

# Dividing wall revamp boosts octane and throughput

Dividing wall column technology reduces energy and capex, but increasingly contributes to higher revenues from better products, as in this application to light naphtha isomerisation

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Economic growth and environmental awareness require refineries to produce clean, high-octane gasoline products. The octane number or RON is primarily the knock resistance measure of gasoline. It has a numerical value from 0 to 100 and primarily describes the behaviour of the fuel in the engine during combustion at lower temperatures and speeds. To take RON values to higher levels, the reforming and light naphtha isomerisation process became an integral part of refineries. Light naphtha isomerisation not only produces high octane isomerate products but it also takes care of the latest stringent gasoline specifications. Isomerisation units can handle the benzene content of the gasoline pool and most benzene and its precursors are diverted to the light naphtha fraction as the feed to this unit. The isomerisation unit saturates benzene to cyclohexane. The configuration of an isomerisation unit depends on the required RON value of the gasoline pool.

## Overview of a light naphtha isomerisation unit

Isomerisation and reforming are processes which help to improve the octane barrel of the end product by either converting straight chain paraffins to their branched isomers or by changing linear hydrocarbons into branched alkanes and cyclic naphthenes which are then partially dehydrogenated to produce high-octane aromatic hydrocarbons.

Isomerisation reactions are reversible and mildly exothermic. Conversion to iso-paraffins does not reach completion since the reaction is equilibrium governed.

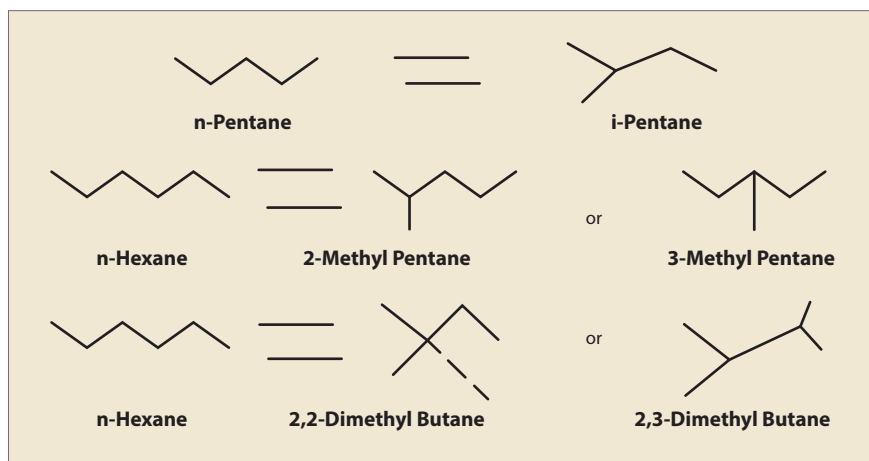


Figure 1 Primary reactions in a light naphtha isomerisation unit

### RON values of individual components in a light naphtha isomerisation unit

Component	Boiling point, °C	RON
i-Pentane	27.8	93.5
n-Pentane	36.1	61.7
2,2-Dimethylbutane	48.7	93
Cyclopentane	49.3	101.3
2,3-Dimethylbutane	58	104
2-Methylpentane	60.3	73.4
3-Methylpentane	63.3	74.5
n-Hexane	68.7	30
Methylcyclopentane	71.8	95
Benzene	80	>100
Cyclohexane	80.7	83

Table 1

The presence of other components in the feed such as benzene and naphthenes tends to raise the reaction temperature as benzene saturation and naphthene ring opening are highly exothermic, while low temperatures favour the conversion of n-paraffins to iso-paraffins. However, operating at low temperatures will decrease the reaction rate, so to overcome this a very active catalyst is usually employed.

Light naphtha isomerisation is

evaluated on the basis of the product yields and the RON of the isomerate product. The liquid product yield is determined principally by the extent of hydrocracking which takes in the isomerisation unit. Hydrocracking is an undesirable side reaction which converts light naphtha into light hydrocarbon gas molecules which are low RON components. There is an inbuilt tendency in molecules with higher molecular number such as the heptanes and above to crack and produce undesirable components.  $C_7+$  molecules are diverted to the CCR unit instead of the isomerisation unit, and benzene and benzene precursors help to manage this well.

Figure 1 shows the primary light naphtha isomerisation reactions.

The isomerisation reaction enhances the octane values of straight chain alkanes by isomerising the n-pentane ( $nC_5$ , RON value 62) to iso-pentane ( $iC_5$ , RON 93.5). Other low RON components like  $nC_6$  (RON 31) are isomerised to 2-methylpentane (2MP, RON

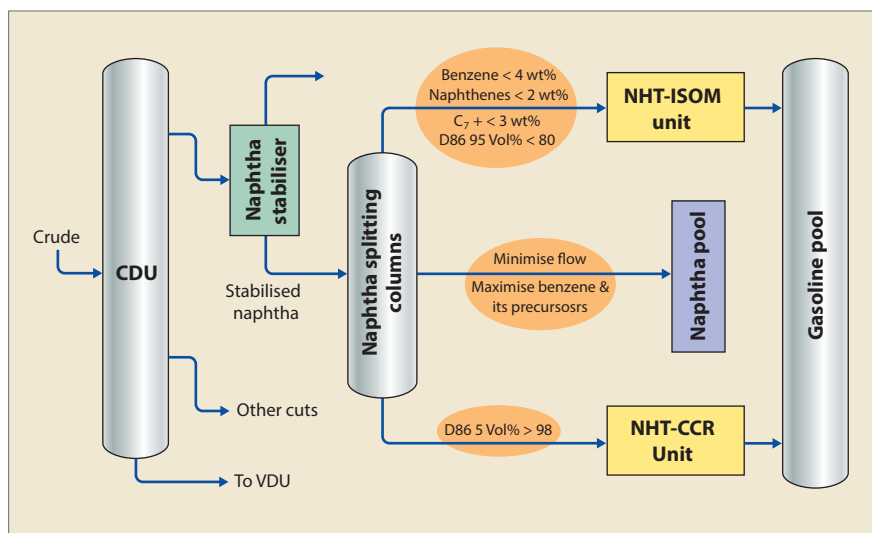


Figure 2 Typical location of a light naphtha isomerisation unit in a refinery

74) and 3-methylpentane (3MP, RON 76). These 2MP and 3MP molecules are then isomerised to 2,2-dimethylbutane (22DMB) with a RON of 94 and 2,3-dimethylbutane (23DMB) with a RON of 104. **Table 1** shows the comparative RON values of individual components in an isomerisation unit.

### Unit configurations to meet RON requirements

As isomerisation reactions are in equilibrium, various methods are used to push the reactions in the forward direction. The target RON desired for the combined isomerate product depends on two criteria, the first being removal of products from the isomerate stream and the other recycling low octane molecules from the product back to the isomerisation reactors. For this purpose, the depentaniser and deisopentaniser are installed. It can be concluded that, since the isom-

erisation reactions are in equilibrium, the product octane number is defined by the number of separation units in the process. The sequence of columns used for separation of isopentanes or isohexanes clubbed with the isomerisation unit with recycle give benefits on account of managing the equilibrium of the reactions taking place in the isomerisation unit to maximise RON. As the benchmark for RON is increased, there is an increase in reboiler duties which can be attributed to the following factors:

- Increase in RON requires a sharp separation between low and high-octane molecules due to which the reboiler load of the column increases.
- RON can also be increased by recycling low RON components back to the reactor, which increases the reboiler duties of the downstream columns.

Apart from increased opex, the

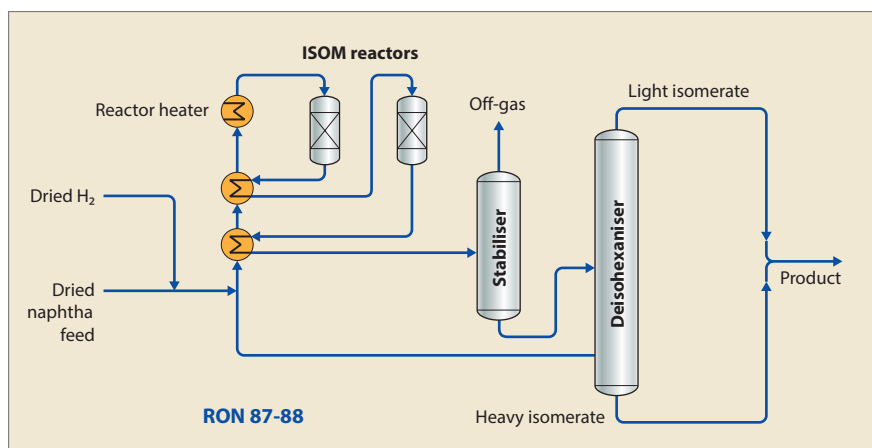


Figure 3 Typical configuration of a light naphtha isomerisation unit with hexane recycle

capex involved in deploying various columns in the process of boosting octane makes the technocrats in the facility rethink other options. Also, with facilities that have already invested in these columns, further enhancement of RON is always on the table. In this article, we will be discussing the various configurations of an isomerisation unit. **Figure 2** shows the typical location of an isomerisation unit in a refinery. The top product from the naphtha splitter with  $C_7$  less than 3% is sent to the isomerisation unit.

### Typical configurations of isomerisation units in a refinery Once-through vs hexane recycle

The simplest isomerisation units are once-through units. Fresh feed is sent to a feed pretreatment section and then passes through a series of isomerisation reactors after mixing with hydrogen gas where it comes into contact with the catalyst. The reactor effluent is sent to a stabiliser column where hydrogen and light hydrocarbons produced due to hydrocracking are removed from the top as off-gas and the isomerate is removed from the stabiliser bottoms. The RON achievable through these once-through processes is about 85.

Refineries that want to achieve RON beyond a value of 85 deploy ways to recycle low octane molecules back to the isomerisation reactor. Facilities which have an isomerisation reactor followed by a deisohexaniser (DIH) column can achieve a product RON of up to 88 by recycling a high percentage of the n-hexane, 2-methylpentane, and 3-methylpentane, which are low in RON, back to the reactor.

This is achieved by drawing the mid-cut from the DIH column. The DIH produces a light isomerate distillate product consisting of  $C_5$  and branched  $C_6$  molecules (rich in DMBs), a  $C_6$  recycle side draw, and a  $C_7+$  bottoms product. For a recycle stream at 60% of the fresh feed, an octane increase of several points is achieved compared to the once-through operation. Typically, one can expect a RON increase from 83-84 to 87-88 with DIH column hexane recycle to the isom-



# Rewriting the fate of your refinery

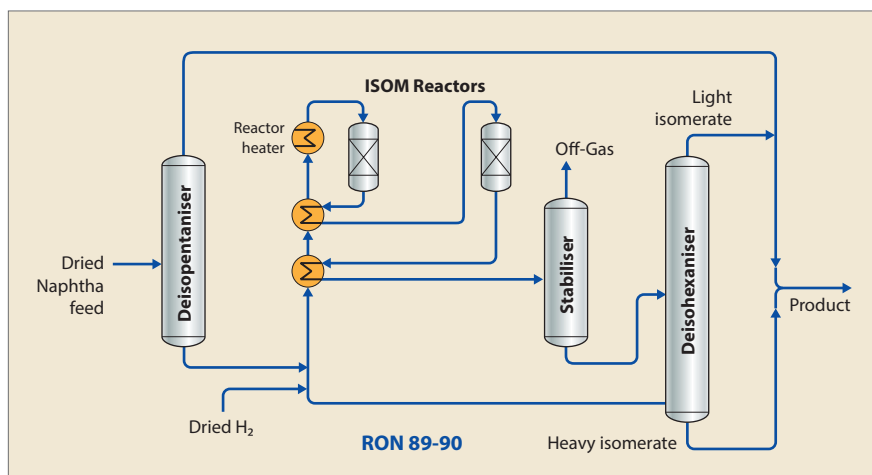
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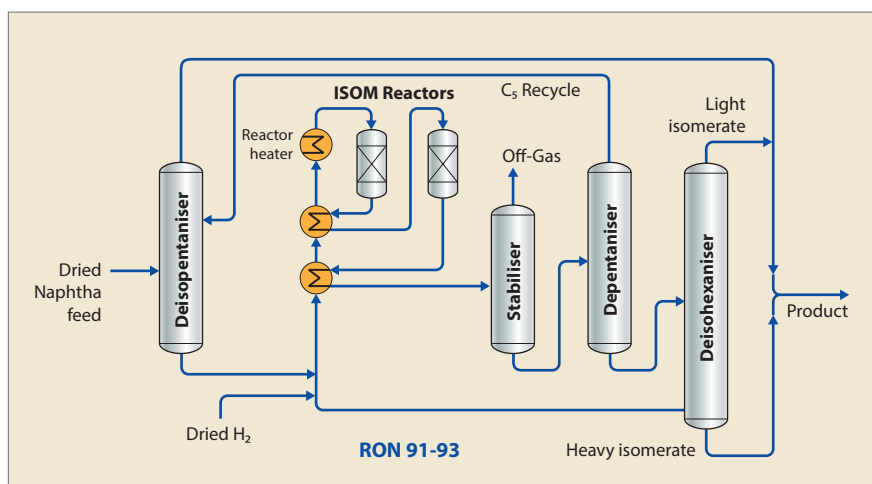
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**Figure 4** Typical light naphtha isomerisation unit with hexane recycle and deisopentanised feed



**Figure 5** Isomerisation unit with hexane recycle, deisopentanised feed, and C<sub>5</sub> recycle

erisation reactor. **Figure 3** shows a typical configuration of a light naphtha isomerisation unit with hexane recycle.

#### Isomerisation unit with hexane recycle and deisopentanised feed

Some facilities, in addition to a DIH column with recycle, have a deisopentaniser (DIP) column installed before the isomerisation reactor. This helps in achieving an isomerate product of RON up to 90. As the DIP is placed in a feed fraction-

ation section, it removes iC<sub>5</sub> from the feed as overhead distillate product, which pushes the reaction in the forward direction. The balance of the feed is sent to isomerisation reactors and the reactor effluent is sent to a DIH column to separate high octane C<sub>5</sub>/C<sub>6</sub> isomerate product from low octane C<sub>6</sub> molecules which are recycled to the isomerisation reactor. Thus the addition of a DIP increases the RON over that of a 'DIH only' configuration (see **Figure 4**).

Typical RON for various isomerisation unit configurations		
Isomerisation unit process configuration	No of column	RON of isomerate product
Once-through	Stabiliser	81-84
Hexane recycle	Stabiliser + deisohexaniser	87-88
Deisopentanised feed and hexane recycle	Deisopentaniser + stabiliser + deisohexaniser	89-90
Pentane and hexane recycle	Deisopentaniser + stabiliser + Depentaniser + deisohexaniser	91-93

**Table 2**

#### Isomerisation unit with hexane recycle, deisopentanised feed, and C<sub>5</sub> recycle

Unconverted n-pentanes with RON values as low as 61 are sent to the DIH distillate and thus become a part of the final isomerate product. For full conversion of all normal paraffins, recycling is required via a depentaniser (DP) installed before the DIH column. This helps to make a sharper separation between the DMB-rich C<sub>6</sub> isomerate product and the iC<sub>5</sub>/nC<sub>5</sub> recycle stream. The DP column removes iC<sub>5</sub>/nC<sub>5</sub> as an overhead distillate product upstream of the DIH and recycles it back to the deisopentaniser column, which in turn separates iC<sub>5</sub> as the high RON top product, and nC<sub>5</sub> is recycled back to the reactor via bottoms product. This again helps in pushing the equilibrium reactions in the forward direction. The configuration (see **Figure 5**) improves RON up to 93.

**Table 2** shows how the introduction of DP/DIP/DIH columns in the isomerisation loop in various combinations, clubbed with the type of process employed, impacts the achievable RON.

#### Developments in dividing wall column technology applied to isomerisation

Advances in distillation play a key role in minimising the costs of new and revamped projects in a refinery. Dividing wall column (DWC) technology had limited acceptance 20 years ago but is now reshaping our distillation processes. DWC technology is increasingly used to modernise conventional distillation sequences, especially in revamps of existing units. Besides energy and throughput improvements, a DWC revamp significantly improves the performance of downstream units.

The alignment of the dividing wall inside the column plays a dominant role in the selection of DWC for a particular separation. The middle DWC is an ideal alternative for side cut columns, which helps to increase throughput and gives better product specifications. The top DWC provides an additional source of heat integration

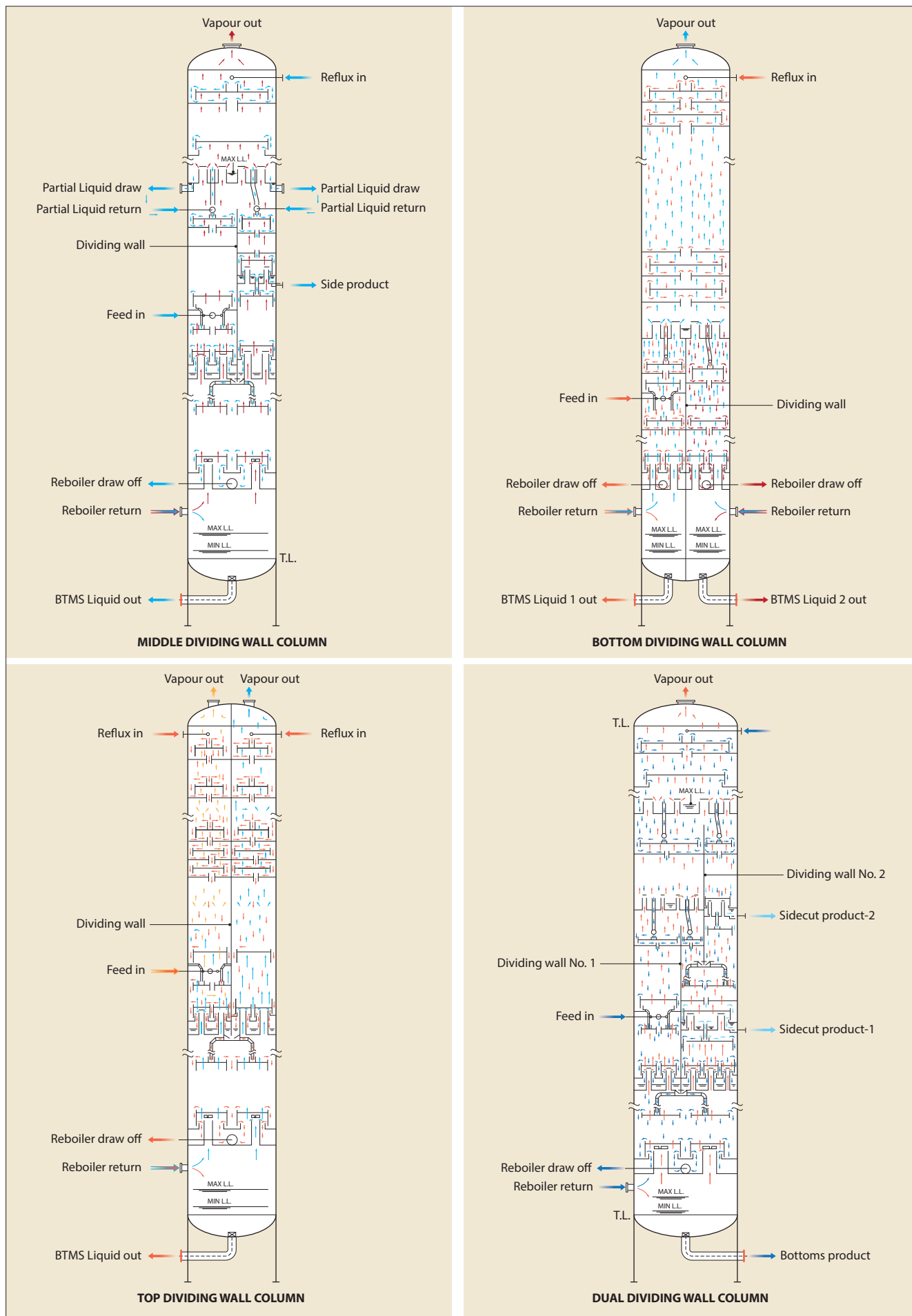
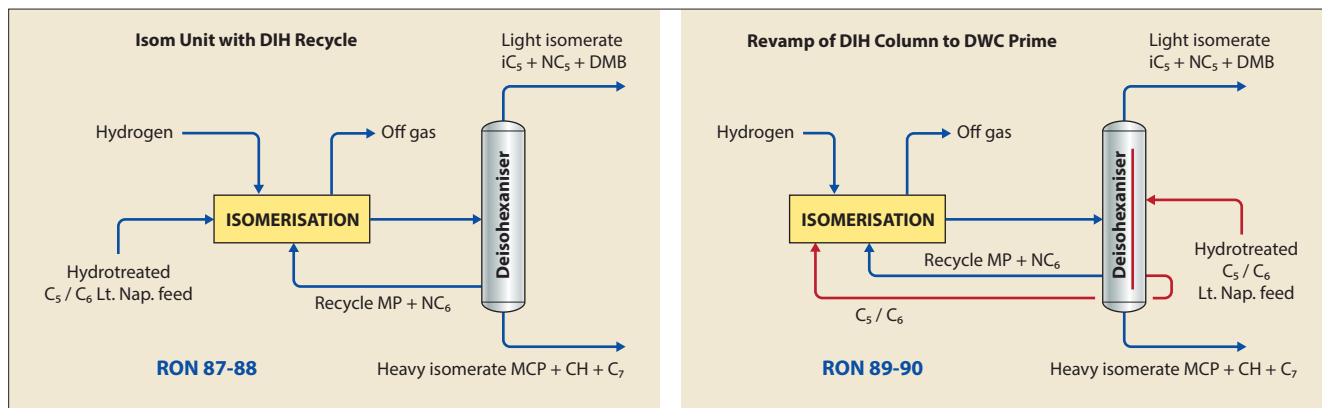


Figure 6 Elevation of commonly used dividing wall columns Source: DWC Innovations



**Figure 7** Revamp of a DIH column to DWC in an isomerisation unit with hexane recycle

with other process streams. On the other hand, the bottom DWC has the advantage of replacing a two-column arrangement in an indirect sequence.

The latest advance in DWC technology is dual wall dividing columns which are known to have a higher thermodynamic efficiency than their counterparts. From the outside, it is no different from a simple DWC but has the capability to deliver four or more high purity products from a single column. As dual wall columns are robust, flexible, and easy to operate, this technology has become viable. **Figure 6** shows the elevations of commonly used DWCs.

### Revamp of a deisohexaniser column using DWC technology

DWC technology plays a key role in enhancing the performance of isomerisation units. Facilities that want to improve the RON of the final isomerate find divided wall column technology lucrative as this involves only the deisohexaniser (DIH) column being revamped, so as to include the additional func-

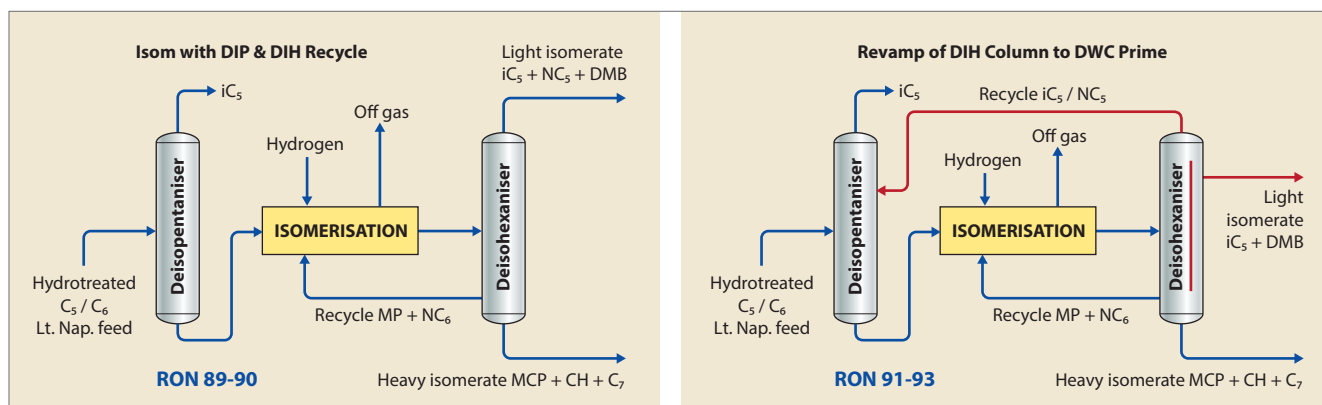
tionality of DIP or DP columns as the case may be. Besides enhancing separation, DWC revamps provide considerable energy savings when compared to conventional distillation column flow schemes. The use of DWC technology in an isomerisation unit not only targets improvement in RON but brings the added advantage of increased throughput which would otherwise require installation of new columns. The remaining part of this article focuses on the applications and outcomes of revamping the DIH column in various configurations.

### Application of DWC in isomerisation units with hexane recycle

The DIH column recirculates unbranched molecules, mainly n-hexanes and methylpentanes, after removal of branched, high-RON molecules back to the isomerisation reactor. The top product, the light isomerate, contains mainly isopentanes, dimethylbutanes, and methylpentanes. The less the amount of methylpentanes going to the top product, the better the

RON value of the final isomerate. Although this configuration definitely gives a higher RON than a once-through process, the RON can be further increased by recirculating methylpentanes back to the reactor. Also, separation of isopentanes present in the fresh feed going to the isomerisation reactor contribute to higher RON values. The isopentanes present in the fresh feed take a free ride in the isomerisation reaction process and restrict the forward reaction to produce more branched chain components. The conventional method for removing isopentanes from fresh feed is to install a DIP column upstream of the isomerisation reactor.

The revamp of an existing DIH column to a DWC enables it to have the dual functionality of a deisopentaniser. Hydrotreated naphtha is first sent to the revamped DIH column which now produces four sharp cuts. As **Figure 7** shows, the light/heavy isomerate and the recycle are managed in a way similar to that before the revamp, while the fourth cut is the fresh feed to the isomerisation reactor without iso-



**Figure 8** Revamp of a DIH column to DWC in an isomerisation unit with hexane recycle and deisopentanised feed

Performance of an isomerisation unit after revamp of a DIH column to DWC

No of columns in isomerisation unit configuration	RON of existing isomerisation unit	Performance of isomerisation unit after revamp of deisohexaniser column to dividing wall column		Remarks
		RON	Increase in throughput	
Stabiliser + deisohexaniser (DIH)	87-88	89-90	10-20%	Existing DIH column performs dual functionality of hexane recycle & deisopentaniser after the revamp to DWC
Deisopentaniser (DIP) + stabiliser + deisohexaniser (DIH)	89-90	91-93	5-10%	Existing DIH column performs dual functionality of hexane recycle & depentaniser after the revamp to DWC

Table 3

pentanes. This is an attractive and lucrative scheme as a DWC revamp of a DIH saves the installation of a DIP column, though offering the same benefits.

The advantage of this revamp is a boost in RON to 90, from 87 previously, along with a fresh feed increase of 10-20%. **Figure 7** compares a conventional DIH to a post-revamp version converted to a DWC configuration unit with hexane recycle.

A conventional configuration of an isomerisation unit with hexane recycle and a DIP column can attain a RON close to 90 as the presence of the DIP column helps remove most  $iC_5$  before the reactor which in turn affects the reaction equilibrium in the forward direction. But to achieve RON values beyond this number, unreacted  $nC_5$  needs to be recirculated back to the reactor. The DIH column in the conventional configuration is not able to restrict  $nC_5$  going to the light isomerate, hence maximum conversion of  $nC_5$  to its high-octane isomer is not achieved. Also, because some portion of  $nC_5$  becomes a part of the light isomerate this affects the RON adversely. By revamping the conventional DIH column to dividing wall, more of the sharper cuts can be obtained and the RON of the isomerate can be improved further.

**Figure 8** shows that, to improve the RON of the final product further, the DIH column is revamped to a DWC so as to draw four cuts from the column. The light and the heavy isomerate are combined and sent to the gasoline pool, while the third cut is recycled to the reactor in a manner similar to the conventional scheme. The fourth cut drawn from the DIH column primarily consists of  $iC_5$  along with unreacted  $nC_5$  which is recycled back to the DIP column. The deisopentaniser column removes isopentanes from the fresh feed along with the recycle stream from the revamped DIH column. The bottoms of the DIP column are rich in straight chain components and are routed to the isomerisation reactor. The revamp of a DIH column in this configuration provides the dual functionality of a DP column and helps in achieving a RON of 91-93 in the final isomerate product.

**Table 3** summarises the benefits of DWC technology for various isomerisation configurations.

## Conclusion

The benefits of DWC technology have grown beyond reduction in energy consumption or capex. Refineries are using DWC technology for maximising revenue from newer or better products. It is increasingly used in debottlenecking existing units in the refinery. Light naphtha isomerisation is one such example, in which the simple revamp of a DIH column improves the unit's performance by improving RON along with an increase in throughput.

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