WHITE PAPER

MAXIMIZE MARGINS IN ISOMERIZATION UNIT USING DIVIDING WALL COLUMN TECHNOLOGY

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Background of Isomerization:

The increasing demand for more efficient and low emission fuels on account of new stringent environmental policies and growing environmental awareness lead to the refineries looking for options on the enhancement of RON of the final product. This made the isomerization process gain immense importance across the globe and it became an intrinsic part of almost all refineries. The isomerization process is not only capable of upgrading the octane number of naphtha fractions specially the C5's and C6's but also simultaneously reducing the benzene content of naphtha by saturation of the benzene fraction. This efficiently converts low grade straight run naphtha to more marketable and valued product because of the improved RON. Isomerization is preferred not only because it is simple and cost effective for octane enhancement as compared to other octane-improving processes but also because it gives isomerate product with very low sulfur and benzene, making it an ideal blending component in refinery gasoline pool.

Talking on the structural level the straight-chain paraffins get converted into their branched-chain counterparts known as isomers which improve the RON of the isomerate and this has made this process gain popularity in the petrochemical facilities. Technology companies offer various options of isomerization processes, be it once through or recycle. Benefits of RON of the final product clubbed with capex and opex involved in revamps govern the decision of refineries in taking up the isomerization unit a must part of their facility.

A few examples of this transformation of compounds into any of its isomeric forms through the process of isomerization which have the same chemical composition but different structure and different physical and chemical properties, are depicted in figure below.

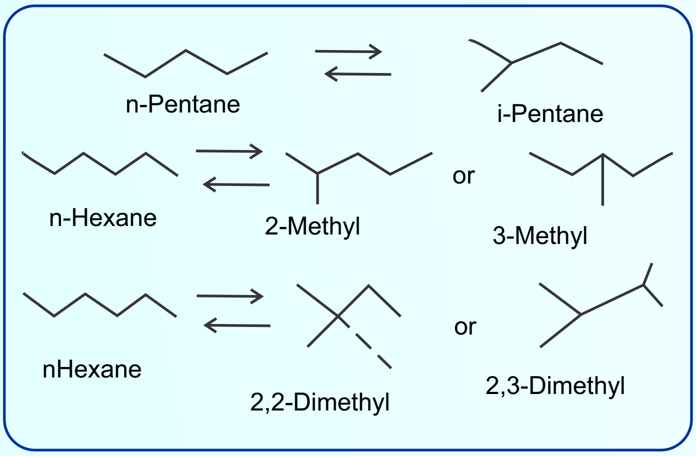

Figure 1: Primary reactions in an Isomerization Process

As the isomerization process itself is mildly exothermic, low temperature favors the reaction in forward direction, hence highly active catalyst are employed. To avoid the formation of olefins in low-temperature process, the feed to the isomerization plant is premixed with hydrogen. Processes are capable of upgrading low octane C5/C6 streams to products with octane ranging from 80 RON up to 93 RON. It has been observed that once through processes give product in range of 80-84 RON while recycle processes with deisopentanizer and deisohexanizer columns can give products with RON as high as 93.

Process flow scheme in an Isomerization unit with recycle

Besides the Isomerization Reactor, a typical isomerization unit consists of three columns. The deisopentanizer (DIP) column stands at the front end of the unit before the reactor while the other two i.e. the stabilizer and the Deisohexanizer (DIH) columns are at the back end of the unit i.e. after the reactor. The product stream from the isomerization unit is stabilized and then send to the DIH column. The column splits the isomerate stream into three streams i.e. the light isomerate, DIH recycle and heavy isomerate. The light isomerate and the heavy isomerate streams are combined and sent to the battery limits for storage. The DIH recycle stream is sent back to the isomerization reactor. The process flow of a typical isomerization unit is shown in Figure 2.

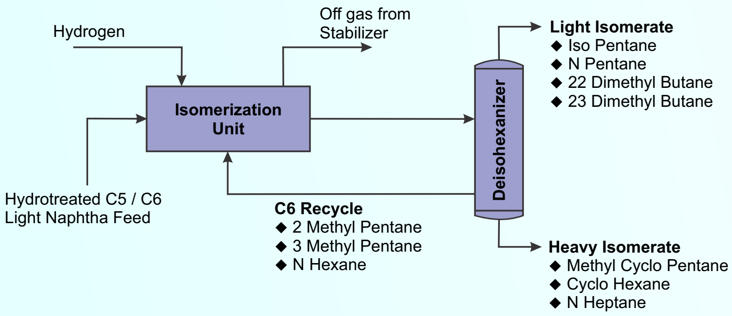

Figure 2: Block flow diagram of a typical Isomerization Unit

The compositions of the light isomerate and the heavy isomerate stream can be seen at a glance from the above process flow sheet. The light isomerate is mainly composed of four components i.e. Isopentane, N-pentane, 2 methyl butane and 3 methyl butane and the focus on improving the RON of this stream has made technology companies invest time and money for further improvements in processes and catalysts. The recycle stream which is send back to the reactor is mainly a mixture of 2 methyl pentanes (2MP) , 3 methyl pentanes(3MP) and N-hexane. Lesser the quantities of 2MP & 3MP in recycle stream, there is a rise in the tendency of the equilibrium to shift in a direction so as to lower values of 2 Methyl Butane(2MB) & 3 Methyl Butane (3MB) in the product stream, which are critical components that contribute to RON of total isomerate. Thus the recycle stream should have requisite amount of 2MP and 3MP in order to obtain desired product specification. But this eventually leads to the third component of the recycle stream i.e. N-hexane to build up in the recycle loop which effects the throughput of the Isom reactor and it becomes a bottleneck when it comes to capacity augmentation.

The above bottleneck lead to recognizing the novel idea of drawing N-hexane out of the recycle loop and using it to make few values added products. N-hexane drawn from the loop can be converted to marketable products like the food grade/polymer grade/ pharma grade hexanes and isohexanes. Not only does these marketable products bring in additional revenue to the facility but as the recycle to the Isom reactor decreases more feed can be pushed through the reactor. This is an added benefit for facilities specially where Isom unit is bottleneck.

Figure: 3 help in understanding the compositions of feed and product stream DIH column. It also helps to get an idea of what are the set targets and specifications of the outlet streams when it comes to DIH column. As newer technologies with recycle offer benefits on RON, so facilities across the globe who use this technology look forward to remove the intrinsic drawbacks associated with this technology.

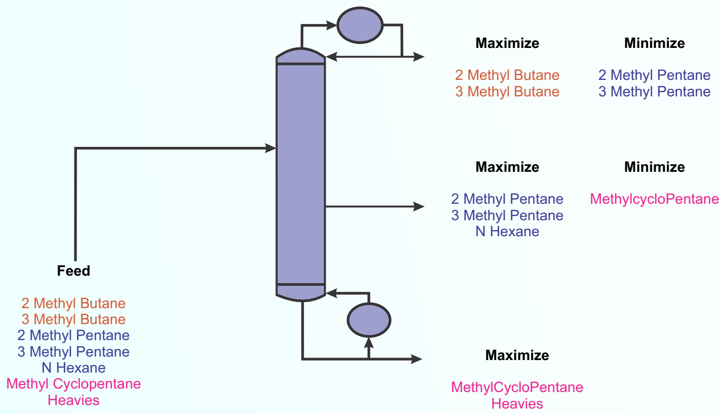

Figure 3: A closer look at Deisohexanizer column component split

Why FGH production post Isom is more attractive than other routes:

An alternate route for production of Food Grade Hexane and SBP solvents is by selective extraction of dearomatized light naphtha fraction post hydrotreating. In this sulpholane is used as solvent so as to get FGH as the midcut while the top and the bottom products are mixed to get the SBP solvents. Though this technology is used widely but has few shortcomings when compared with the production of FGH post ISOM unit because:

- The later does not require any ARU unit to be installed to get dearomatized Naphtha.
- When FGH is produced from Isom unit stream i.e. from the DIH column no additional column is required while the former requires a couple of columns in series.
- Also when n-hexane is produced post Isom, the stream which has the lowest RON is used. Hence by this revamp a valuable product like FGH is produced from a stream containing undesirable products like N - Hexane .
- Not only does the revamp to produce FGH from the DIH column brings additional revenue it also debottlenecks the Isom in terms of capacity by at least 25%.
- There is an increase in total octane barrel by the route of FGH production through ISOM.

In a case study for a facility in South Asia the option of producing FGH through Isom was found very lucrative. The team whom eventually were looking at FGH production from the perspective of debottlenecking the Isom analysed its cost/ton was way lower than FGH their facility produced through the dearomatisation route; so they decided to meet the demand they had by producing FGH through DIH and close the existing unit.

Alternate C6 products from Isom Unit

The following CG products can be produced from the Isom Unit :

Food Grade Hexane (FGH): Food grade hexane is a colorless solvent. They are primarily used in the extraction of edible oils. This calls for very high purity levels of hexane, followed by safe and careful storage. It also finds usage in a limited manner in preparation of rubber adhesives, can sealing compounds etc.

Polymer Grade Hexane (PGH): Polymer Grade Hexane is a fast evaporating hydrocarbon solvent that consists essentially of hexane isomers. A concentration of approximately 40% makes n-hexane the major component in this mixture. Polymer grade hexane is used as polymerization medium and in the manufacture of catalysts.

Isohexane: This is another compound of interest which also can be drawn from the recycle stream. It is a solvent used in industrial, professional, and consumer applications such as manufacturing process solvent, metal working, and coatings. It is not sold directly to the public for general consumer uses; however, this product may be an ingredient in consumer and commercial product applications such as cleaning agents and coatings.

Special Boiling Point Spirit: Sometimes on the market demand one more product is made from the recycle stream called the Special Boiling Point Spirit 55/115. It is used in the rubber industry particularly during the process of vulcanization in tyre manufacturing or in preparation of certain rubber mixes, cements and adhesives. It is also used as thinner for varnish, paint and printing inks formulation where quick drying is required and as diluent for lacquer, enamels, high grade leather drops.

The table below gives the typical specifications of the products discussed above at a glance.

Property	Units	Food Grade Hexane	Polymer Grade Hexane	Special Boiling Point	Iso Hexane
Color	Saybolt		Min 30	Min 25	Min 30
Density (at 20C)	kg/m3	0.660-0.687	0.660-0.687		0.665-0.686
Moisture	mg/kg	50	Max 100		Max 100
Bromine Index	mg Br/100g	Max 50	Max 10		Max 5
Refractive Index		1.3750-1.3840	1.3750-1.3840	-	1.373
Copper Strip Corrosion for 3 hrs at 50 C			<1	<1	<1
Doctor Test		-	Negative	-	Negative
Distillation Range					
Initial Boiling Point	C	65	64	50	59
Final Boiling Point	C	69	70	120	63
Residue on evaporation	mg/100ml		5	5	1
Components					
N-Pentane		-	-	-	Max 1
N-Hexane	wt%	Min 40	Min 44		Max 5
IsoHexane	wt%	30-45			Min 95
Methyl Cyclo Pentane	wt%	Max 20			
Cyclo Hexane	wt%	Max 3			
Benzene	ppmwt	Max 500	Max 3		Max 100
Aromatics	ppmwt		Max 10	Max 3500	
Lead as Pb	mg/kg	Max 1	Max 1		
Tota sulfur	mg/kg	Max 5	Max 2		Max 1

Table 1: Specifications for C6 Products

Why Dividing Wall Columns offer better revamp options :

Wall Columns (DWCs) have gained popularity both in grassroots and revamps in petrochemical industry. The technology works on refurbishing of conventional distillation columns, which are the most energy intensive areas of refining and chemical industries. Use of this technology has made facilities reap maximum benefits and of late many revamps are being taken up by the refineries to harness the benefits of DWC in areas which were bottleneck otherwise.

Revamps of conventional columns to DWC can reap the following benefits :

- Ideal alternative for revamp of side cut columns when high purity is required from the three product streams.
- Lower foot print as equipment count is reduced by half.
- Equipment turnaround time and other miscellaneous expenditure are reduced.
- The operational and capital expenditure are reduced by approximately 20-50%.

Structurally from outside a dividing wall column looks like a conventional distillation column but inside they have a defining wall in the column to separate the tower into two sections. Different fractionation zones are created in the column due to this wall. The zone in the column where the feed is introduced works to effectively separate the heaviest and the lightest key. Because this wall removes the intrinsic mixing which takes place in the conventional column by creating different separation zones, hence these columns are thermodynamically more efficient in comparison to their counterparts hence benefit in terms of operating cost.

Dividing wall column in DIH vs new column post DIH for producing FGH.

As demand of C6 products surged the refineries could foresee an additional source of revenue and galloped to take up making FGH by the conventional route or by drawing FGH from the recycle stream by installing new FGH columns post DIH column. As in our previous discussion we could conclude that obtaining FGH through the ISOM route is more attractive than the de-aromatization route .

The usual way of obtaining FGH from the recycle stream is by installing two new columns post DIH column. Figure 4 shows the typical configuration of producing food grade hexane by DIH route. In this process a new FGH column is installed after the DIH column so as to divert the mid cut/recycle stream to this column. The next column in series, receives the top cut of the previous column and gives two cuts, one of which is the FGH stream and other is the recycle to the reactor.

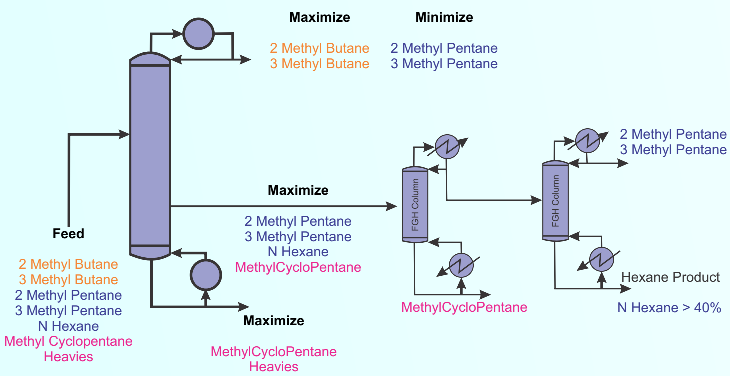

Figure 4: Typical Configuration for producing Hexane Products in Industry using conventional sequence of columns

This route when compared with revamping DIH column itself using divided wall scores less as it involves capex of two columns, it has a requirement of more plot space and also has higher operating cost in terms of steam consumption per ton of FGH produced. This way of producing FGH though brings additional revenue to the refinery but viability of the project on account of above cons pushed this revamp to take a backseat. Also the facilities who had already taken up this route of making FGH looked forward to make FGH by revamping the DIH column by using dividing wall column technology so that they could at least save on the operating cost.

For the facilities the revamp of DIH column to divided wall column can be of immense benefits. The existing DIH column can be revamped to a dividing wall column to produce four cuts ie the DIH can give light and heavy isomerate as top and bottom products, along with FGH and the recycle stream as other two cuts. This option is explicitly described in the figure below showing how a middle dividing wall column takes care of the overlap of the heavy isomerate and the recycle stream as it reduces the number of stages required for the desired specs in comparison to the conventional column and these spare stages are available in obtaining the fourth cut .

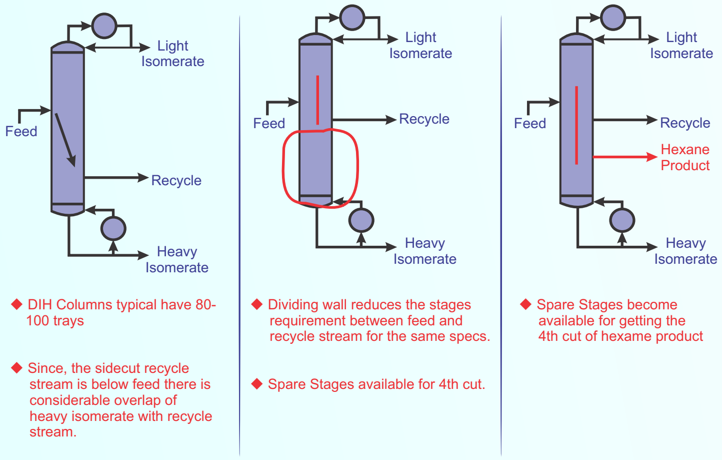

Figure 5: Use of DWC Technology for revamp of Deisohexanizer

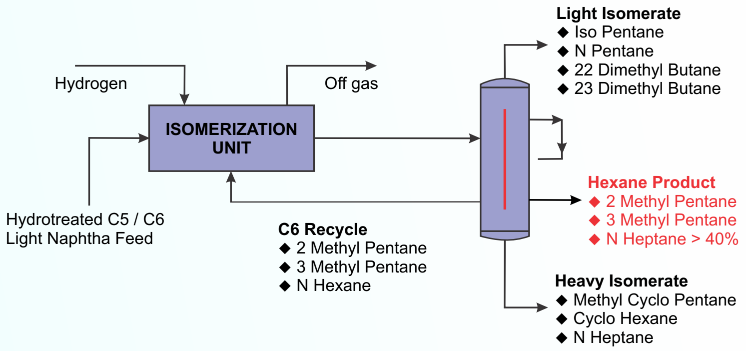

Figure 6: Hexane Production in Isomerization Unit using DWC Technology

This option of getting four cuts from the DIH column is not only attractive in terms of lower capex and opex but is flexible enough as the column is capable of operating in two modes i.e. the FGH Mode in which is column will produce a fourth cut i.e. Food grade Hexane and the DIH Mode in which the column operates on the a conventional mode with recycle to Isom Unit and there is no FGH Production. For producing the fourth cut the alignment of the wall inside the column is customized so as to meet the desired product specs, quantities and simultaneously targeting on minimizing the heat loads. This process advantages are enough to prompt the facilities to take up such processes for beneficial production of FGH.

Figure 6 shows the process flow and the components of the four cuts of the DIH column post revamp. The benefits can be summarized as below:

- There is a balance between FGH Production and Maximization of RON
- With the drawing of FGH i.e. n-hexane from the recycle stream as the fourth cut, the recycle rate to the Isom reactor is reduced. This helps in pushing more feed through the reactor and is helpful in capacity augumentation.

Case Study : Studies have been done for a refinery in Asia and the use of this technology in production of food grade hexane shows immense benefits in terms of following analysis. The unit in concern has light naphtha isomerization unit which produces 30t/hr of isomerate with octane value of 88.0 RON. In the case study done for the unit which was limited to economic analysis of DIH column and its associated equipment (condenser & reboiler) helped in drawing the following conclusions :

- Revenue increased by producing high value hexane products
- The RON of isomerate products remains unchanged.
- The isomerization unit can process an additional 8-15% of light naphtha feed without any modifications to the isomerization units
- Typical project payback is 2-10 months.

Analysis on cost basis and typical payback for the unit are summarized in the table below stating the investments vs the total revenue post revamping a DIH column into a divided wall column for the facility in concern with the above mentioned feed rates.

Stream Factor	8000	Hrs
MP Steam Cost	20.0	$/MT
Power Cost	86.8	$/MW
Food Grade Hexane Cost	709.8	$/MT
Light & Heavy Isomerate Cost	651.6	$/MT
Deisohexanizer Feed Cost	549.3	$/MT

Table 2: Cost basis for economic evaluation

Total Project Investment	**3.4**	MMUSD
Net Renenue after revamp of Deisohexanizer Column to 4 Cut DWC	5.3	MMUSD
Payback	7.7	Months

Table 3: Project Payback

Conclusion

The refineries are forging way and looking forward to taking up the production of Food grade/pharma grade hexane through the route **of using dividing wall column technology by revamping the DIH column to a four cut column**. This is a promising venture as with only some modification in the existing DIH column in terms of the installation of divided wall and change limited to few trays the revamp can be done easily in 25 man in man out days which are typically available during the annual shutdown in the facility. As summarized in the table the payback is extremely attractive i.e. less than a year and with demands of C6 products rising this seems to be an attractive venture.