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FULL LENGTH ARTICLE

Improving gasoline quality produced from MIDOR light naphtha isomerization unit

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Isomerization unit;
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De-hexanize;
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Abstract Isomerization process became one of the best gasoline production sources, as it gives a high octane product while saving environment from pollution impacts. This paper presents a practical study that aims to improve the gasoline quality and economic income of an existing light naphtha isomerization unit used for octane improvement. The study included selecting the optimum combination of isomerization unit equipment that gives better product specifications for a specified feed. Eight scenarios were studied and simulated to predict the product specs. The original studied unit is MIDOR light naphtha isomerization unit at Alexandria-Egypt that recycles the unconverted hexane (C6). The other studied scenarios were adding fractionators for separating feed iso-pentanes, and recycling unconverted pentanes, hexanes and/or combinations of these fractionators. The results show a change in octane number of gasoline product for a specific feed. Once through process with no extra fractionators has lower octane number of 81 while that with de-iso-pentanizer–de-pentanizer and de-hexanizer produces gasoline with 92.3 octane number. Detailed economic study was done to calculate the return on investment "ROI" for each process option based on equipment, utilities, feed and product prices. Once through simple isomerization unit had the lowest ROI of 14.3% per year while the combination of De-iso-pentanizer with the De-hexanizer had the best ROI of 26.6% per year.

1. Introduction

Isomerization unit is a petroleum refining process that improves the octane number of gasoline, by converting the strait chains of paraffin molecules to the branched form of iso-paraffin. Previously catalytic reforming was the main octane number improving process that produces gasoline with high content of aromatic compounds, and catalytic reforming product has a bad effect on environment as it increases CO_2 emissions and causes cancer compared with isomerization product [1,2].

Chuzlov et al. [3] presented a mathematical model for optimizing the process including catalytic isomerization unit and separation columns. Chekantsev et al. [4] provided a new mathematical model of light alkanes isomerization process.

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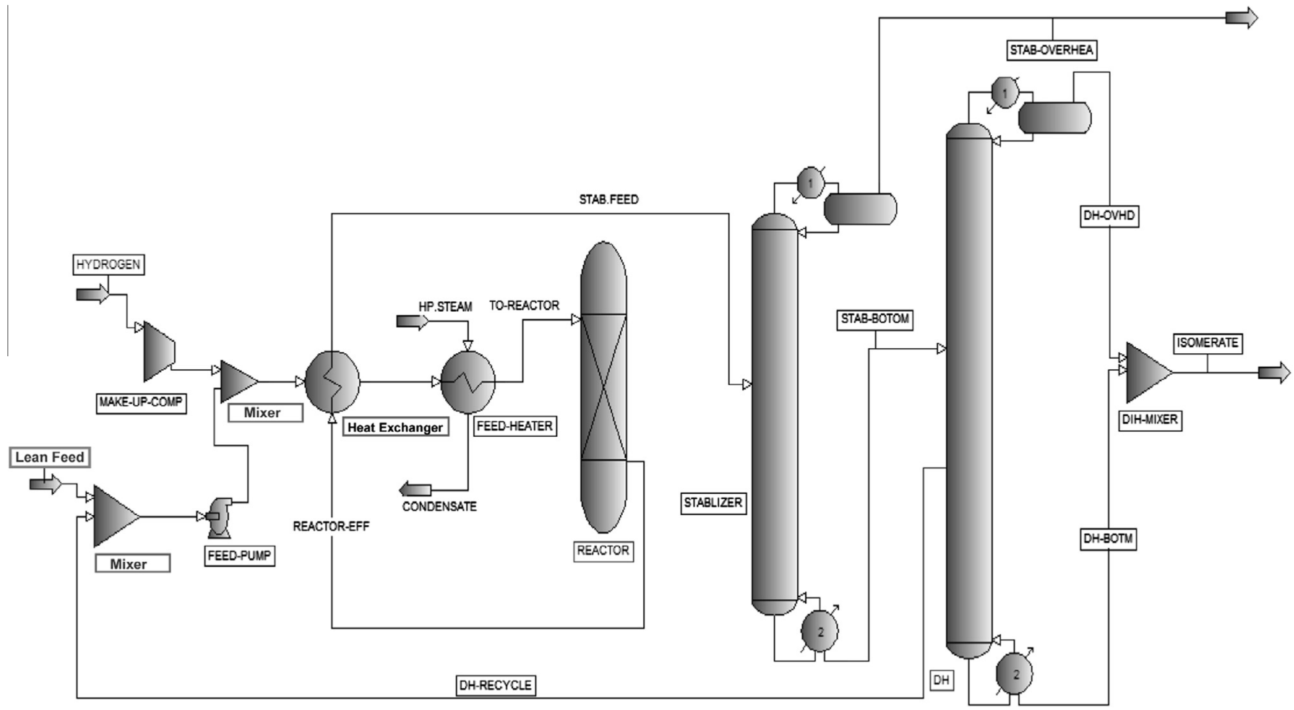

Figure 1 Isomerization unit process flow diagram.

Table 1 Studied light naphtha composition.

Component	Units	Composition
Butane	% mole	0.11
Iso-pentane	% mole	11.69
N-pentane	% mole	13.3
Cyclo-pentane (CP)	% mole	1.95
2,2-Di-methyle-butane (2,2 DMB)	% mole	0.49
2,3-Di-methyle-butane (2,3 DMB)	% mole	1.66
2-Methyl-pentane (2 MP)	% mole	10.4
3-Methyl-pentane (3 MP)	% mole	9.37
N-hexane	% mole	30.72
Methyl-cyclo-pentane (MCP)	% mole	8.69
Cyclo-hexane (CH)	% mole	5.84
Benzene	% mole	3.18
Heptanes	% mole	2.6
Copper	Ppb*	20
Lead	Ppb	10
Arsenic	Ppb	1
Fluorides	Ppb	0.1
Mercury	Ppb	< 1
HCl	Ppm**	0.5
Sulphur	Ppm	0.5
Nitrogen	Ppm	0.5

* Part per billion.
** Part per million.

Table 2 Light naphtha specifications.

Specification	Units	Value
Density	kg/m^3	671.4
Molecular weight	kg/kg mole	81.88
Bromine number	mgBr2/100 g	4

Table 3 Make-up hydrogen analysis.

Component	Composition, % mole
Hydrogen	90.09
Methane	3.18
Ethane	2.82
Propane	2.33
Iso-butane	0.55
N-pentane	0.63
Iso-pentane	0.13
N-pentene	0.06
2,2-Di-methyle-butane	0.01
2,3-Di-methyle-butane	0.02
2-Methyl-pentane	0.04
3-Methyl-pentane	0.01
N-hexane	0.01
Water	0.12

This mathematical model can be used for different raw materials composition and catalyst and also it can be used to compare the efficiency of different modules isomerization work and choose the most appropriate alternative of process optimization for a given raw material. This work aims to improve product octane number of an existing isomerization unit with small equipment modification and low utility consumption. Eight process scenarios were proposed for modification of existing isomerization unit, and each process scenario was studied using process simulation software. The equipment data and product predicted octane number were calculated. Economic evaluation study was done for each scenario, since the evaluation included raw material cost, and the other operating cost items, equipment fixed cost, product selling price and profit. Optimum modified isomerization process was selected based on best economic return on investment and minimum pay-back time.

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Table 4 Investigated process scenarios for isomerization unit.

Scenarios	Feed fractionation	Product fractionation	Terminology
Process 1	No fractionation	Once through	Simple
Process 2	De-iso-pentanizer	No fractionation	DIP
Process 3	No fractionation	De-pentanizer	DP
Process 4	No fractionation	De-hexanizer	DH
Process 5	De-iso-pentanizer	De-pentanizer	DIP/DP
Process 6	De-iso-pentanizer	De-hexanizer	DIP/DH
Process 7	No fractionation	De-pentanizer & De-hexanizer	DP/DH
Process 8	De-iso-pentanizer	De-pentanizer & De-hexanizer	DIP/DP/DH

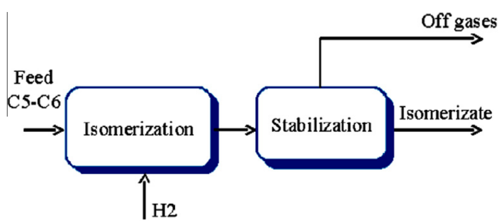

Figure 2 Block diagram for once through isomerization unit "scenario 1".

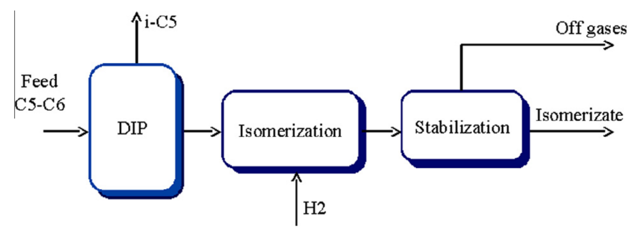

Figure 3 Block diagram for isomerization unit with De-iso-pentanizer (DIP) "scenario 2".

2. Field data analysis for MIDOR light naphtha isomerization plant

2.1. Studied process

Currently light naphtha is fed to existing MIDOR isomerization unit where its octane number is improved from 66.6 to 86.7, and this existing unit is included by the scenario number 4 for de-hexanizer recycling fractionator (DH). Hence, light naphtha is separated from crude oil using atmospheric distillation, and also it is produced from cracking units of hydrocracker and coker units [5–7]. As shown in Fig. 1 light treated naphtha is mixed with hydrogen to reduce coke formation on catalyst. Then feed is exchanged with reactor effluent stream. Reaction temperature is controlled using steam reboiler. Hot feed enters the reactor through top distributer, and reactor

Table 5 Simulation results of once through isomerization unit (scenario 1).

Stream name	Lean feed	Hydrogen	TO-reactor	Reactor-EFF	Stab.feed	Stab-overhead	Product
Phase	Liquid	Vapour	Mixed	Mixed	Mixed	Vapour	Liquid
Temperature, °C	42.0	38.0	138.0	151.0	81.4	37.1	176.4
Pressure, Barg	6.8	44.6	36.5	31.0	15.4	13.9	15.1
Molecular weight	82.1	5.1	56.7	72.2	72.2	26.9	83.9
Rate, kg-mol/hr	582	287	869	869	685	141	545
Total molar comp. per cents							
H_2	0	90.22	29.81	8.68	8.68	42.25	0
Methane	0	3.17	1.05	1.56	1.56	7.59	0
Ethane	0	2.82	0.93	1.29	1.29	6.27	0
Propane	0	2.33	0.77	4.09	4.09	19.9	0
i-butane	0	0.55	0.18	3.87	3.87	18.56	0.07
Butane	0.11	0.63	0.28	0.86	0.86	3.84	0.09
i-pentane	11.69	0.13	7.87	9.45	9.45	1.53	11.5
Pentane	13.3	0.06	8.93	3.02	3.02	0.06	3.78
CP	1.95	0	1.31	0.64	0.64	0	0.8
2,2 DMB	0.49	0.01	0.33	16.8	16.8	0	21.15
2,3 DMB	1.66	0.02	1.12	5.67	5.67	0	7.13
2MP	10.4	0.04	6.97	18.32	18.32	0	23.06
3MP	9.37	0.01	6.28	9.74	9.74	0	12.26
Hexane	30.72	0.01	20.57	6.11	6.11	0	7.69
MCP	8.69	0	5.82	4.17	4.17	0	5.24
CH	5.84	0	3.91	4.21	4.21	0	5.3
Benzene	3.18	0	2.13	0	0	0	0
Heptane	2.6	0	1.74	1.52	1.52	0	1.93

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Table 6 Simulation results for isomerization unit with De-iso-pentanizer (scenario 2).

Stream name	Lean feed	DIP-OVHD	DIP-bottom	Hydrogen	TO-reactor	Reactor-EFF	Stab.feed	Stab-overhead	Product
Phase	Liquid	Liquid	Liquid	Vapour	Mixed	Mixed	Mixed	Vapour	Liquid
Temperature, °C	72	49.04	82.31	38	138	151	116.71	36.16	171.31
Pressure, Barg	10.3	1	1	44.6	36.54	31.03	15.38	13.93	15.1
Molecular weight	82.14	71.99	83.19	5.1	67.25	75.83	75.83	26.56	82.24
Rate, Kgmol/h	582.14	54.47	527.67	135.36	663.03	663.03	588.03	67.74	520.29
Total molar comp. per cents									
H_2	0	0	0	90.22	18.42	4.92	4.92	42.7	0
Methane	0	0	0	3.17	0.65	0.89	0.89	7.69	0
Ethane	0	0	0	2.82	0.58	0.73	0.73	6.31	0
Propane	0	0	0	2.33	0.48	2.32	2.32	20.12	0
i-butane	0	0	0	0.55	0.11	2.19	2.19	18.47	0.07
Butane	0.11	1.17	0	0.63	0.13	0.41	0.41	3.09	0.06
i-pentane	11.69	95.82	3	0.13	2.41	15.62	15.62	1.53	17.46
Pentane	13.3	3.01	14.37	0.06	11.45	6.34	6.34	0.09	7.15
CP	1.95	0	2.15	0	1.71	1.36	1.36	0	1.54
2,2 DMB	0.49	0	0.54	0.01	0.43	20.71	20.71	0	23.41
2,3 DMB	1.66	0	1.83	0.02	1.46	6.99	6.99	0	7.9
2MP	10.4	0	11.47	0.04	9.14	12.02	12.02	0	13.58
3MP	9.37	0	10.34	0.01	8.23	7.42	7.42	0	8.38
Hexane	30.72	0	33.89	0.01	26.98	9.33	9.33	0	10.54
MCP	8.69	0	9.59	0	7.63	4.56	4.56	0	5.15
CH	5.84	0	6.44	0	5.13	4.19	4.19	0	4.76
Benzene	3.18	0	3.51	0	2.79	0	0	0	0
Heptane	2.6	0	2.87	0	2.27	0	0	0	0

effluent consists of branched hydrocarbons, cracked gases and hydrochloric acid. Gases is separated at sieve tray stripper (stabilizer), then washed by 10% wt caustic solution to remove HCl. Unconverted hexanes are separated from product using sieve tray fractionators called de-hexanizer "DH", then recycled and mixed with feed stream to reactor, and this improves product octane number as normal hexane has low octane number of 24.8 [5,8].

2.2. Feed of isomerization unit

Feed flowrate to isomerization unit is 70.7 m^3/h of treated light naphtha. Such feed is hydrotreated using cobalt, molybdenum and nickel oxide as catalyst. Then the treated naphtha is split into light naphtha with mainly five and six carbon atoms and heavy naphtha with other heavier hydrocarbons [6]. Detailed light naphtha composition and specifications for isomerization feed are listed in Tables 1 and 2. Make up hydrogen is produced at platforming unit, which increases heavy naphtha octane number by converting the naphthenes to aromatics. The molecular weight of make-up gas is 5.12, and detailed make up gas composition is tabulated in Table 3.

2.3. Catalyst type

Catalyst converts normal paraffins, naphthenes, benzene and low octane paraffins to high octane iso-paraffins. It is composed of chlorinated alumina that is impregnated with 0.25 wt% platinum. Catalyst is loaded in fixed-bed reactors, and no oxygen is allowed to contact the catalyst during loading. Chloride-alumina bond is very sensitive to oxygen, so that oxygen compounds are removed before reaction using molecular sieve. Catalyst shape is extruded and dense loaded to increase the amount of catalyst inside the reactors. Perchloroethylene is continuously injected to maintain the same concentration of chlorides at the catalyst [9,10].

3. Results and discussion

The present study uses PRO/II computer software that simulates chemical and refining processes with high power and flexibility for wide range of applications. All studied scenarios are presented in Table 4, and each scenario has a separate simulation model. All scenarios are based on same feed composition

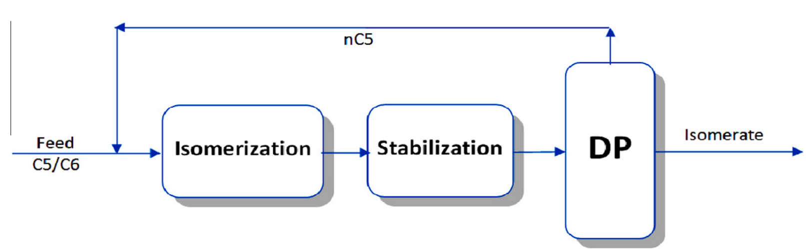

Figure 4 Block diagram for isomerization unit with De-pentanizer "scenario 3".

Table 7 Simulation results for isomerization unit with De-pentanizer (scenario 3).

Stream name	Lean feed	Hydrogen	TO-reactor	Reactor-EFF	Stab-overhead	Stab-bottom	ISO-pentane	NC5-recycle	C6 + isomerate	Product
Phase	Liquid	Vapour	Mixed	Mixed	Vapour	Liquid	Liquid	Liquid	Liquid	Mixed
Temperature, °C	72.00	38.00	138.00	151.00	37.66	164.62	49.10	100.15	128.09	70.35
Pressure, Barg	10.30	44.60	36.54	31.03	13.93	15.10	1.00	5.00	5.00	1.00
Molecular weight	82.14	5.10	60.47	71.79	27.06	80.15	72.07	72.53	85.45	80.99
Rate, Kgmol/h	582.14	241.29	885.10	885.10	116.85	625.48	188.25	61.68	375.55	563.80
Total molar comp. per cents										
H_2	0	90.22	24.6	6.62	42.05	0	0	0	0	0
Methane	0	3.17	0.86	1.18	7.53	0	0	0	0	0
Ethane	0	2.82	0.77	0.98	6.22	0	0	0	0	0
Propane	0	2.33	0.63	3.12	19.83	0	0	0	0	0
i-butane	0	0.55	0.15	2.95	18.35	0.07	0.24	0	0	0
Butane	0.11	0.63	0.24	0.77	4.42	0.09	0.31	0	0	0.11
i-pentane	11.69	0.13	8.22	25.79	1.53	30.33	98.44	7.09	0	11.69
Pentane	13.3	0.06	14.88	8.09	0.07	9.59	1.01	87.82	1.05	13.3
CP	1.95	0	1.43	1.16	0	1.38	0	2.09	1.95	1.95
2,2 DMB	0.49	0.01	0.53	15.71	0	18.65	0	2.97	30.57	0.49
2,3 DMB	1.66	0.02	1.1	5.3	0	6.29	0	0.02	10.47	1.66
2MP	10.4	0.04	6.85	9.07	0	10.76	0	0.01	17.92	10.4
3MP	9.37	0.01	6.17	5.59	0	6.64	0	0	11.06	9.37
Hexane	30.72	0.01	20.21	7.04	0	8.36	0	0	13.92	30.72
MCP	8.69	0	5.71	3.44	0	4.08	0	0	6.8	8.89
CH	5.84	0	3.84	3.19	0	3.76	0	0	6.26	5.84
Benzene	3.18	0	2.09	0	0	0	0	0	0	3.18
Heptane	2.6	0	1.72	0	0	0	0	0	0	2.4

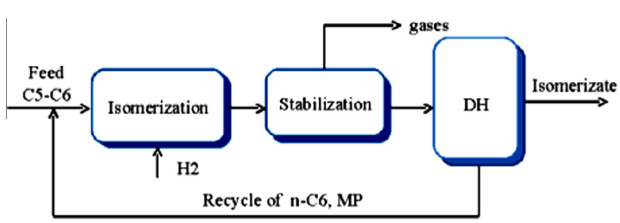

Figure 5 Block diagram for Isomerization unit with De-hexanizer (DH) “scenario 4”.

and flowrate, stream analysis is obtained, and then octane number is calculated. These different scenarios are based on the separation of pentanes, hexanes and its isomers. Hence new fractionators are installed at feed and product in order to separate high octane number components and recycle the unconverted hydrocarbons from product.

3.1. Once through isomerization unit “Scenario 1”

Once through isomerization unit contains only the reaction section then product stabilization, and no extra fractionation or recycling is installed as shown in Fig. 2. It is the original pentane isomerization process, and once-through scheme without any recycle can be used in case of minimum investment available with the company owners. Once through stream analysis is tabulated in Table 5.In practice it is not quite simple because feed is usually de-butanized and treated to remove sulphur and nitrogen. Hydrogen purge is necessary since there is a small amount of cracking with the requirement of saturation of the resulting olefins. However, hydrogen consumption is minimal and mostly is employed for carbon suppression. This once through operation will normally yield a research octane number (RON) improvement depending on the distribution of the various isomers in the feed stream. To achieve higher octane, several schemes which have lower octane components should be separated and recycled back to the reactors [9–11].

3.2. Unit with De-iso-pentanizer DIP “Scenario 2”

Isomerization unit with de-iso-pentanizer then reaction section then stabilizer is shown in Fig. 3. Iso-pentane can be removed from the feed, reducing throughput and increasing the driving force for isomerization. Simulation results of isomerization unit with de-iso-pentanizer are indicated in Table 6. This can be accomplished with a de-iso-pentanizer ahead of the feed drying system. The scheme with de-iso-pentanizer (DIP) before the reactor section allows the production of isomerate with high octane number, since increasing the conversion level of n-pentanes and reducing the reactor duty and space velocity increase the contact time between light naphtha and catalyst [10]. DIP overhead product is normally rich in iso-pentane, and is routed to gasoline blending along with other high octane components. The DIP bottom, which is rich in n-C5 and C6 paraffins, is routed to the light naphtha isomerization unit. Tower may be originally designed as a naphtha splitter, to separate light naphtha from catalytic reformer feed. The tower is converted to a de-iso-pentanizer to remove i-C5 from the

Table 8 Simulation results for isomerization unit with De-hexanizer (scenario 4).

Stream name	Lean feed	Hydrogen	TO-reactor	Reactor-EFF	Stab-overhead	Stab-bottom	DH. bottom	DH-overhead	Product
Phase	Liquid	Vapour	Mixed	Mixed	Vapour	Liquid	Liquid	Liquid	Liquid
Temperature, °C	72.00	38.00	138.00	151.00	37.28	176.15	126.74	66.94	74.15
Pressure, Barg	10.30	44.60	36.54	31.03	13.93	15.10	2.00	1.03	36.54
Molecular weight	82.14	5.10	67.60	77.98	26.93	84.07	91.74	81.45	82.79
Rate, Kgmol/h	582.14	241.29	1174.86	1174.86	118.90	997.43	84.53	561.48	646.01
Total molar comp. per cents									
H_2	0	90.22	18.53	4.49	42.21	0.00	0.00	0.00	0.00
Methane	0	3.17	0.65	0.81	7.57	0.00	0.00	0.00	0.00
Ethane	0	2.82	0.58	0.67	6.31	0.00	0.00	0.00	0.00
Propane	0	2.33	0.48	2.12	19.89	0.00	0.00	0.00	0.00
i-butane	0	0.55	0.11	2.00	18.21	0.07	0.00	0.13	0.11
Butane	0.11	0.63	0.18	0.53	4.24	0.08	0.00	0.15	0.13
i-pentane	11.69	0.13	5.82	12.71	1.52	14.04	0.00	24.94	21.68
Pentane	13.3	0.06	6.60	3.33	0.05	3.72	0.00	6.60	5.74
CP	1.95	0.00	0.97	0.70	0.00	0.79	0.00	1.40	1.21
2,2 DMB	0.49	0.01	0.55	20.47	0.00	22.91	0.01	40.06	34.82
2,3 DMB	1.66	0.02	3.64	6.90	0.00	7.72	0.43	7.77	6.81
2MP	10.4	0.04	14.02	16.82	0.00	18.83	1.87	14.62	12.95
3MP	9.37	0.01	11.345	9.32	0.00	10.43	3.45	4.00	3.93
Hexane	30.72	0.01	20.59	6.48	0.00	7.25	9.30	0.25	1.43
MCP	8.69	0.00	7.22	3.94	0.00	4.41	10.99	0.08	1.51
CH	5.84	0.00	4.50	3.37	0.00	3.77	22.10	0.00	2.89
Benzene	3.18	0.00	1.57	0.00	0.00	0.00	0.00	0.00	0.00
Heptane	2.6	0.00	2.645	5.34	0.00	5.98	51.85	0.00	6.79

isomerization unit feed, which increases the refinery's ability to produce premium gasoline. During the revamp, additional condensing capacity was added for the DIP [12,13].

3.3. Unit with De-pentanizer DP "Scenario 3"

Isomerization unit with reaction section then stabilizer then recycling low octane number C5 using de-pentanizer is indicated in Fig. 4, and it deals with high pentane feed, but it increases reaction section capacity. Results of process simulation with de-pentanizer fractionators are indicated in Table 7.

3.4. Unit with De-hexanizer DH "Scenario 4"

Existing isomerization unit at MIDOR has reaction section then stabilizer then recycling low octane number C6 using de-hexanizer as shown in Fig. 5. The DH is used to recover pentanes and product iso-hexane from the stabilized reactor products. The recycle draw is composed primarily of n-hexane and low octane number components of methyl-pentanes. Overhead vapour from the de-hexanizer is condensed via the air cooler and the liquid accumulates in the de-hexanizer receiver. The receiver serves as a reflux drum. A large portion of the overhead liquid is pumped via a reflux pump back to the tower, the balance then is taken off as net product [9]. The DH recycle stream is pumped back to the liquid feed driers. The net product is pumped out by de-hexanizer pump via the de-hexanizer cooler where it is cooled and then directed to storage [5,10]. Simulation results for isomerization unit with de-hexanizer are shown in Table 8.

3.5. Unit with De-iso-pentanizer and De-pentanizer DIP/DP "Scenario 5"

The addition of a de-pentanizer on the product stream to permit n-pentane recycle via the de-iso-pentanizer yields an increase in octane number. Scheme with recycle of n-pentane (with DIP and DP) requires providing with de-pentanizer of isomerizate after the reaction section and de-iso-pentanizer before the reactor as shown in Fig. 6. The normal pentane in the product at essentially equilibrium concentration is recycled to fresh feed that is immediately de-iso-pentanized to make iso-pentane product in this two-step improvement. Simulation results for isomerization unit with de-iso-pentanizer and de-pentanizer are shown in Table 9 [5]. The enriched feed and makeup hydrogen are dried and passed through a heat exchange network to the isomerization reactor with its fixed catalyst bed. The material leaving the reactor is flashed, with the hydrogen may be recycled to the reactor and the liquid product being stabilized. Stabilizer bottom is directed to the splitter that recycles n-pentane and takes the isomeric hexane product as a bottom cut [9].

3.6. Unit with De-iso-pentanizer and De-hexanizer DIP/DH "Scenario 6"

This process scenario has de-iso-pentanizer then reaction section and stabilization then de-hexanizer as shown in Fig. 7. This method is typically used in plants with a significant amount of iso-pentane in the feedstock. If fed to the reactor, the iso-pentane would pass on through unreacted. Because of

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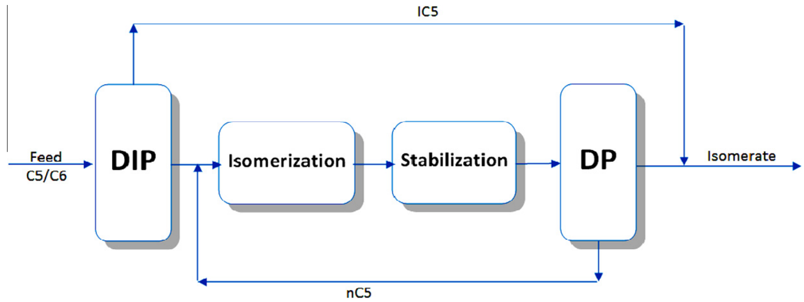

Figure 6 Block diagram for isomerization unit with De-iso-pentanizer (DIP) and De-pentanizer (DP) "scenario 5".

Table 9 Simulation results for isomerization unit with De-iso-pentanizer and De-pentanizer (scenario 5).

Stream name	Lean feed	Hydrogen	TO-reactor	Stab-overhead	ISO-C5	DIP-bottom	Stab-overhead	NC5-recycle	C6 + isomerate	Product
Phase	Liquid	Vapour	Mixed	Mixed	Liquid	Liquid	Vapour	Liquid	Liquid	Mixed
Temperature, °C	72.00	38.00	138.00	151.00	49.04	82.31	36.40	100.26	128.08	68.57
Pressure, Barg	10.30	44.60	36.54	31.03	1.00	1.00	13.93	5.00	5.00	1.00
Molecular weight	82.14	5.10	59.97	71.84	71.99	83.19	26.65	72.53	85.45	80.36
Rate, Kgmol/h	582.14	241.29	847.25	847.25	54.47	527.67	112.83	78.30	367.28	592.30
Total molar comp. per cents										
H_2	0.00	90.22	25.69	6.59	0.00	0.00	42.60	0.00	0.00	0.00
Methane	0.00	3.17	0.90	1.18	0.00	0.00	7.65	0.00	0.00	0.00
Ethane	0.00	2.82	0.80	0.97	0.00	0.00	6.28	0.00	0.00	0.00
Propane	0.00	2.33	0.66	3.115	0.00	0.00	20.08	0.00	0.00	0.00
i-butane	0.00	0.55	0.16	2.94	0.00	0.00	18.59	0.00	0.00	0.08
Butane	0.11	0.63	0.18	0.55	1.173	0.00	3.18	0.00	0.00	0.18
i-pentane	11.69	0.13	2.43	23.89	95.82	3.00	1.53	5.69	0.00	37.18
Pentane	13.30	0.06	17.23	10.39	3.007	14.37	0.09	89.42	1.07	1.23
CP	1.95	0.00	1.52	1.17	0.00	2.15	0.00	1.89	1.93	1.18
2,2 DMB	0.49	0.01	0.615	15.715	0.00	0.54	0.00	2.97	30.55	18.95
2,3 DMB	1.66	0.02	1.15	5.30	0.00	1.83	0.00	0.02	10.51	6.52
2MP	10.40	0.04	7.16	9.03	0.00	11.47	0.00	0.01	17.92	11.11
3MP	9.37	0.01	6.44	5.58	0.00	10.34	0.00	0.00	11.07	6.86
Hexane	30.72	0.01	21.11	7.01	0.00	33.89	0.00	0.00	13.91	8.62
MCP	8.69	0.00	5.97	3.42	0.00	9.59	0.00	0.00	6.79	4.21
CH	5.84	0.00	4.01	3.15	0.00	6.44	0.00	0.00	6.25	3.88
Benzene	3.18	0.00	2.185	0.00	0.00	3.51	0.00	0.00	0.00	0.00
Heptane	2.6	0.00	1.79	0.00	0.00	2.87	0.00	0.00	0.00	0.00

the equilibrium reaction, less of the normal pentane would be able to isomerize because the iso-pentane in the feed would limit the total concentration. By removing the iso pentane from the feed, the equilibrium is pushed forward and more of the normal-pentanes can react to form iso-pentanes. There will be less normal-pentanes in the reactor effluent. This is particularly important since a de-hexanizer column is being used to separate the isomerate product [5,13]. Remember that all the pentanes go overhead in a de-hexanizer, both normal and iso. Using de-iso-pentanizer plus de-hexanizer increases octane. Of course, adding separation equipment also increases your capital cost. Simulation results for isomerization unit with de-iso-pentanizer and de-hexanizer are listed in Table 10.

3.7. Unit with De-pentanizer and De-hexanizer DP/DH "Scenario 7"

Unit with reaction section then stabilizer and de-pentanizer followed by de-hexanizer is shown in Fig. 8. This option has the highest recycle amount for unconverted pentanes and hexanes, and the simulation results for DP/DH isomerization unit are listed in Table 11 [9,13].

3.8. Unit with De-iso-pentanizer, De-pentanizer and De-hexanizer DIP/DP/DH "Scenario 8"

Scheme with iso-pentanes separation then recycling of unconverted n-pentane and n-hexane is shown in Fig. 9. Total con-

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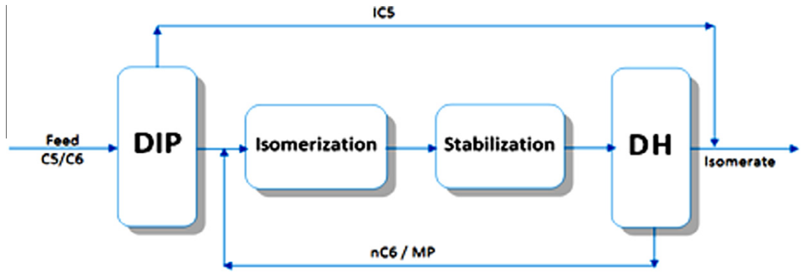

Figure 7 Block diagram for isomerization unit with De-iso-pentanizer (DIP) and De-hexanizer (DH) “scenario 6”.

Table 10 Simulation results for isomerization unit with De-iso-pentanizer and De-hexanizer (scenario 6).

Stream name	Lean feed	Hydrogen	TO-reactor	Stab-overhead	Stab-overhead	ISO-pentane	DH-bottom	DH-recycle	DH-overhead	Product
Phase	Liquid	Vapour	Mixed	Mixed	Vapour	Vapour	Liquid	Liquid	Liquid	Mixed
Temperature, °C	72.00	38.00	138.00	151.00	36.10	49.40	124.98	101.54	69.69	70.24
Pressure, Barg	10.30	44.60	36.54	31.03	13.93	1.00	2.00	1.86	1.03	1.00
Molecular weight	82.14	5.10	68.03	78.54	26.54	71.99	90.95	86.23	82.65	82.60
Rate, Kgmol/h	582.14	241.29	1163.68	1163.68	116.32	54.47	66.02	394.72	533.98	654.48
Total molar comp. per cent										
H_2	0.00	90.22	18.71	4.48	42.76	0.00	0.00	0.00	0.00	0.00
Methane	0.00	3.17	0.66	0.80	7.63	0.00	0.00	0.00	0.00	0.00
Ethane	0.00	2.82	0.58	0.67	6.36	0.00	0.00	0.00	0.00	0.00
Propane	0.00	2.33	0.48	2.11	20.15	0.00	0.00	0.00	0.00	0.00
i-butane	0.00	0.55	0.11	2.00	18.45	0.00	0.00	0.00	0.14	0.11
Butane	0.11	0.63	0.13	0.37	3.035	1.173	0.00	0.00	0.11	0.19
i-pentane	11.69	0.13	1.39	7.98	1.53	95.82	0.00	0.00	16.27	21.25
Pentane	13.30	0.06	6.53	3.24	0.085	3.007	0.00	0.00	6.72	5.73
CP	1.95	0.00	0.98	0.70	0.00	0.00	0.00	0.00	1.45	1.18
2,2 DMB	0.49	0.01	0.59	22.18	0.00	0.00	0.01	1.02	45.38	37.03
2,3 DMB	1.66	0.02	4.04	7.48	0.00	0.00	0.46	9.45	8.51	6.99
2MP	10.40	0.04	16.46	20.17	0.00	0.00	2.23	33.18	17.18	14.24
3MP	9.37	0.01	12.55	10.38	0.00	0.00	3.82	23.16	4.00	3.65
Hexane	30.72	0.01	20.85	6.38	0.00	0.00	9.30	16.16	0.18	1.09
MCP	8.69	0.00	7.43	3.94	0.00	0.00	11.63	9.10	0.06	1.22
CH	5.84	0.00	4.65	3.40	0.00	0.00	26.72	5.10	0.00	2.70
Benzene	3.18	0.00	1.59	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Heptane	2.6	0.00	2.27	3.72	0.00	0.00	45.83	2.83	0.00	4.62

version of all linear paraffins (not only n-C6 but also n-C5) into isomers can be realized by set of distillation columns with de-iso-pentanizer, de-hexanizer and de-pentanizer (DIP, DH and DP) [5,9,10,13]. This process option has the biggest amount of equipment while obtaining the best product quality, and simulation results for process streams are shown in Table 12.

3.9. Simulation results analysis

Simulation was done for light naphtha isomerization unit using actual detailed component composition, and many process scenarios were proposed: first scenario was removing the existing MIDOR de-hexanizer tower, another two scenarios were proposed for replacing the existing de-hexanizer tower with de-iso-pentanizer and de-pentanizer. Installing two fractionators was studied as per scenario 5 till 7. Finally, installing de-iso-pentanizer, de-pentanizer and de-hexanizer at the same time was studied as per scenario 8. Product octane number obtained from each fractionation option is summarized in Fig. 10. High quality product was obtained from isomerization unit with DIP/DP/DH fractionators, because of concentrating the normal paraffins at reactor feed that force the reaction towards more isomerization. As the concentration of normal hexane is higher than normal pentane and iso-pentane, accordingly octane number for isomerization unit with de-hexanizer is higher than unit with de-pentanizer and de-iso-pentanizer.

4. Economic study

For the previous isomerization unit scenarios, complete economic models were done to select the best scenario that has a high economic benefit; all chemical process items are included such as equipment, instruments, electrical, utilities,

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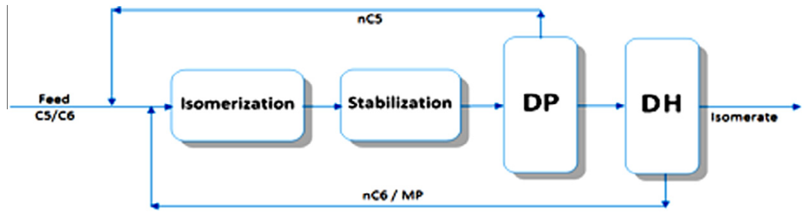

Figure 8 Block diagram for isomerization unit with De-pentanizer (DP) and De-hexanizer (DH) "scenario 7".

civil work, operating costs, feed and product prices. Profit is obtained as a net income after eliminating all operating costs and raw material prices. Pay-back time and return on investment are calculated based on total fixed cost and profit, and good investment will have small pay-back time and high return on investment as a percentage per year [14].

4.1. Predicted income based on octane number

Produced gasoline is evaluated based on its main quality indicator of octane number, and gasoline is basically classified into high octane number with a famous name of premium gasoline and less octane number that is called regular gasoline. United States energy information administration gives a monthly update for gasoline prices for different gasoline grades as described in Table 13, and product income values are calculated using Eq. (1) and shown in Fig. 11 [15].

$$\text{Product income} = \text{Product flowrate} * \text{selling price} \tag{1}$$

4.2. Operating cost

Based on process simulation, each isomerization scenario had certain amounts of raw materials, utilities, catalyst, chemicals, electrical requirements and labour costs. Each item of operating costs was concluded for each scenario. As presented in Eq. (2) and shown in Fig. 12 the operating cost is the summation of raw material cost (naphtha cost) (C_{raw}), electricity cost (C_{Elec}), steam cost ($C_{st.}$), cooling water cost ($C_{wat.}$), labour cost ($C_{lab.}$), catalyst cost ($C_{catl.}$), chemicals cost ($C_{chem.}$), and make-up hydrogen cost ($C_{hydrogen}$) [16–18].

$$\text{Operating cost} = C_{raw} + C_{Elec} + C_{st.} + C_{wat.} + C_{lab.} + C_{cat.} + C_{chem.} + C_{hyd.} \tag{2}$$

Table 11 Simulation results for isomerization unit with De-pentanizer and De-hexanizer (scenario 7).

Stream name	Lean feed	Hydrogen	TO-reactor	Stab-overhead	STAB. FEED	Stab-overhead	Stab-bottom	DH-overhead	DH-recycle	Product
Phase	Liquid	Vapour	Mixed	Liquid	Mixed	Vapour	Liquid	Liquid	Liquid	Liquid
Temperature, °C	72.00	38.00	138.00	151.00	156.84	36.16	187.45	116.79	141.80	101.32
Pressure, Barg	10.30	44.60	36.54	31.03	15.38	13.93	15.10	5.00	5.00	36.54
Molecular weight	82.14	5.10	80.33	84.52	84.52	26.47	87.63	84.11	90.10	80.91
Rate, Kgmol/h	582.14	241.29	2602.85	2602.85	2520.14	128.05	2392.09	452.77	1763.16	612.62
Total molar comp. per cent										
H_2	0.00	90.22	8.36	2.18	2.18	42.76	0.00	0.00	0.00	0.00
Methane	0.00	3.17	0.29	0.39	0.39	7.69	0.00	0.00	0.00	0.00
Ethane	0.00	2.82	0.26	0.32	0.32	6.25	0.00	0.00	0.00	0.00
Propane	0.00	2.33	0.223	1.03	1.03	20.17	0.00	0.00	0.00	0.00
i-butane	0.00	0.55	0.05	0.97	0.97	17.606	0.07	0.00	0.00	0.29
Butane	0.11	0.63	0.081	0.26	0.26	3.93	0.06	0.00	0.00	0.23
i-pentane	11.69	0.13	2.90	7.11	7.11	1.524	7.41	3.332	0.00	27.74
Pentane	13.30	0.06	3.30	1.96	1.96	0.06	2.06	8.66	0.00	6.66
CP	1.95	0.00	0.492	0.49	0.49	0.00	0.523	2.401	0.07	1.78
2,2 DMB	0.49	0.01	7.83	20.60	20.60	0.01	21.70	70.26	11.37	51.95
2,3 DMB	1.66	0.02	6.17	6.95	6.95	0.00	7.32	5.343	8.56	3.95
2MP	10.40	0.04	19.51	19.39	19.39	0.00	20.424	9.12	25.37	6.75
3MP	9.37	0.01	8.094	6.34	6.34	0.00	6.68	0.832	8.84	0.61
Hexane	30.72	0.01	9.98	3.22	3.22	0.00	3.39	0.04	4.59	0.03
MCP	8.69	0.00	4.11	2.24	2.24	0.00	2.353	0.012	3.20	0.01
CH	5.84	0.00	4.07	2.85	2.85	0.00	3.00	0.00	4.07	0.00
Benzene	3.18	0.00	0.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Heptane	2.6	0.00	23.57	23.7	23.7	0.00	25.01	0.00	33.93	0.00

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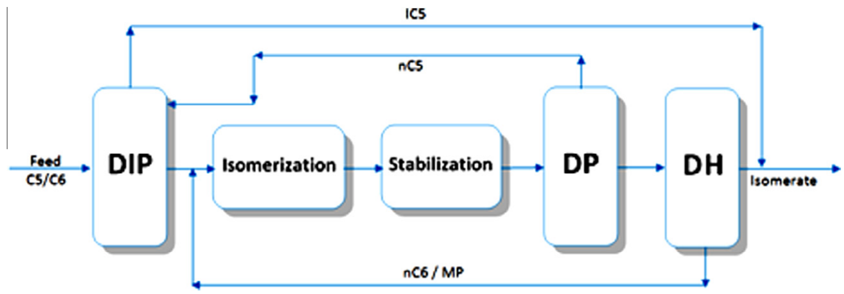

Figure 9 Block diagram for isomerization unit with De-iso-pentanizer (DIP)/De-pentanizer (DP) and De-hexanizer (DH) "scenario 8".

4.3. Profit calculation

Profit is net cash flow for the refinery in dollars per time units. Profit can be simply calculated as direct cash flow from selling produced gasoline after extracting the money spent for buying raw materials and the other operating costs. Profit Value for all isomerization process scenarios is calculated using Eq. (3):

$$\text{Profit}(\$/\text{h}) = \text{Product income} - \text{Operating cost} \quad (3)$$

The operating cost items are tabulated in Table 13 [14,19]. As shown in Fig. 13, scenario 8, "DIP/DP/DH" has the best profit due to high product quality, although scenario 8 has high operating and fixed costs, since the income from selling the high quality gasoline will overcome the required operating costs. De-hexanizer units "processes 4–8" have high profit due to recycling unconverted hexanes, as hexane components have high concentrations. Simple once through isomerization "process 1" has low profit, as low product quality and income are obtained compared with operating costs [14,19].

4.4. Total fixed cost

Equipment cost base was collected on January 2000 [14], and Eq. (4) indicates the capacity correction for cost:

$$C_e = C_b * (Q_e/Q_b)^m \quad (4)$$

where:

C_e: required equipment cost
C_b: base equipment cost
Q_e: equipment capacity
Q_b: base equipment capacity
m: constant depends on equipment type

Table 12 Simulation results for isomerization unit with De-iso-pentanizer, De-pentanizer and De-hexanizer (scenario 8).

Stream name	Lean feed	Hydrogen	TO-reactor	Stab-overhead	ISO-C5	Stab-overhead	NC5-recycle	DH-overhead	DH-bottom	Product
Phase	Liquid	Vapour	Mixed	Liquid	Liquid	Vapour	Liquid	Liquid	Liquid	Mixed
Temperature, °C	72.00	38.00	138.00	151.00	49.04	35.27	97.75	73.16	86.50	65.15
Pressure, Barg	10.30	44.60	36.54	31.03	1.00	13.93	5.00	1.00	1.00	1.00
Molecular weight	82.14	5.10	72.24	81.54	71.99	26.19	72.56	84.98	85.87	81.52
Rate, Kgmol/h	582.14	241.29	1559.62	1373.59	54.47	64.23	26.37	425.88	757.30	580.16
Total molar comp. per cent										
H_2	0.00	90.22	14.02	2.02	0.00	43.28	0.00	0.00	0.00	0.00
Methane	0.00	3.17	0.49	0.36	0.00	7.691	0.00	0.00	0.00	0.00
Ethane	0.00	2.82	0.435	0.30	0.00	6.352	0.00	0.00	0.00	0.00
Propane	0.00	2.33	0.36	0.95	0.00	20.381	0.00	0.00	0.00	0.00
i-butane	0.00	0.55	0.09	0.91	0.001	17.94	0.00	0.00	0.00	0.16
Butane	0.11	0.63	0.10	0.17	1.171	2.731	0.00	0.00	0.00	0.21
i-pentane	11.69	0.13	1.565	8.03	95.823	1.533	31.24	0.91	0.00	26.42
Pentane	13.30	0.06	6.00	3.27	3.002	0.092	65.10	6.28	0.00	5.06
CP	1.95	0.00	0.74	0.37	0.003	0.00	0.66	1.15	0.00	0.84
2,2 DMB	0.49	0.01	0.24	22.56	0.00	0.00	2.95	72.57	0.00	53.27
2,3 DMB	1.66	0.02	4.04	7.61	0.00	0.00	0.02	12.09	7.00	8.88
2MP	10.40	0.04	29.33	30.87	0.00	0.00	0.03	6.86	52.13	5.06
3MP	9.37	0.01	12.53	10.24	0.00	0.00	0.00	0.14	18.49	0.10
Hexane	30.72	0.01	15.08	4.02	0.00	0.00	0.00	0.00	7.29	0.00
MCP	8.69	0.00	6.24	3.37	0.00	0.00	0.00	0.00	6.12	0.00
CH	5.84	0.00	6.57	4.95	0.00	0.00	0.00	0.00	8.97	0.00
Benzene	3.18	0.00	1.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Heptane	2.6	0.00	0.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00

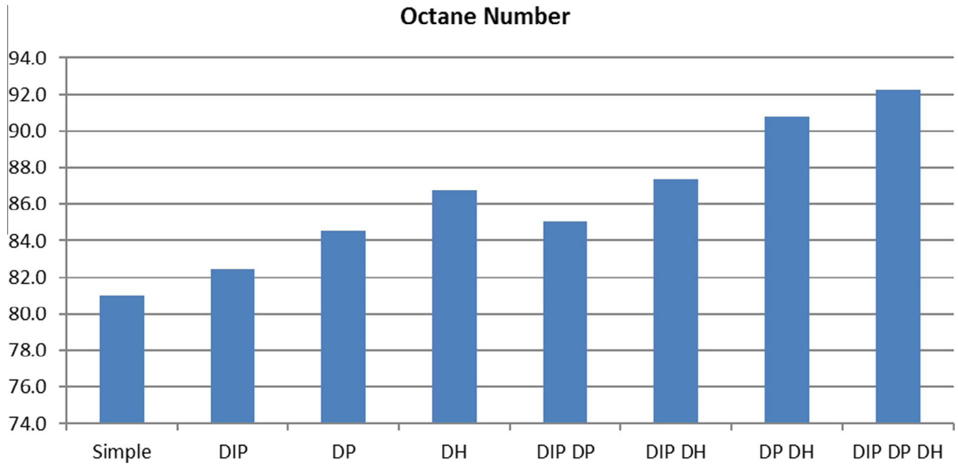

Figure 10 Product octane number for different process scenarios.

Cost change by time was updated using the chemical engineering cost index [14]. Design temperature, pressure and material were corrected using Robin factors as indicated in Eq. (5):

$$C_e = C_b * \left(\frac{Q_e}{Q_b}\right)^m * \frac{INDEXe}{INDEXb} * F_m * F_p * F_t \quad (5)$$

where:
$INDEXe$: latest year cost index
$INDEXb$: base time cost index
F_m: material cost correction factor
F_p: pressure cost correction factor
F_t: temperature cost correction factor

Other capital cost was included based on practical applied data for constructed chemical plants. Instrument, control cost, electrical requirements, piping, erection, utilities connections, off site preparation, civil work, equipment transportation and installation costs were considered [19–22]. Total fixed cost for process scenarios is shown in Fig. 14. It can be concluded that scenario 8 "DIP/DP/DH" has the highest fixed costs with many installed fractionators and expensive equipment required for high recycling rate for unconverted pentane and hexanes. Fixed cost increases with the number of installed fractionators, as more reboilers, condensers, exchangers and pumps are needed. Isomerization unit with de-pentanizer or de-hexanizer "Scenarios 3–8" has a higher fixed cost compared with de-iso-pentanizer units, as bigger reaction section equipment are needed with high recycling flow. Units with de-pentanizer and de-hexanizer at the same time "scenarios 7 and 8" have the highest fixed cost due to double recycling for pentanes and hexanes, so that reaction section becomes bigger than single recycle "scenarios 3–6".

Table 13 Gasoline price and utilities cost.

Items	Cost
Raw material cost \$/ton	638
Electricity cost \$/kw	0.0511
Steam cost for low pressure \$/ton	5.5
Steam cost for medium pressure \$/ton	8.8
Steam cost for high pressure \$/ton	12.1
Cooling water cost \$/m^3	0.022
Labour cost M\$/yr	1.75–2
Catalyst & chemicals cost \$/bbl	0.2
Hydrogen cost \$/gigajoule	30
81 gasoline price (\$/gallon)	2.06
82.4 gasoline price (\$/gallon)	2.17
84.5 gasoline price (\$/gallon)	2.33
85.1 gasoline price (\$/gallon)	2.37
86.74 gasoline price (\$/gallon)	2.49
87.35 gasoline price (\$/gallon)	2.54
90.8 gasoline price (\$/gallon)	2.80
92.3 gasoline price (\$/gallon)	2.91

4.5. Investment evaluation

Selecting the best isomerization design should be based on economical comparisons, refinery process requires two types of costs to obtain the target profits, first fixed cost is needed to construct the process and then operating cost is needed during process operation [22–25]. At the beginning the profit is consumed for returning back the initial investment then profit will be a gain for the project. Good investment will have a quick time to return the initial investment. So that, payback time is calculated as the time to recoup the capital investment. Return on investment "ROI" is an important expression in economics that indicated the ability to return back the initial investment, and ROI can be calculated from the following Eq. (6) [13,14]:

$$\text{ROI\%} = [\text{Average yearly profit/total fixed cost}] * 100 \quad (6)$$

Calculated values for investment payback time are listed in Table 14, and also a comparison between the return on investment as a percentage per year is shown in Fig. 15. Scenario 6 "DIP/DH" has the best process economics of payback and return on investment based on equipment fixed cost calculations in addition to profit obtained. This is due to high product quality with low fixed costs. Although high octane number is produced with process numbers 7 and 8 "DP/DH and DIP/DP/DH", its return on investment is low due to excessive requirements for equipment fixed costs. Simple once through isomerization unit "process 1" has a low return on investment as the profit gained from this process is very low.

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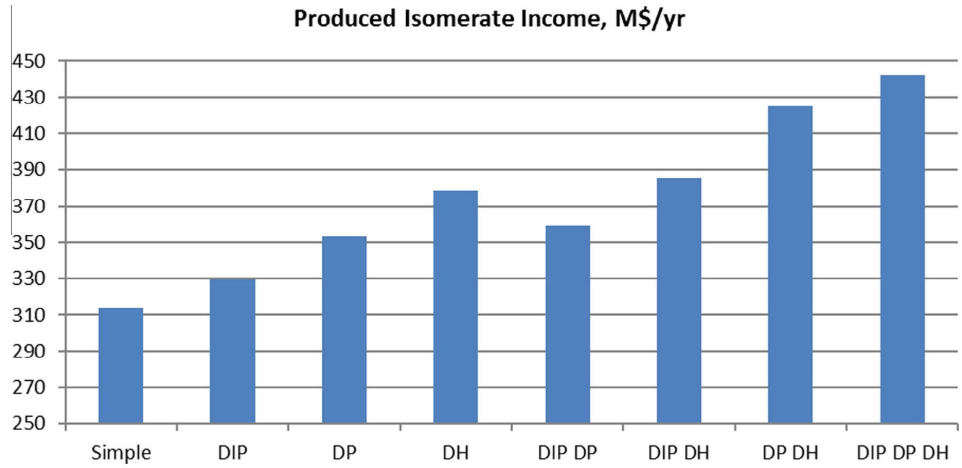

Figure 11 Product income comparison for different process scenarios.

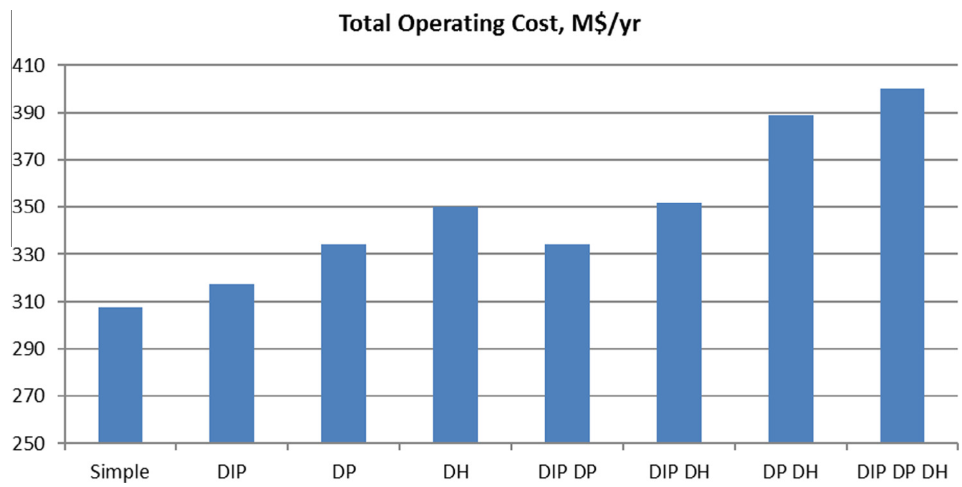

Figure 12 Total operating cost for different process scenarios.

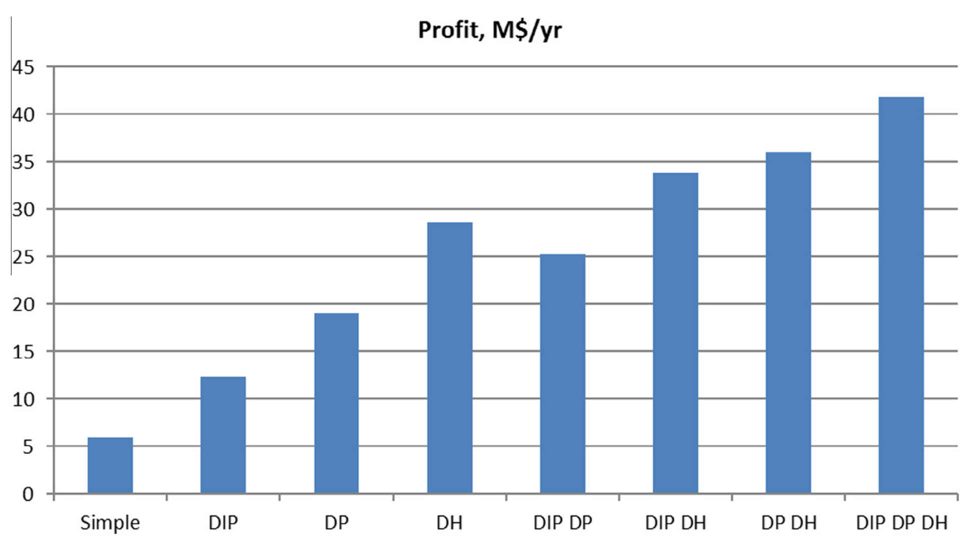

Figure 13 Profit values for different process scenarios.

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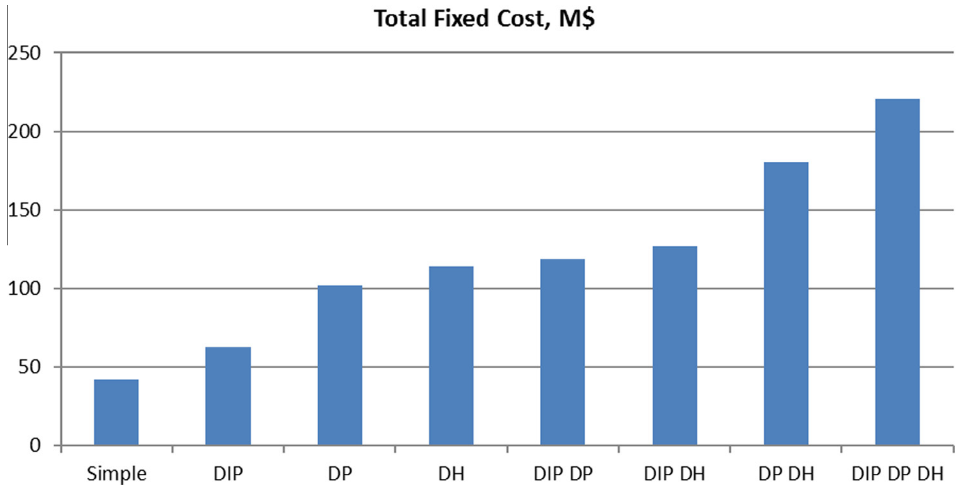

Figure 14 Total fixed cost.

Table 14 Economic data for all scenarios.

Investment evaluation	Simple	DIP	DP	DH	DIP DP	DIP DH	DP DH	DIP DP DH
Octane number	81.0	82.4	84.5	86.7	85.1	87.4	90.8	92.3
Produced isomerate income, M$/yr	314	330	353	379	359	386	425	442
Total operating cost, M$/yr	308	317	334	350	334	352	389	400
Profit, M$/yr	5.94	12.37	19.09	28.58	25.24	33.85	36.01	41.84
Total fixed cost, M$	41.6	63.1	101.6	114.3	118.8	127.1	180.0	220.5
Payback time, yr	7.0	5.1	5.3	4.0	4.7	3.8	5.0	5.3
ROI% per yr	14.3	19.6	18.8	25.0	21.3	26.6	20.0	19.0

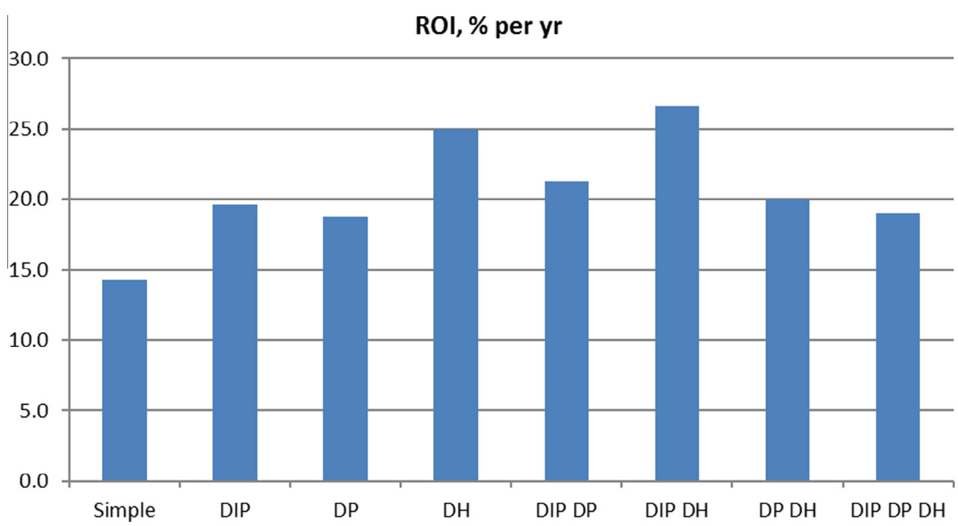

Figure 15 Return on investment "ROI" for different process scenarios.

In conclusion for feed with 13.3% mole pentane and 30.72% mole hexane, process with de-iso-pentanizer, de-pentanizer and de-hexanizer produces isomerate with 92.3 octane number, while minimum product octane number of 81 was obtained with simple once through isomerization unit. Replacing the existing de-hexanizer tower of MIDOR isomerization unit with de-iso-pentanizer tower will reduce return on investment by about 5.4% per year, while replacing the de-hexanizer with de-pentanizer tower will reduce ROI by about 6.2% per year, as the octane number will decrease by about 4.3 and 2.2 consequently. Adding de-iso-pentanizer tower to existing MIDOR isomerization unit is the best economic scenario, as it will increase return on investment to 26.6% per year, that is higher than adding de-pentanizer tower by 6.6%

per year, and operating costs are lower by 10%. Also, de-iso-pentanizer modification is better than adding both de-iso-pentanizer and de-pentanizer to existing de-hexanizer as the ROI is higher by about 7.6% per year with 14% lower operating costs.

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