(\frac{2379}{10000} \right)^{0.6}$$

$$C_n = 15 \text{ \$ million}$$

Chapter 5 Conclusion and Recommendation

5.1 Conclusions:

In this project we've studied the effect of adding the alkylation unit to the Khartoum refinery company and we've found the product of alkylate yield from this unit is economical. We've also studied a correlation by (fundamentals of petroleum refinery) to predict the amount of iso-butane and 1-butene consumed during reaction and we've found some variation in comparison with the real operation data and simulation results.

5.2 Recommendations:

For further study of alkylation unit we suggest to use the hydrofluoric acid as a catalyst to the unit and show the difference between it and sulfuric acid.

Also in this study we used the 1-butene as olefin to react with iso-butane to get the alkylate, so for further study it can be replaced with other olefin such as propene or iso-butene and show the difference.

Finally we recommend to add an alkylation unit to Khartoum refinery company in order to obtain a high gasoline yield with high octane number.

5.3 References:

- Amico et al. (2006). "Amico, V. D., Gieseeman, J., Brockhoven, E., Rooijen, E., and Nousiainen, H. (2006).
- TheFahim, M. A. (2010). "Fundamentals of petroleum refining Includes index."
- Fahim, M. A., et al. (2009). Fundamentals of petroleum refining, Elsevier.
- Jones, D. S. J. (2015). "Introduction to Crude Oil and Petroleum Processing.
- Kranz, K., and Graves ((1988)). "Olefin interaction in sulfuric acid catalyzed alkylation.215th National Meeting, American Chemical Society (Division of Petroleum Chemistry),Dallas, TX."
- Rase, H. F. ((1977).). "'Chemical Reactor Design for Process Plants,' vol. 1.Wiley-Interscience,New York."