Increasing octane number through minor modifications in an existing PENEX-DIH unit, A case study

A. F. Nassar, A. Safwat, R. S. Ettouney, and M.A. El-Rifai

Chemical Engineering Department, Faculty of Engineering, Cairo University, Giza, Egypt

Abstract

The purpose of this study is to suggest some minor design modifications into an existing unit in a refinery with a view to maximizing the octane number of the gasoline product. The function of the studied UOP PENEX-DIH unit at MIDOR refinery is to process hydro-treated light Naphtha to improve the gasoline quality by converting low octane paraffins into higher octane iso-paraffins. The process involves two distillation columns; a stabilizer and a de-isohexanizer. HYSYS software was used to simulate the selected unit. The search for the conditions corresponding to maximum octane number of the product stream is done by considering the effect of changing five operating variables. These are the operating pressures of the stabilizer and the de-isohexanizer, their feed plate positions and the cut plate position of the side stream in the de-isohexanizer. These changes are associated with changes of the reflux ratio inside the de-isohexanizer. It was found that the octane number of the design case can be improved by moving the feed plate position 7 plates toward the bottom of the column and moving the cut plate position 8 plates toward the top of the de-isohexanizer. By comparing the different processes used to separate normal and iso-paraffins, the de-isohexanizer was found to match the purpose of the existing PENEX- DIH unit.

1. Introduction

Gasoline is probably among the most important refinery products owing to the fact that it is readily and widely used by the general public. Among the most important parameters in the manufacture of gasoline is its resistance to knocking which limits the power that can be developed by the engine/fuel combination.

Octane numbers are a measure of a gasoline's resistance to knock in the cylinder of a gasoline engine. The higher this resistance the higher the efficiency of the fuel to produce work. A relationship exists between the antiknock characteristic of the gasoline (Octane number) and the compression ratio of the engine in which it is to be used. The higher the octane number of the fuel, the higher the compression ratio of the engine in which it can be used. By definition, an Octane number is that percentage of isooctane in a blend of isooctane and normal heptanes that exactly matches the knock behavior of the gasoline. Thus, a 90 Octane gasoline matches the knock characteristic of a blend containing 90% isooctane and 10% n-heptane [1, 2].

The processing of the gasoline fraction to obtain a high quality product is usually undertaken through the use of a set of fractionation columns. To design a distillation column for the fractionation of a certain multi-component mixture, the number of independent variables that need to be defined is first determined. This is followed by plate to plate calculation. In this work, both numerical and graphical methods have been first used and the results compared with those obtained from a simulation program for the studied distillation system.

Manual calculations were undertaken by using the Lewis and Matheson method, the Lewis and Cope method, and the Relative Volatility method. All are based on the assumption of constant heat of vaporization leading to equi-molar overflow on all the plates.

A number of simulation programs are available for steady state calculation of fractionation systems. The software which are mostly used include Aspen Plus, VMG and Pro II and Aspen HYSYS Version 3.1 [3, 4, 5, 6].

This version provides the framework suitable for supporting steady state process design, asset planning and utilization, and real time optimization. This allows further leverage for investment modeling to asses real business benefits.

The studied unit is the PENEX- DIH unit at MIDOR refinery which includes two distillation columns: a stabilizer and a de-isohexanizer. The purpose of this work is to introduce some minor design modifications into this unit with a view to maximizing the octane number of the gasoline product.

2. Process Description

Hydrotreated light Naphtha is processed in the UOP PENEX-DIH unit outlined in Figure (1). In this unit low octane paraffins are converted into higher octane iso-paraffins through a reversible reaction. Due to the change in structure, gasoline quality will be improved since branched paraffins resist self ignition more than straight paraffins.

To prevent catalyst deactivation, the gasoline is first desulfurized in a sulfur guard bed, it then flows to the feed driers to remove any mist before entering the surge drum. Sulfur causes temporary poisoning while the presence of water reduces the life expectancy of the reactor catalyst (permanent poison) [7].

The makeup hydrogen flows to gas driers, similar to those on the gasoline feedstock. Liquid feed from the charge surge drum is first mixed with makeup hydrogen and before entering the reactors, the combined feed is heated first by heat exchange against reactor effluent and then by a steam charge heater.

Although not essential to the success of the process, the PENEX-DIH system will normally employ two reactors in a series flow configuration with the total required catalyst being equally distributed between the two vessels. Valves and piping are provided which permit reversal of the processing positions of the two vessels and the isolation of either for partial catalyst replacement [8].

Chlorinated-alumina based catalysts are the most active and supply the highest isomerizate yield and isomerizate octane number. It should be noted that during isomerization catalysts loose chlorine, consequently the activity is reduced. That is why chlorine compound injection to the feed (usually CCl_4) is provided for keeping high activity. This necessitates caustic soda washing from organic chloride in special scrubbers. A drawback of this type of catalyst is its high sensitivity to poisonous impurities such as the oxygen compounds including water, and sulfur. This requires feedstock pretreatment and drying. Additional problems occur during regeneration [9, 10, 11].

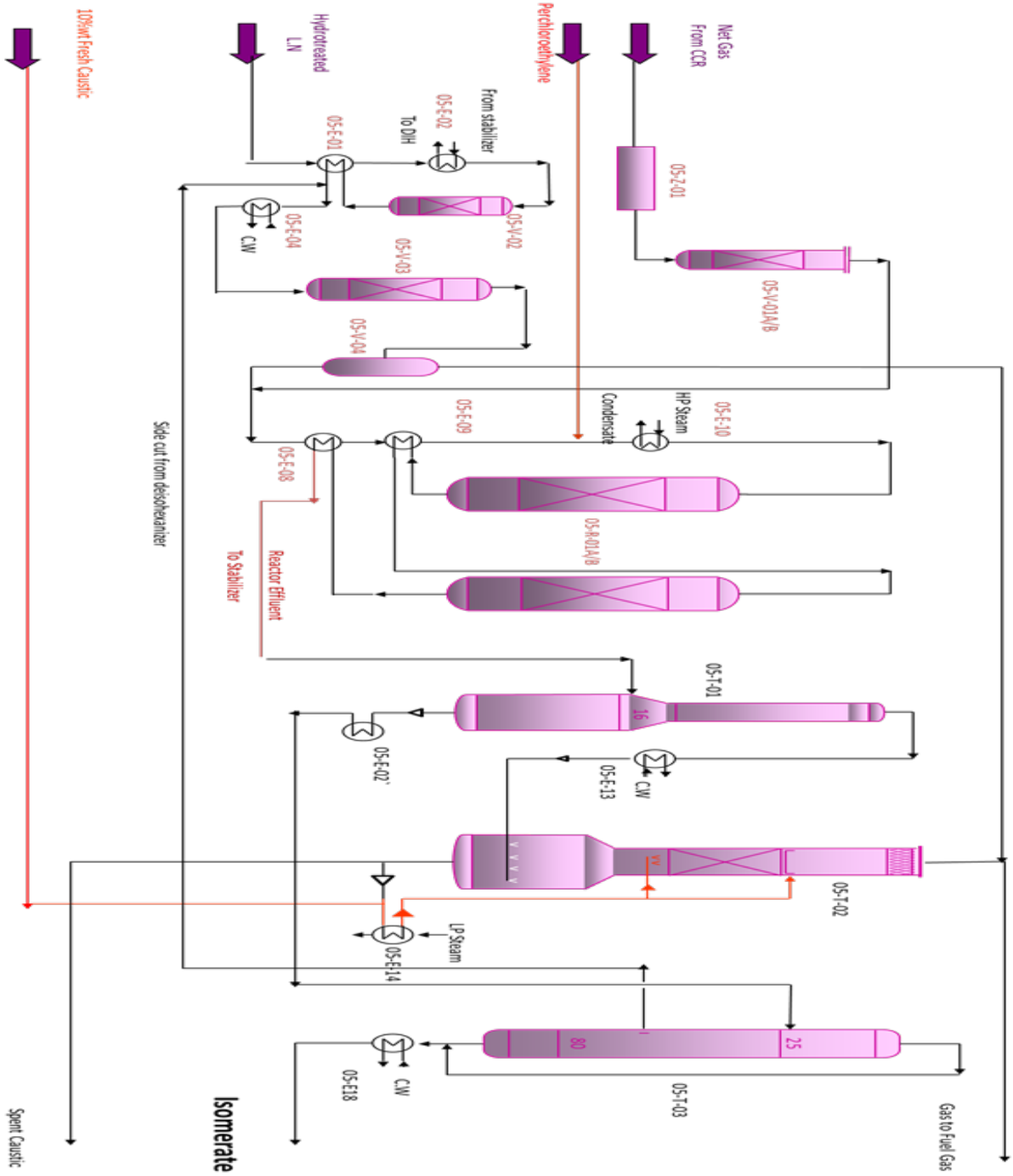

Figure (1) Outline of the flow scheme

The stabilizer off gas product containing HCl, Hydrogen and light hydrocarbons, such as byproduct methane, ethane, propane and butane gases, flows to the Caustic Scrubber Column. This off-gas is scrubbed with a caustic solution to treat the hydrogen chloride before flowing to the fuel gas system. The caustic solution is circulated by a pump at the bottom of the Caustic Scrubber Column. The stabilized, isomerized, liquid product from the bottom of the Stabilizer Column passes to the de-isohexanizer column (DIH) [12].

In the de-isohexanizer column a split is made between the higher octane dimethylbutanes and the lower octane methylpentanes. The dimethylbutanes and lower boiling components are then taken overhead from the column and separated from the methylpentanes and normal hexane, which are recycled as a side-cut to the reactors. The small bottoms drag stream, contains C7 and cyclic components to be withdrawn from the system, which is of lower octane than the product and would normally be sent either to a catalytic reformer or can be included with the product [13, 14, 15, 16, 17, 18].

The minor modifications targeted by this study envisage the investigation of the effect of changing the position of the feed plates to both columns, operating pressures in both columns, and the position of the hexane/methyl pentane side stream withdrawal from the de-isohexanizer to be recycled back to the isomerization reactor.

3. Simulation Results

3.1. Stream Compositions

The design of the stabilizer and the de-isohexanizer of the PENEX-DIH unit at MIDOR refinery have been performed on the HYSYS simulation software. The composition of the feed stream to the stabilizer was taken from the design case data [19] and is given in the first column of Table (1). The composition of stabilizer and de-isohexanizer product streams obtained from the simulation results are also given in Table (1).

Table (1) Process stream composition from HYSYS results

	Feed to Stabilizer	Top of Stabilizer	Bottom of Stabilizer	Top of DIH	Bottom of DIH	Cut	Isomerate
H_2	75.39	75.39	6.71856E-09	6.7186E-09	3.2776E-29	4.7364E-28	6.719E-09
Methane	9.14	9.14	6.23285E-07	6.2328E-07	3.2861E-29	4.7487E-28	6.233E-07
Ethane	7.65	7.65	0.000203085	0.00020309	3.2737E-29	4.7307E-28	0.0002031
Propane	21.03	20.98	0.05	0.04982039	3.2831E-29	6.7096E-27	0.0498204
I-Butane	19.06	17.93	1.13	1.13	6.8879E-24	1.1059E-18	1.13
N-Butane	5.42	4.55	0.87	0.87	4.1235E-21	2.1806E-16	0.87
i-Pentane	111.19	6.76	104.43	104.43	1.0228E-10	2.5078E-07	104.43
N-Pentane	47.09	0.87	46.22	46.22	7.3765E-09	8.1008E-06	46.22
Cyclopentane	8.90	0.0272218	8.88	8.88	2.1123E-06	0.00059008	8.88
22-Methylbutane	173.73	0.1852218	173.55	172.96	0.00377871	0.59	172.96
23-Methylbutane	67.02	0.0176784	67.00	50.70	0.20	16.10	50.90
2-Methylpentane	230.03	0.0460805	229.98	113.47	1.65	114.86	115.12
3-methylpentane	132.35	0.0150211	132.33	19.21	2.41	110.72	21.62
N-Hexane	114.96	0.0051096	114.96	1.73	4.49	108.73	6.22
Methylcyclopentane	63.52	0.0019138	63.52	0.41	3.80	59.31	4.21
Cyclohexane	62.44	0.0005344	62.44	0.03	8.43	53.98	8.46
Benzene	0.00687999	2.337E-07	0.006879756	3.8116E-05	0.00047805	0.0063635865	0.0005162
2-MHexane	3.87	2.864E-06	3.87	1.0646E-05	1.25	2.61	1.25
N-Heptane	3.13	5.737E-07	3.13	4.4349E-07	1.66	1.47	1.66
Methylcyclohexane	14.84	2.306E-06	14.84	2.1638E-06	8.92	5.92	8.92
Total (kgmole/h)	1170.76	143.57	1027.19	520.08	32.82	474.30	552.90

The flow rates of each component in the product stream (isomerate stream) corresponding to the design case and those obtained from the simulation results are compared in Table (2). This confirms the validity of studying these two columns using HYSYS results. Figure (2) also presents the comparison.

Table (2) Comparison between the isomerate design composition and the simulation results

Components	Isomerate (design)	Isomerate (HYSYS)
H_2	0	0
Methane	0	0
Ethane	0	2.03E-04
Propane	0	0.05
I-Butane	0.72	1.13
N-Butane	0.73	0.87
i-Pentane	115.79	104.43
N-Pentane	42.09	46.22
Cyclopentane	6.92	8.88
22-Methylbutane	171.3	172.96
23-Methylbutane	42.85	50.9
2-Methylpentane	108.1	115.12
3-methylpentane	34.46	21.62
N-Hexane	6.27	6.22
Methylcyclopentane	3.56	4.21
Cyclohexane	9.56	8.46
Benzene	0	0
2-MHexane	1.72	1.25
N-Heptane	0	1.66
Methylcyclohexane	9.53	8.92
Total (kgmole/h)	**553.6**	**552.8986896**

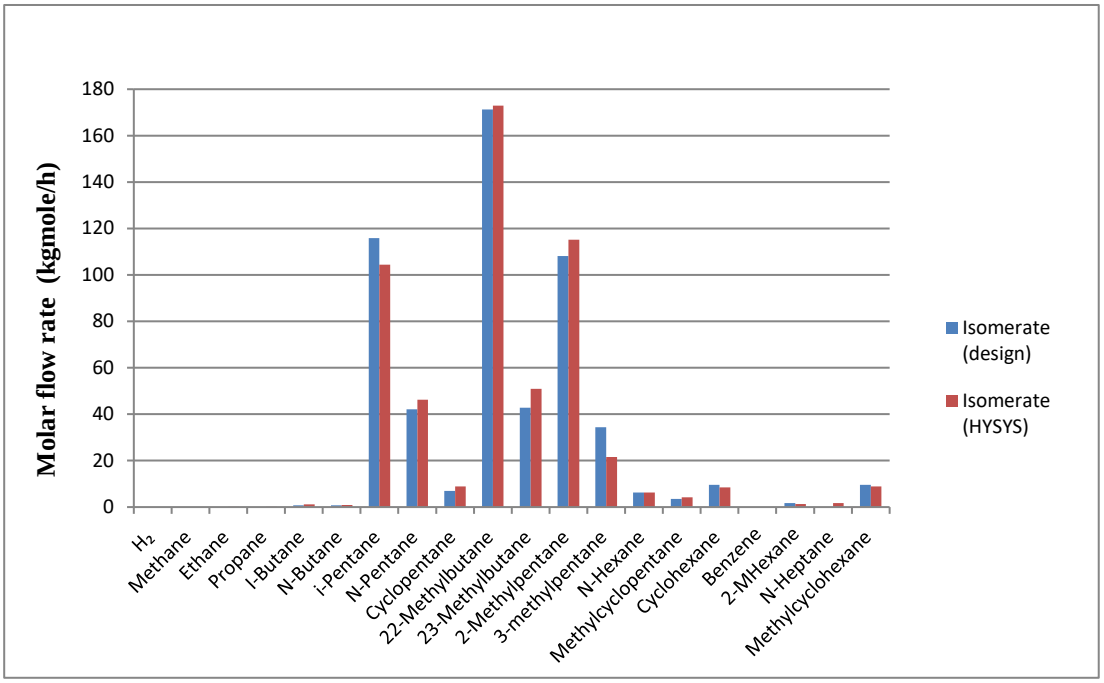

Figure (2) Flow rates of the different components in the isomerate stream

It is seen that the results given by HYSYS have almost the same flow rates of the design case. This justifies study of the composition profile inside both the stabilizer and the de-isohexanizer using the simulation model.

3.2. Calculation of the Octane Number

MIDOR's laboratory provided values of the constants that are relevant to the calculation of the product stream octane number. These constants are listed in Table (3) for each component present in the PENEX-DIH unit.

Table (3) Constants measured by MIDOR's laboratory for the calculation of the octane number

Constants	Sp. Gr. (60F/60F)	RVP (psi)	Molecular Weight	Octane (RON)	Octane (MON)	Averge octane number
Isobutane	0.5631	71.90	58.120	100.2	97.6	98.9
N-Butane	0.5844	51.50	58.120	95.0	93.5	94.25
IsoPentane	0.6248	18.93	72.146	93.5	89.5	91.5
N-Pentane	0.6312	14.42	72.146	61.7	61.3	61.5
CycloPentane	0.7505	9.18	70.130	102.3	85.0	93.65
2-2 DMB	0.6540	9.13	86.172	94.0	95.5	94.75
2-3-DMB	0.6664	6.85	86.172	105.0	104.3	104.65
2 Methyl Pentane	0.6579	6.27	86.172	74.4	74.9	74.65
3 Methyl Pentane	0.6690	5.56	86.172	75.5	76.0	75.75
N Hexane	0.6640	4.59	86.172	31.0	30.0	30.5
Methyl Cyclopentane	0.7535	4.17	84.156	96.0	85.0	90.5
Cyclohexane	0.7834	3.02	84.156	84.0	77.2	80.6
Benzene	0.8846	2.98	78.108	120.0	114.8	117.4

C7+ (Product)	0.6830	2.10	100.198	82.0	71.0	76.5

In order to calculate the average octane number for any stream, the research octane number and the motor octane number have been calculated by multiplying the constants by the volume percentages of each component then calculating their averages to get the total average octane number. Figure (3) shows a comparison between the octane number values corresponding to both the design case composition and the HYSYS model calculated compositions. This provides a further check on the flow rates and compositions computed by the simulation program.

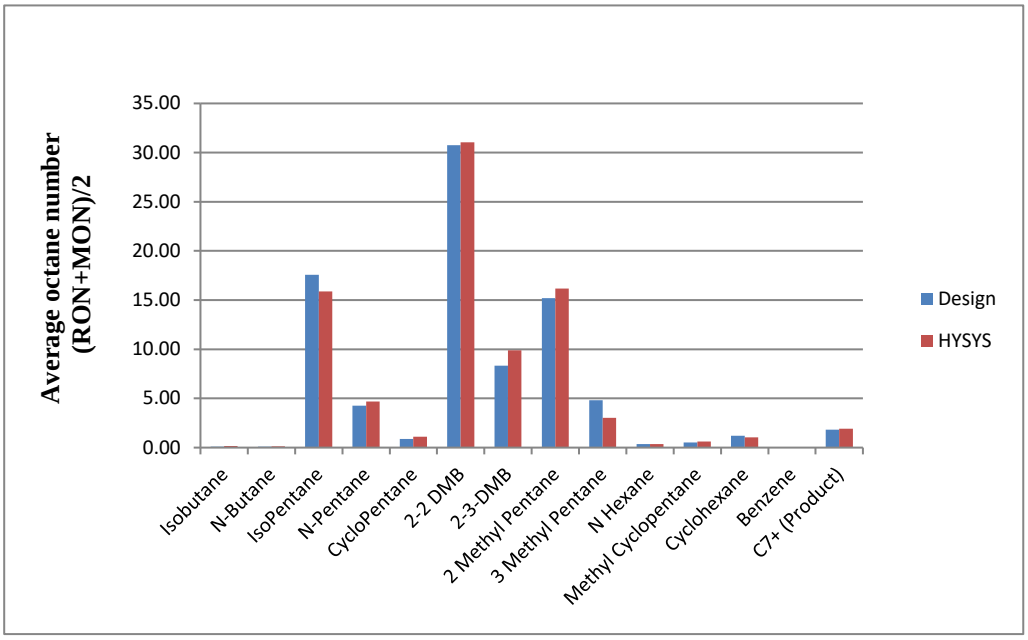

Figure (3) Octane number of components present in the isomerate stream

3.3. Composition Profiles

In the actual application, the fractionation column operates with approximately 50% efficiency. This has been considered with the column operating with half the actual plates number, so the stabilizer on HYSYS operates with 15 theoretical plates (30 actual plates), and the de-isohexanizer operates with 40 theoretical plates (80 actual plates). The composition of each component on the de-isohexanizer plates has been calculated in the simulation and presented in Figure (4).

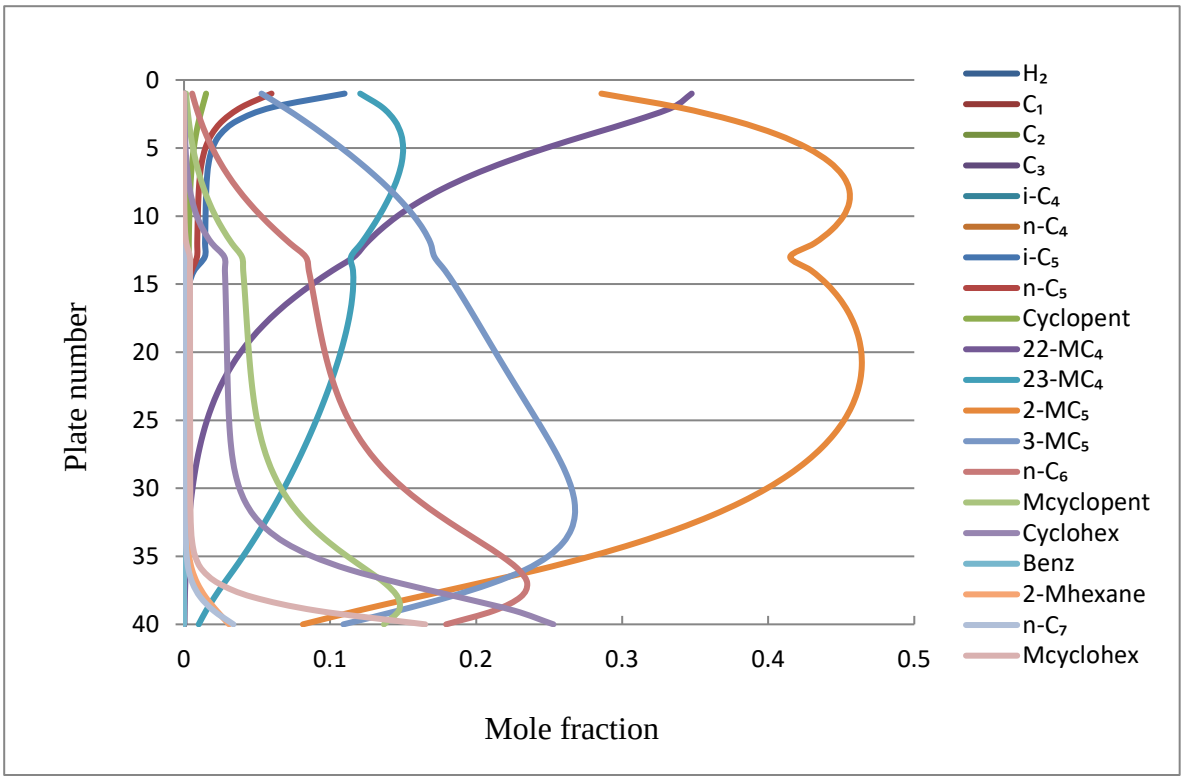

Figure (4) Plate composition in the de-isohexanizer

The composition profiles are characterized by a sharp discontinuity at the 13th theoretical plate which is the feed plate. The side cut is withdrawn from plate 36. In order to give a better view of the composition variation of the light components, their composition profiles have been drawn separately in Figure (5).

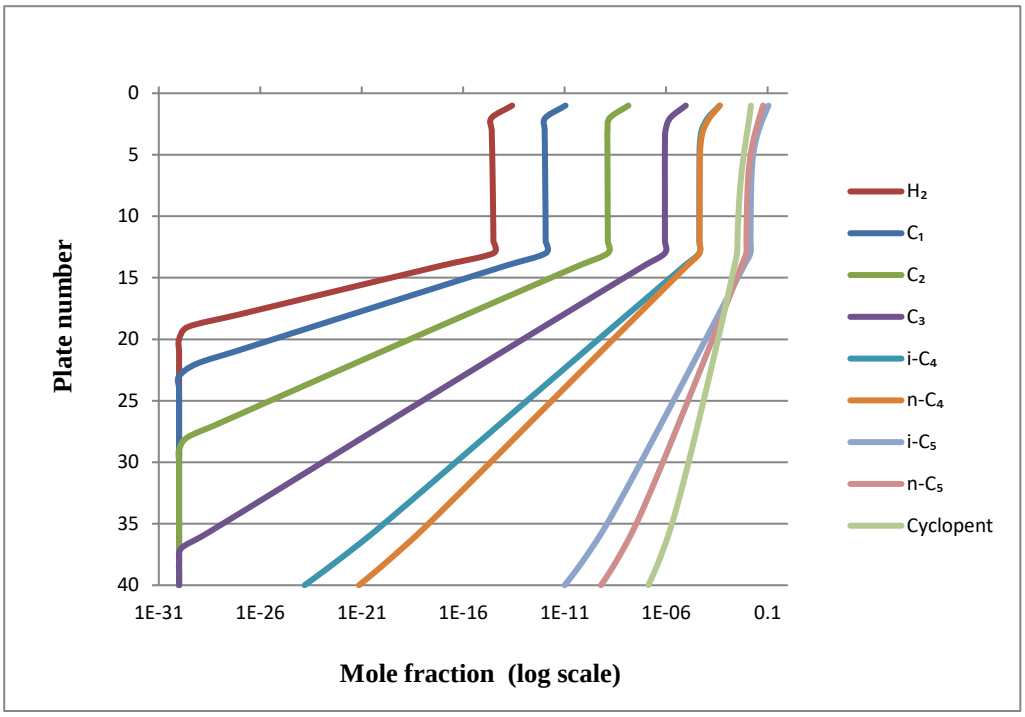

Figure (5) Light components composition profiles

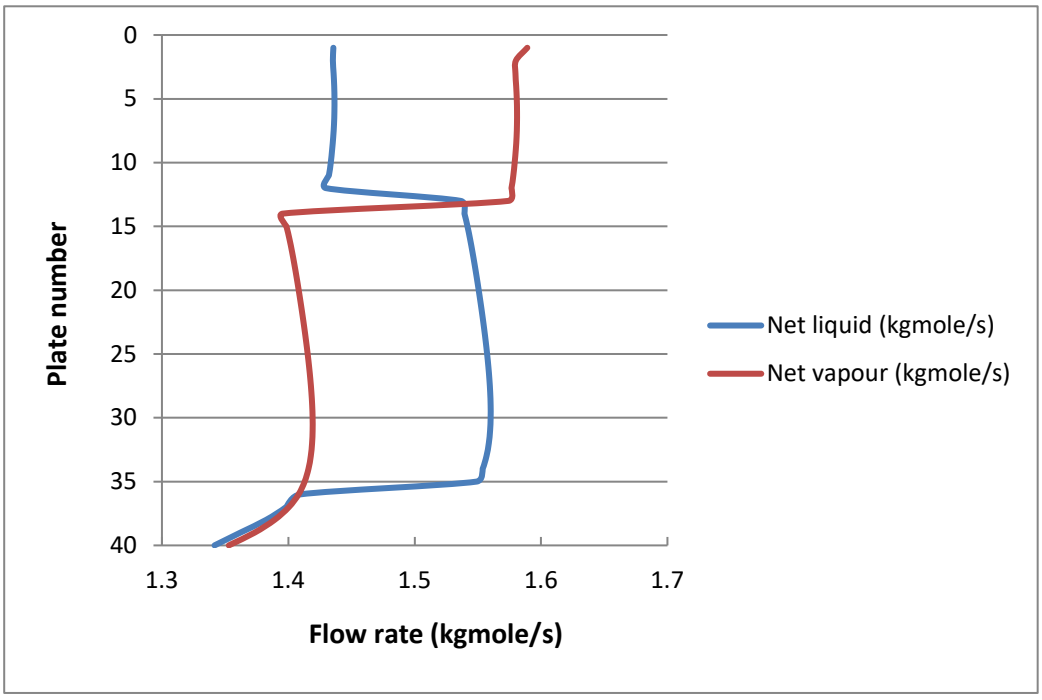

Figure (6) Liquid and vapour flow rates on each plate in deisohexanizer

As seen from Figure (6) the vapor flow rate rising from the reboiler starts with a low value in the bottom of the column, then it increases from plate 40 to plate 35. It then becomes almost constant from plate 35 to plate 13 (feed plate) where it increases

suddenly with the entrance of the feed which flashes on this plate. Above the feed plate the flow rate of the vapor remains constant till it reaches the condenser. The liquid flow rate is constant in the top plates (and less than the flow rate of the vapor). It then increases on the feed plate, remains constant till the 35th plate where the cut stream is withdrawn.

3.4. Manual Calculation

The simulation programs widely serve chemical engineers as they enable to perform tedious calculations with inherently large number of equations and thermodynamic data much faster compared to manual calculations. In the studied work, the theory behind the results provided by these programs is the plate to plate calculation procedures described previously. In order to ensure confidence in the generated simulation results it was found appropriate to test the results using manual calculations before undertaking the parametric study by repeated application of the software.

As previously mentioned, the fractionation and mass transfer calculations inside the different distillation columns can be performed using several methods including graphical or plate to plate calculations. In this work plate to plate calculations were carried out using the relative volatility method since this method is characterized by the ease of determining the plate composition, and there is no need for pressure estimation or trial and error calculations [20].

The plate to plate calculations gives good results and a good estimation of the fractionation happening inside the deisohexanizer, since the number of the theoretical plates calculated is 43 while that of the HYSYS model is 40 theoretical plates (using the plate efficiency calculated by the O'Connell correlation) as shown in table (4).

Table (4) Comparison between the deisohexanizer used in the simulation and that of the plate to plate calculations

	Calculation	**HYSYS**
Total number of plates	43	40
Feed plate	15	13
Cut plate	40	36

The feed plate position in the calculation (which is the plate that has the same vapor/liquid composition of the feed) is plate number 15 while that of the design case was plate 13, and finally the cut plate position in the calculation was found to be pate number 40 instead of 36.

4. Optimization

4.1. Range of Variation of the Operating Variables in a parametric study

In order to get the best octane number of the product stream, a parametric study has been conducted in which five variables have been changed. These variables are the operating pressures of the stabilizer and the de-isohexanizer, their feed plate positions and the cut plate position of the side stream in the de-isohexanizer. The permutation of this system of variables corresponds to a total of 243 runs. The ranges within which the variables are changed are given in Table (5).

Table (5) Range of variables considered in estimating the octane number

Stabilizer operating pressure (bar-g)	**Feed plate position in stabilizer (theoretical)**	**Deisohexanizer operating pressure (bar-g)**	**Feed plate position in Deisohexanizer (theoretical)**	**Cut plate position in Deisohexanizer (theoretical)**
14.38	7	1.5	12	35
15.38	8	1.59	13	36
16.38	9	1.7	14	37

The octane number of the product stream in each run has been calculated and compared to the other runs to determine the effect of changing each variable on the quality of the gasoline product.

4.2. Effect of de-isohexanizer and Stabilizer Pressures

Changing the operating pressure of either or both the stabilizer and de-isohexanizer does not affect the octane number.

4.3. Effect of Stabilizer and de-isohexanizer Feed Plate

Changing the feed plate of the stabilizer doesn't change the octane number. Figure (7) on the other hand, shows the variation of the octane number of the isomerate versus the feed plate and the cut plate positions in the de-isohexanizer. This trend has been persistent on variation of the other variables but the different runs resulted in a slight variation in the product streams composition. This indicates that these two variables have the more pronounced effect on the octane number. Figure (7) also indicates that taking plate 14 as the feed plate to the de-isohexanizer gives a higher octane number compared to plates 12 or 13.

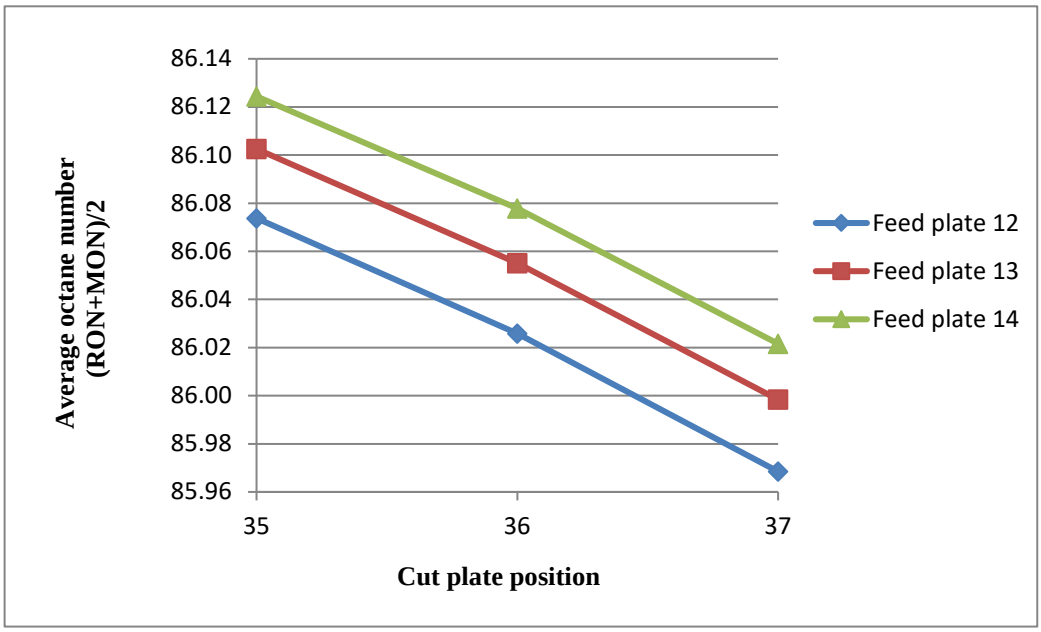

Figure (7) Effect of changing de-isohexanizer cut and feed plate positions on the octane number

4.4. Effect of Cut Plate Position

It is clear from Figure (7) that the octane number decreases when the cut plate position moves toward the bottom of the column. Plate 35 gives higher octane number than plates 36 and 37.

4.5. Optimum Feed Plate and Cut Plate Positions

The previous results suggested to zoom in on plates 14 and 35 respectively as feed and cut plate positions in the de-isohexanizer. The results also indicated that the variation of the studied variables had only a slight effect on stream compositions and octane number.

Ninety (90) runs have been carried out in order to localize the combination corresponding to the maximum octane number of the isomerate. The results shown

in Figure (8) indicate that the maximum octane number of 86.21 occurs when the feed is at plate 16 and the side cut withdrawn from plate 31 of the de-isohexanizer.

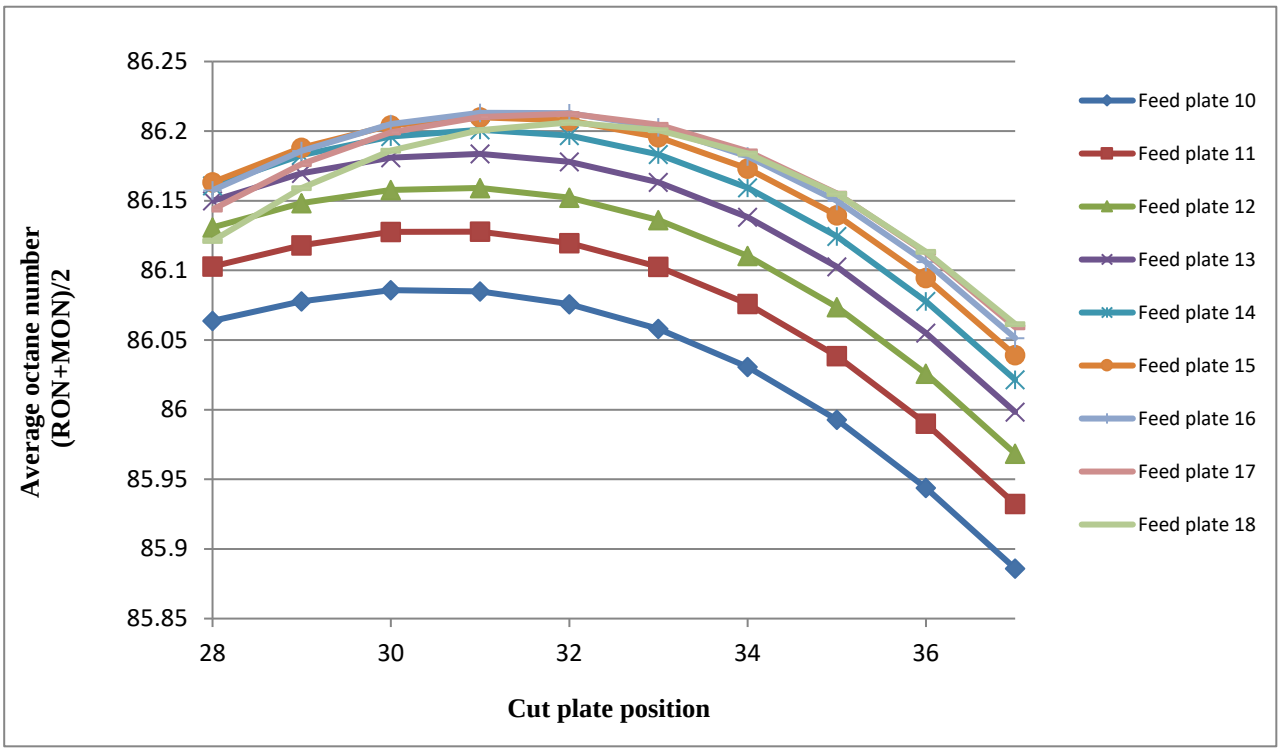

Figure (8) Variation of the octane number with feed plate and cut plate positions

4.6. Value Added

In order to determine the value added for the change in the octane number from **86.05** to **86.2132,** an economic evaluation has been done using the data provided by U.S. Energy Information Administration website, which gives the U.S. Total Gasoline Retail Sales by Refiners (Dollars per Gallon) of the different gasoline grades which are given in Table (6).

Table (6) U.S. Total Gasoline Retail Sales by Refiners (Dollars per Gallon) in 2012 for the different grades of gasoline [21]

Type of Gasoline	Octane Number	U.S. Total Gasoline Retail Sales by Refiners (Dollars per Gallon) in 2012
Regular Gasoline	87	3.118

Midgrade Gasoline	**89**	**3.29**
Premium Gasoline	**91**	**3.4**

To have a rough estimation of the value added by this change in the octane number, a graph depicted in Figure (9) was used to get the retail sales by refiners (Dollars per Gallon) of every slight change in the octane number of the gasoline final product.

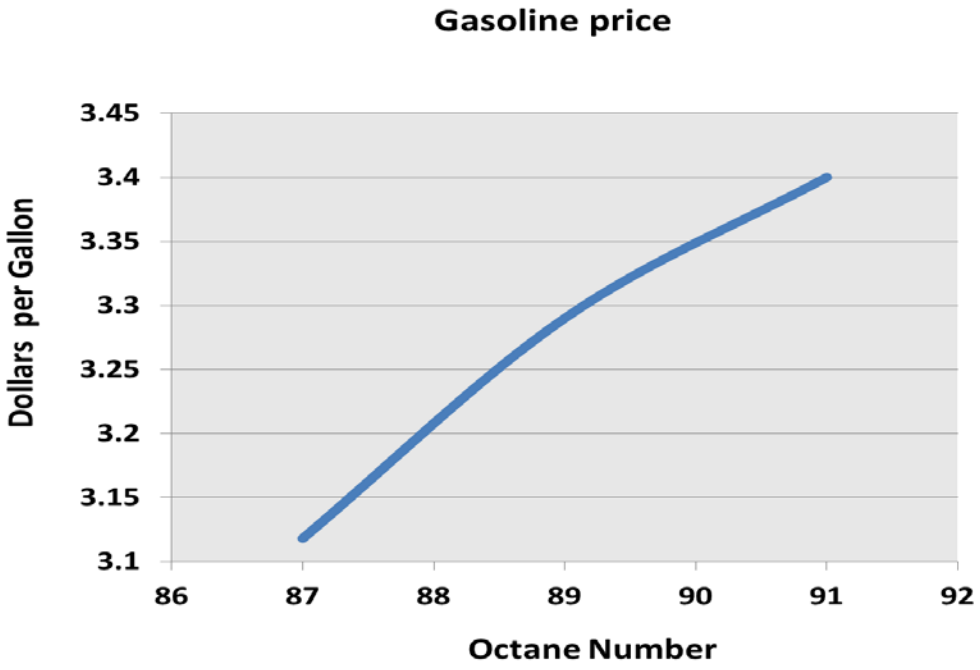

Figure (9) An estimation of the retail sales by refiners (Dollars per Gallon) of the different gasoline grades

It is seen from Figure (9) that the retail sales price by refiners (Dollars per Gallon) of the gasoline obtained from the design case with an octane number of 86.05 is equal to **3.385** and that produced from the optimum case is **3.405.** Table (7) calculate the value added to from this change in the octane number.

Table (7) Value added by the optimization

	Octane Number	**U.S. Total Gasoline Retail Sales by Refiners (Dollars per Gallon) in 2012**

Design	**86.05**	**3.385**
Optimum	**86.213**	**3.405**
Difference	**0.163**	**0.020**
Flow rate (kgmole/h)		**552.899**
Volume (USGPG)		**18362**
Profit (USD/year)		**3.3 Million USD/Year**

It may be concluded that the PENEX-DIH unit operating with an actual feed plate 32 and cut plate 62 gives a product with a better quality (octane number) than that produced when the feed plate is plate number 25, and cut plate 70.

4.7. Effect of Reflux Ratio

All the above reported trials were done at a reflux ratio of 10. This ratio has been changed both for the design case and the optimum case. The octane number is affected by this ratio as shown in Figure (10). It is seen that on increasing the reflux ratio, higher octane numbers are achievable both for the design base case and for the case of optimum positioning of the feed and cut plates.

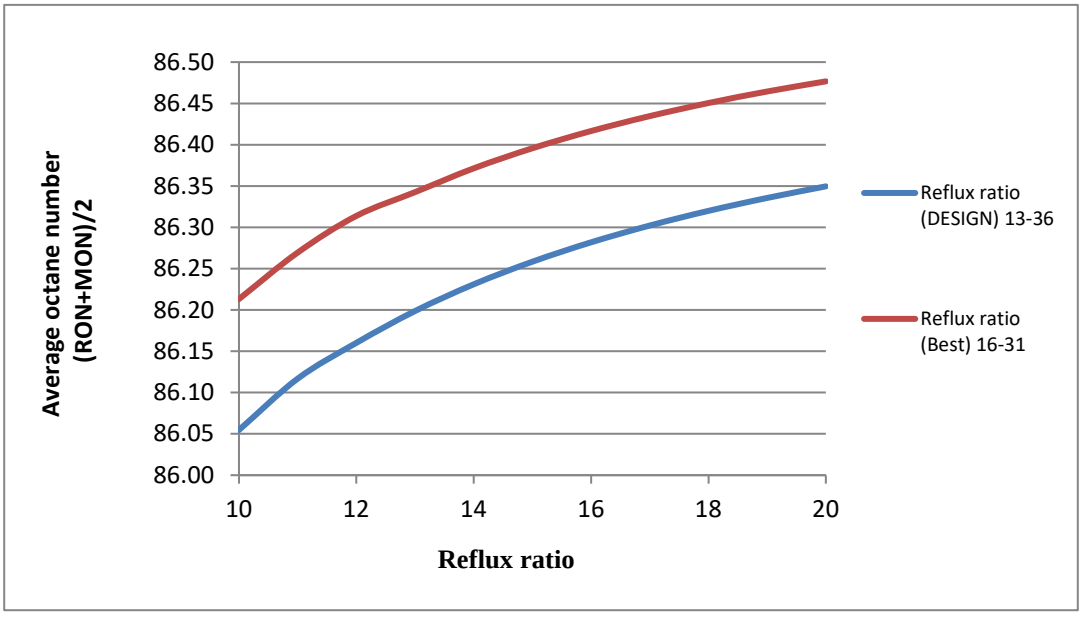

Figure (10) Octane number versus de-isohexanizer reflux ratio

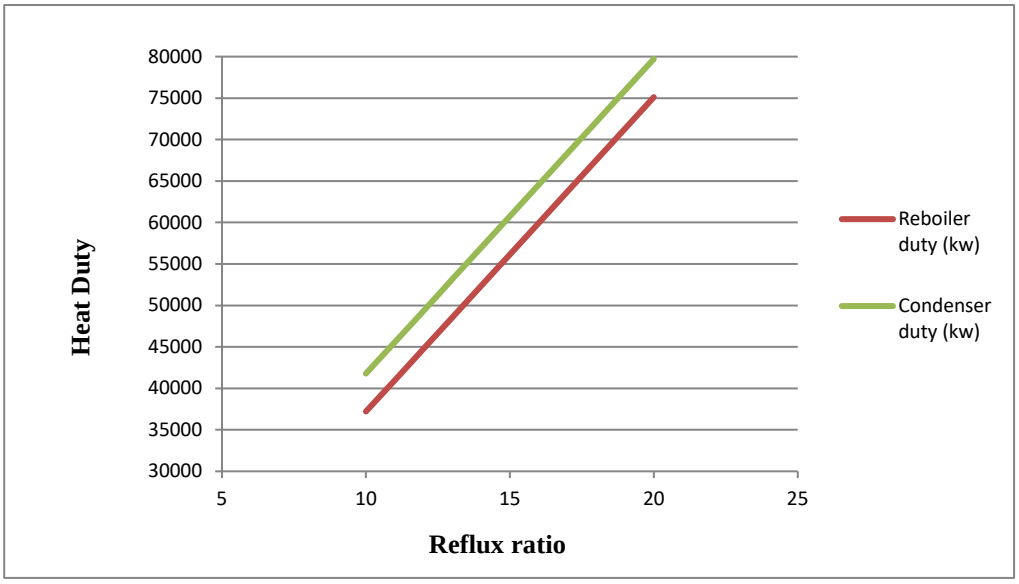

Figure (11) Reflux ratio of Opt. case versus Duties

It is also seen that an octane number of 86.48 may be obtained in the latter case. This is however associated with an increase in both the condenser and reboiler heat duties as shown in Figure (11).

5. Suitability of PENEX- DIH Unit to MIDOR

The PENEX-DIH unit at MIDOR Refinery aims at producing iso-paraffins from normal Pentane and normal Hexane. The iso-paraffins are separated from the normal paraffins by fractionation in the de-isohexanizer. Normal hexane and the methylpentanes are separated and recycled to the reactor.

Although the de-isohexanizer scheme is simple in concept and it increases the C6 isomer content, it does not alter the structure of the C5 components. Thus the unconverted normal pentane, 61 RON, are present in the de-isohexanizer distillate and thus appear in the final isomerate product [17].

5.1. The MOLEX Unit

The Molex process is used along with PENEX process to recycle normal C5/C6 back to the PENEX reactor to improve the octane number. In the PENEX-MOLEX combined process, the C5/C6 hydrocarbons are isomerized on a chlorinated alumina catalyst followed by adsorption on a liquid phase molecular sieve of the normal paraffin from the bottom of the stabilizer [9].

The hydrocarbon fraction of the reactor effluent stream is circulated through a zeolitic molecular sieve adsorbent bed where the normal hydrocarbons are selectively adsorbed while the branched ones are not retained and are carried along the adsorber effluent as an isomerate product. The normal paraffins are then desorbed from the bed and recycled back to be introduced to the reactor with the fresh feed [8, 23, 25].

Table (8) shows the flow rates of the different components of the two streams; the bottom product of the stabilizer (feed to de-isohexanizer or MOLEX process) and the isomerate from the de-isohexanizer of the studied case.

It is seen from Table (8) that normal pentane was not separated from the isomerate product and that its quantity is very small when compared to those of the 2-methyl pentane and the 3-methyl pentanes that were almost separated using the de-isohexanizer, which cannot be done using the MOLEX process, that is why fractionation is preferable for our case.

5.2. The De-isopentanizer

An important modification that can be done to a PENEX unit is to put a de-isopentanizer (DIP) upstream of the reactor. The DIP is used to separate the iso-pentane from the feed then mix it with the product. Since the isomerization reaction is equilibrium limited, the separation of iso-pentane from the feed enables to obtain more conversion of normal pentane into iso-pentane. This column is effective when there is a significant amount of iso-pentane in the feed [24, 25].

Table (8) Flow rate of the feed and product to the De-isohexanizer

Components	Bottom of Stabilizer	Isomerate from DIH	Avg ON
H_2	0.00	0.00	
Methane	0.00	0.00	
Ethane	2.03E-04	2.03E-04	
Propane	0.05	0.05	
I-Butane	1.13	1.13	98.9
N-Butane	0.87	0.87	94.25
I-Pentane	104.43	104.43	91.5
N-Pentane	46.22	46.22	61.5
Cyclopentane	8.88	8.88	93.65
22-Methylbutane	173.55	172.96	94.75
23-Methylbutane	67.00	50.90	104.65
2-Methylpentane	229.98	115.12	74.65
3-methylpentane	132.33	21.62	75.75
N-Hexane	114.96	6.22	30.5
Methylcyclopentane	63.52	4.21	90.5
Cyclohexane	62.44	8.46	80.6
Benzene	0.01	0.00	117.4
2-MHexane	3.87	1.25	76.5
N-Heptane	3.13	1.66	76.5
Methylcyclohexane	14.84	8.92	76.5
Total (kgmole/h)	1027.194723	552.8986896	-------

Conclusion

The presented study is aiming to perform a minor modification to an existing PENEX-DIH unit in order to increase the gasoline quality.
This was done by simulating the fractionation part in this unit, which consists of two distillation towers, a stabilizer and a de-isohexanizer, and the consistency of the simulation results was confirmed by comparing them with the design data.

A parametric study was done to determine the effect of five parameters on the octane number of the final product, however, this study showed that only two variables had affected on the quality of the gasoline product, these variables are the feed plate and the cut plate positions inside the de-isohexanizer, giving a slight change in the octane number with taking plate 32 as a feed plate instead of plate 25, and plate 64 as the cut plate instead of plate 70. The added value arising from the increased octane number through this simple modification of the position of the feed and cut plates is estimated (based on international prices) at about U.S. $ 3.3 million per year.

The reflux ratio change has been also affected the quality of the product but this change is accompanied with a tremendous amount of heat duties needed in the reboiler and the condenser of the de-isohexanizer.
Finally, after studying the alternative schemes to the PENEX-DIH, it has been found that this unit is the optimum choice for MIDOR refinery.

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