WHITE PAPER

CARBON DISULFIDE REMOVAL TO MEET NEW SPECIFICATIONS FOR PETROCHEMICAL NAPHTHA USING DIVIDING WALL COLUMN TECHNOLOGY

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Background for Surge in Petrochemical Demand

In the era of unprecedented competition refineries have to continuously explore new opportunities in order to sustain and grow. Apart from energy integration of upstream and downstream operations the other option is finding out ways to divert the available feedstock into more marketable and in demand products. Some variations listed below in the existing facilities can help in improving profit margins of the facility.

- Focussing on refining and petrochemical integration
- Exploring options of feedstock flexibility
- Exploring options on energy integration
- Adding on existing petrochemicals manufacturing capacity

The downhill trend of transportation fuel demand is the main driver for closer integration between refining and petrochemical assets. Considering this scenario, the alternatives capable of minimizing the naphtha production to gasoline is an attractive way to ensure higher value addition. With new stringent laws governing the global scenario with newer version of vehicles having better fuel efficiency on road combined with growing market of electric vehicles, the market of conventional fuel is bound to show a downward trend. There is the opportunity and space to use the feed stocks to make raw materials which can produce lower cost products like ethylene which is the most widely used monomer in the petrochemical industry, along with other petrochemicals like benzene, toluene, paraxylenes etc.

Over the past few years, global ethylene demand has grown rapidly which has provided enough impetus for many facilities globally in augmenting with new ethylene capacity in house or in market, so diversifying to petrochemical Naphtha has made sense. As a consequence of this many countries have seen their facilities invest heavily in new cracker projects too. Due to the expected significant growth in the petrochemicals demand in the coming times the facilities are working on calculated integration of petrochemical assets in order to improve their refining margins and ensure participation in a growing market too. Petrochemical Naphtha can be converted into the following compounds which has varied uses; some of which are listed below:

- **Ethylene** is commonly used to make different types of films and plastics. It can be found in cleaning agents such as detergents as well as lubricants.
- **Benzene** is used to make nylons which are helpful in the packaging industry.
- **Paraxylene** is the raw material in large scale synthesis of various polymers.
- **Propylene** is used to produce polypropylene plastics for injection molding and fibers and for manufacturing cumene.

Challenges in diversifying to Petrochemical Naphtha (PCN) & presence of CS2

Though shifting to petrochemicals not only requires changes in the existing setup but there are more challenges to be faced mainly because of compliance with the strict specifications of petrochemicals. The crude oil refining processes in the facilities have to cater to crude feed with lesser impurities as compared to the Petrochemical Naphtha so are designed accordingly. Typically, the petrochemical grade naphtha is composed of the lighter fraction of straight run naphtha wherein a cause of concern is the stringent compliance of carbon disulphide (CS2) content in it. Though it was recognised early that carbon disulphide is a potent poison to the catalysts used in petrochemical processes (Ziegler-Natta) but off late this norm has become more stringent after realizing the irreversible damage it does to the catalyst.CS2 is also known to induce fragility and imperfections in the polymeric chain, primarily in isoprene which is an intermediate to rubber production.

Lighter fraction of naphtha carries most of the CS2 because of the temperature range in which the boiling point of CS2 lies. Moreover, the higher chemical stability of CS2 makes it stable to steam cracking process and this helps it staying in there. Because of these reasons, controls of the CS2 in petrochemical grade naphtha has been a cause of concern and needs to be managed very wisely. The various sources which contribute to the CS2 in petrochemical Naphtha are listed below:

- Crude Oil Reserves
- Natural Gas Liquids
- Refinery Processes
- Shale Fracking Solvents

The reason for CS2 entrainment in crude can be multiple, one being the ageing of wells wherein to counter the extraction difficulties due to presence of hydrogen sulphides and heavy metals amines, formaldehydes are used. These additives have tendency to react with the crude oil and form complexes which eventually crack and release CS2. Sometimes the presence ofCS2 is directly related to the naphtha source also.

More insight into catalyst deactivation with CS2

It has been observed that H2S has the strongest poisoning effect and CS2 has the second strongest. The strong poisoning effect of CS2 has been confirmed in industrial units and the presence of a few ppm of CS2 in the feed, a reactor temperature is required to be increased to compensate the catalyst deactivation. With CS2 present in the feed above the defined specifications the catalyst activity shifts from from the top part of the catalyst bed to the bottom part. This is strong evidence enough to show that CS2 has a strong impact on catalyst activity and the top bed deactivates even with a few parts per million of CS2.

It is seen that CS2 acts as a strong inhibitor for the palladium-based catalyst. Many pygas unit operating with a nickel-based catalyst have also observed that the catalyst is poisoned in presence of CS2 and a specific catalyst treatment is required to recover its activity back. It is seen that the nickel-based catalyst can tolerate CS2 contamination in the range of 10-20 ppm with mild temperature elevation as compared to palladium catalyst. But with further increase in CS2 level they also tend to be poisoned. However, aspalladium-based catalyst is more active than a nickel catalyst and it recovers its activity more easily without any specific treatment as soon as feed conditions come back to their initial level with CS2 in specified range. On the other hand, the residual activity of nickel catalyst becomes low with CS2 poisoning and its impossible to recover the initial activity once it had operated with feed containing a high amount of CS2. Thus, while keeping in pace with the growing demand for petrochemicals technocrats face greater technological challenges because of the stricter specifications of petrochemical derivatives in comparison with transportation fuels.

Processes for producing Petrochemical Naphtha:

When facilities were finding ways to diversify looking into the downhill side of the fuel market, producing Petrochemical naphtha came up as a lucrative option. Petrochemical Naphtha is light naphtha without CS2 and as it tends to concentrate in the light fraction of naphtha only, light Naphtha has to be treated for CS2 removal. Mostly in refineries across the globe, Naphtha splitter separates full range naphtha into heavy naphtha which is routed to the CCR unit while the light naphtha which is primarily used as fuel is mostly upgraded to a higher RON through the process of isomerisation. Chemically light naphtha is the fraction which boils between 30 °C and 90 °C and consists of molecules with 5–6 carbon atoms while the heavy naphtha boils between 90 °C and 200 °C and consists of molecules with 6–12 carbon atoms.

Petrochemical Naphtha typically has an IBP of 40°C and FBP of 130°C.With light Naphtha being converted to Petrochemical Naphtha(PCN) by processes which help in removal of CS2,it caters to making of ethylene. Steam cracking helps PCN to get converted to ethylene which is the raw material for most of the plastics; other route being use of ethane and propane as the feedstock. Table 1 below shows the typical specifications of Petrochemical grade Naphtha where the CS2 specification is as low as 1-2 ppm.

Ways of CS2 removal in PCN and challenges

***CS2 removal by Naphtha Hydrotreating unit*:**

Naphtha hydrotreating unit is an important unit in the refinery which performs hydro-desulfurization (HDS) of hydrocarbon feed. It is used in petroleum refining to remove sulfur and nitrogen compounds from natural gas and other refined petroleum products like diesel, gasoline, and jet fuel. The is the first choice of facilities when it comes to removal of CS2 from naphtha subjected to the availability of processing. The process flow diagram for a typical naphtha hydrotreating unit is shown in figure 1.The unit operates in presence of hydrogen wherein CS2 is converted into H2S according to the following reaction. The effluent is routed to a stripper from where the H2S produced is recovered from the top product and send to the sulphur recovery unit.

$$CS_2 + 4H_2 \rightleftarrows CH_4 + 2H_2S$$

Table 1: Specifications for Petrochemical Naphtha

S.no.	Parameter	Specification	Std. Method	Typical Analysis
1	Colour, Saybolt	Plus 30	ASTM D 156	Plus 30
2	Density @ 15 deg. C, kg/m^3, Max	700	ASTM D 4052	690
3	***Allowable CS2 in ppm***	***1-2 ppm***		***1 ppm***
4	Total Paraffins, % by Vol, Max	60-65*	ASTM D 5134	65
5	Olefins, % by Volume, Max	1.0	ASTM D 5134	<1.0
6	Aromatics, % by Volume	10-12	ASTM D 5134	10-12
7	Napthenes, % by Vol, Max	By Balance		By Balance
8	ASTM Distillation		ASTM D 86	
	IBP, ^{0}C	Report		40
	FBP, ^{0}C, Max	130		130

The figure below shows the hydrotreating unit in operation which typically receives feed which is the top product of the Naphtha splitter. This is premixed with hydrogen before routing it to the hydrotreater reactor which converts the sulphur present in the feed into H2S and gives product which is free from sulphur.

***CS2 removal by Physical Adsorption*:**

Another processing route to control the CS2 content in the petrochemical grade naphtha is the physical adsorption. For adsorption process to be effective the contaminant concentration and temperature are important parameters. As these processes are fixed bed type, continuous regeneration is needed. This makes the process opex intensive as well as tedious and for reasons mentioned, technocrats look forward to process which are less opex and capex intensive and help in attaining the desired purity of PCN.

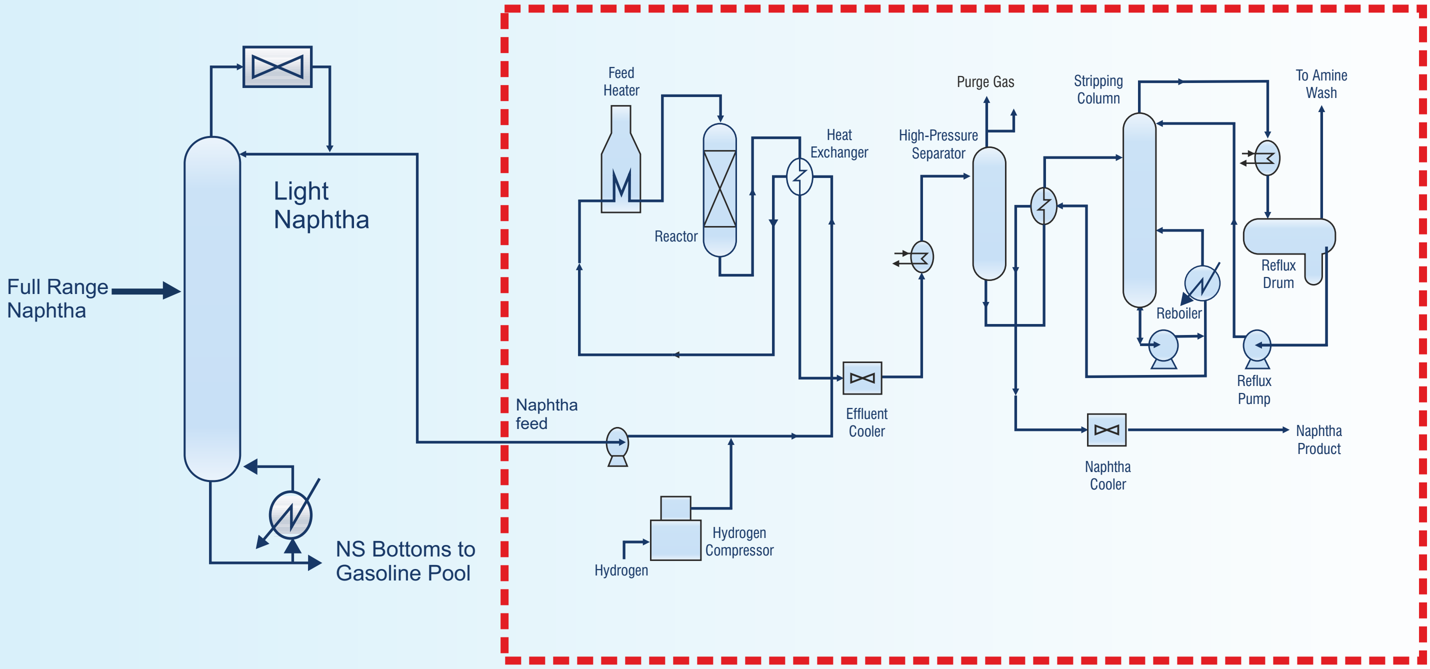

Figure 1: CS2 Removal by Hydrotreating Unit

Though hydrotreating is process of choice when it comes to attaining the desired specification with respect to the CS2 content in the Petrochemical Naphtha but only in case when the facility has the available capacity in the hydrotreating unit along with surplus hydrogen. In refineries where the existing hydrotreating units are already bottlenecked, treating light Naphtha by this route becomes very capital intensive. Also, a big reason for facilities not considering the hydrotreating of petrochemical grade naphtha because this stream is otherwise low in contaminants and for this reason going through this process brings in substantial rise in the operating costs.

CS2 removal by Distillation

As CS2 has a boiling point higher than C5's and lower than C6 hydrocarbons; CS2 can be effectively removed along with C5's via distillation. Though an accurate thermodynamic model is required to predict the behavior of CS2 in PCN but still it is another promising and interesting method for removal of CS2 from PCN. As distillation takes the advantage of the boiling point of CS2 lying between isopentane and hexane it is possible to use distillation and obtain three cuts from the column. By this isopentanes and normal pentane carry most of CS2 while PCN which is withdrawn as the bottom cut will have minimal amount of CS2. Table 2 provides boiling points of components in a typical PCN mix.

The figure below shows PCN production using the distillation method. Though distillation is an effective way to reduce the CS2 content, but employing conventional distillation methods have their own set of limitations:

- High energy consumption in order to get desired PCN specifications
- Top product is predominantly a mix of IC5/NC5.
- Low RON, blending into gasoline pool will lower the overall RON

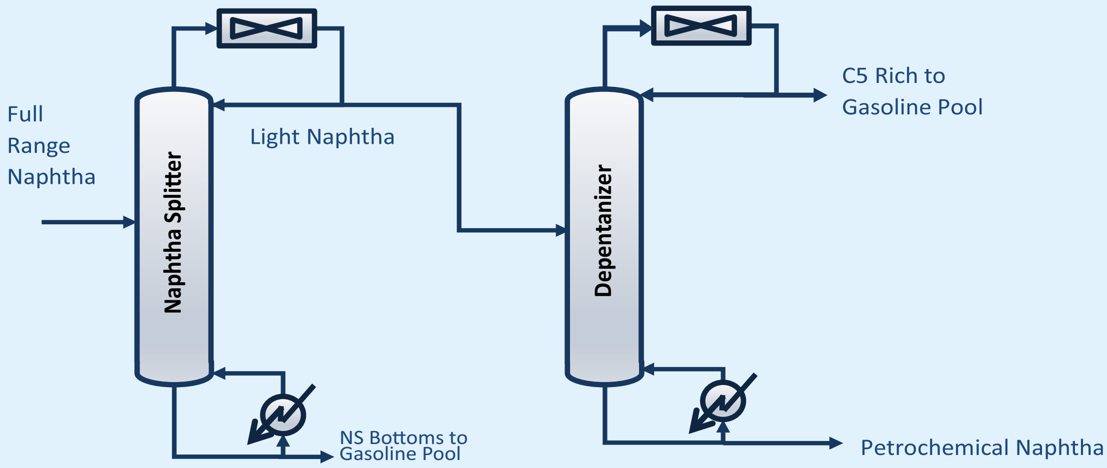

Figure 2: Conventional Distillation scheme for obtaining PCN

Table 2 : Boiling point of components in PCN mix

Typical Components In Petrochemical Naphtha	Boiling Point ˚F
ISOBUTANE	10.9
N-BUTANE	30.2
ISO-PENTANE	82.0
N-PENTANE	97.0
CARBON-DISULFIDE	**115.3**
CYCLOPENTANE	120.6
2,2-DIMETHYL-BUTANE	121.5
2,3-DIMETHYL-BUTANE	136.4
2-METHYL-PENTANE	140.0
3-METHYL-PENTANE	147.2
N-HEXANE	156.2
METHYLCYCLOPENTANE	161.2
BENZENE	176.2
CYCLOHEXANE	177.4
2,2-DIMETHYLPENTANE	174.2
2,4-DIMETHYLPENTANE	176.9
2,2,3-TRIMETHYLBUTANE	177.8
3,3-DIMETHYLPENTANE	186.8

This bottleneck of the conventional distillation schemes was addressed by technocrats who developed new models including the Hybrid schemes by the use of Dividing wall column technology which was implemented successfully in one of the facilities in South east Asia, the case study of which will be put up later in the article.

Why Dividing wall columns:

Off late process optimization techniques specially the Dividing wall columns technology have been found useful to improve the overall profitability through process intensification and optimisation. This is done for better product specifications, decreased energy consumption or capacity augmentation through robust simulation models and engineering. Dividing wall columns have provided an effective way to reinvent age-old distillation methods and offer the benefits of lower capital investment along with lower operational cost when compared to their conventional counterparts. This is a highly adaptable technology in which either a single wall or multiple walls can be installed inside the shell according to the process requirement. The benefits of this technology can be summarized as:

- It can separate the feed into three or more high purity streams from a single column in a sequential distillation.
- 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.
- The operational and capital expenditure are reduced by approximately 20-50%.

It is interesting to see how dividing wall column overcomes the limitation of conventional distillation sequences by adding single or multiple walls that create different fractionation zones inside a single column shell. These walls aim to reduce the intrinsic remixing of components that occur in conventional columns, so higher thermodynamic efficiencies are achieved.

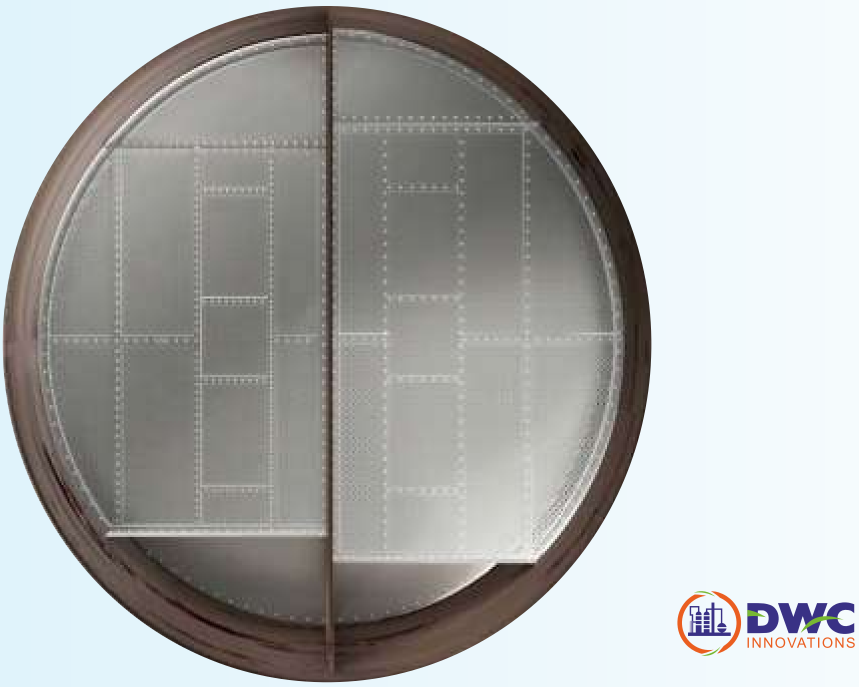

Figure 3A :Top view of dividing wall column. . (Image courtesy of DWC Innovations)

Figure 3B : Dividing wall being installed during a revamp of a conventional column in South East Asia. (Image courtesy of DWC Innovations)

Use of Dividing Wall columns to obtain PCN with iC5 rich stream

In context of the discussed processes and their limitations dividing wall columns are process of choice because they not only are low in capex and opex, but can seamlessly obtain the desired specifications of PCN along with other value-added products like High RON as the top product. One such process scheme is provided in figure 4, wherein the side cut from revamped DWC is diverted to naphtha or gasoline pool.

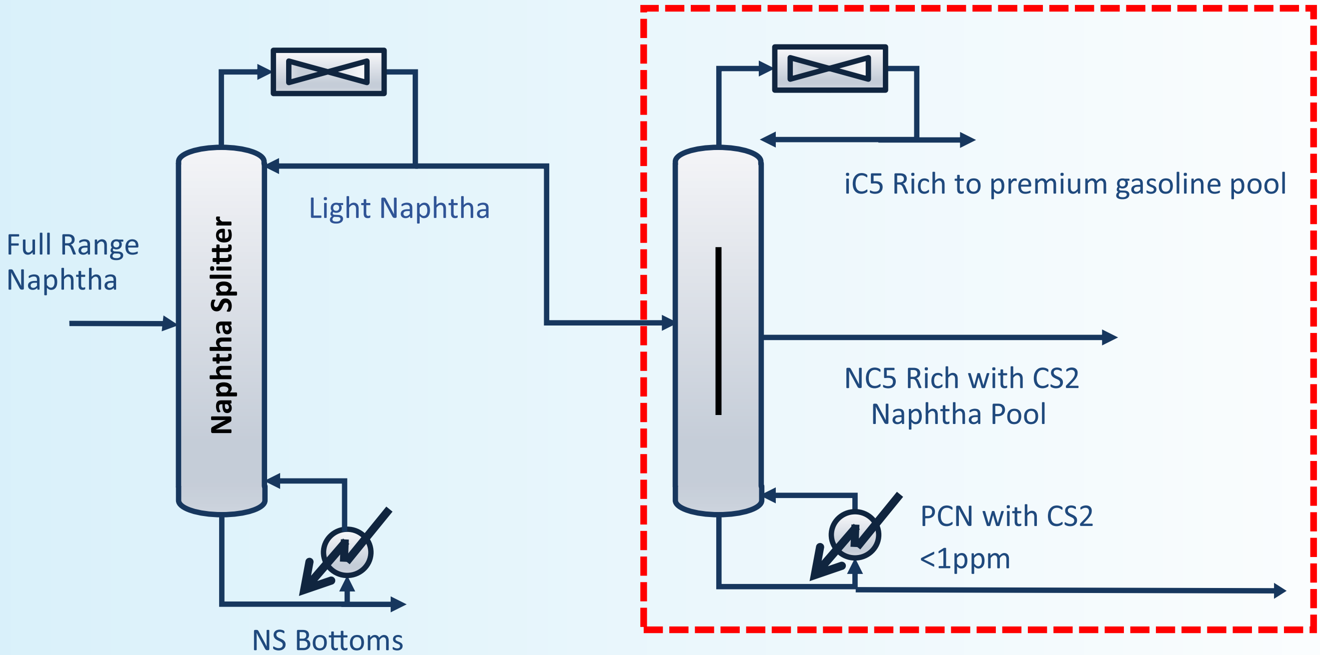

Figure 4 : Flow scheme after revamp of Depentanizer into dividing wall column. The C5 rich sidecut with concentrated CS2 is diverted to naphtha / gasoline pool.

The benefits of revamping the depentanizer column into a dividing wall column can be summarized as:

- Meets CS2 limit in PCN
- No additional load on NHT unit
- Produces premium gasoline improving profitability
- Energy consumption offset by improved margin from producing premium gasoline.
- Retrofits into existing columns.

Case Study incorporating the Hybrid Model

This client in South east Asia was looking forward to major diversification. They were able to identify huge demand to produce PCN keeping in mind the CS2 specification of less than 1 ppm. They could visualize the added benefit to this revamp that was the production of premium gasoline, a stream of 90% iC5 which could be obtained as the top product from the depentanizer column. As most of the CS2 would become a part of the midcut drawn from the column this stream could be either routed to the Naphtha pool or treated in the NHT unit as per the requirement which inturn would offload their NHT unit.

The objective of revamp could be put down as :

- Maximum recovery of i-C5 (> 90 wt%) in overhead product.
- Side cut product would be nC5 with majority of CS2
- Bottom product would be PCN with *CS2 less than 1 ppm*

In their existing configuration at the facility where the full range Naphtha was routed to a series of two columns ie a Naphtha Splitter and a Depentanizer column to get C5 rich and C6 rich streams as top and bottom products. The C5 rich stream was routed to the gasoline pool while the C6 rich was send to the Naphtha pool. The client had an option of proceeding in conventional way by installing a new column after the second column or convert the second column into a side cut column. Both the options were rejected as one of them was Capex intensive while the other would not be able to achieve the desired quality of the product.

The technocrats at the facility decided to take up the revamp by incorporating the *Hybrid Model* by the use of dividing wall column technology. Any facility which takes up this route of obtaining PCN, has to options to choose from:

- Routing the midcut from the column which is mainly NC5 carrying majority of CS2 to the Naphtha /Gasoline pool where it can be put to the desired end use. This option does not put any additional load on the NHT unit. (Figure 3)
- The second option is routing the midcut to the NHT unit to strip of the CS2 contained in it in form pf H2S and mix this stream again with the PCN stream which is the bottom product of the depentanizer column. This in turn increase the production of PCN further.(Figure 5)

The client decided to revamp the depentanizer column to a dividing wall column so as to produce three high purity cuts as discussed. It achieved the desired CS2 specs of PCN wherein the CS2 content remained between 1-2 ppm. The NHT unit was debottlenecked as after the revamp only the midcut which carried majority of CS2 was routed to the NHT unit as shown in the figure below.

The facility also had additional revenue on account of obtaining iC5 rich stream as top product which is sold as premium gasoline. The successful performance test for the revamp was completed in end of 2021. The figure 5 shows the configuration at the facility after the revamp.

The product specifications after the revamp to DWC is summarized in the table below:

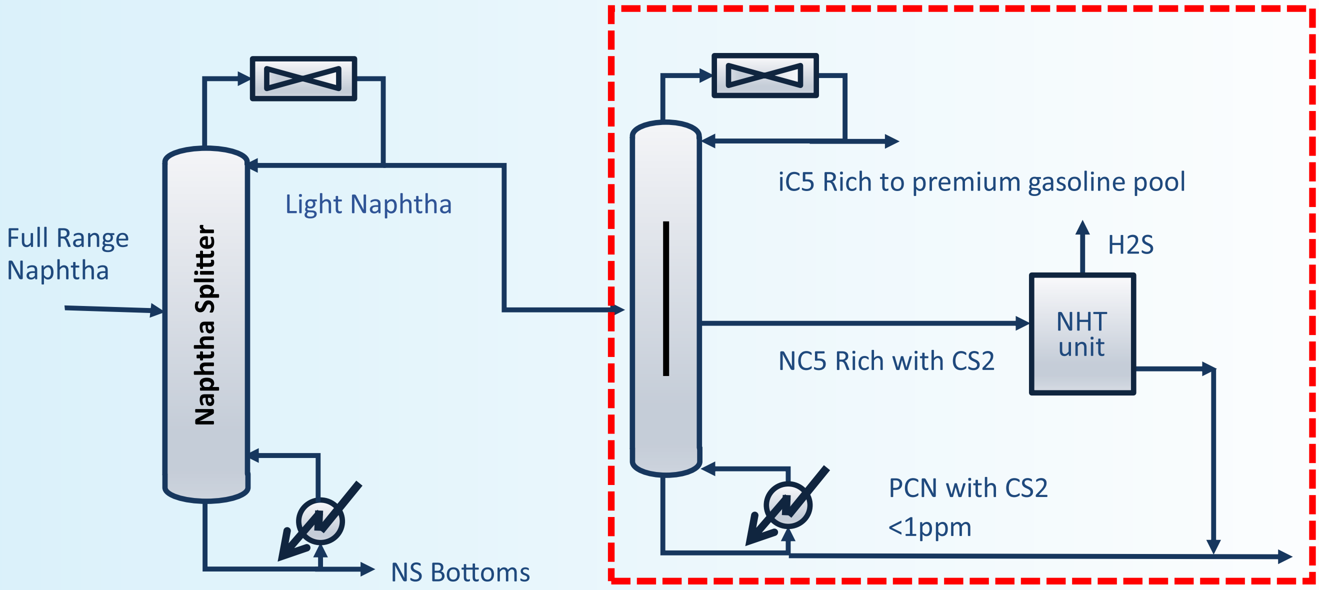

Figure 5 : Flow diagram after revamp of Depentanizer into dividing wall column

Table 3: Product specs after revamp to DWC

Stream Description	Feed	IC5 Product	C5 sidecut mix	Bottoms Petrochemical Naphtha
Total Flow, kg/hr	194,000	18,887	49,952	125,162
Composition (Mass%)				
C4 & Lighter	0.45	4.60	0.001	0.00
IC5	13.97	90.00	19.88	0.13
NC5	15.59	5.24	55.56	1.21
Others	69.99	0.11	24.54	98.66
CS2	70 ppm	100 ppm	200 ppm	<1 ppm

Conclusive Notes

In one of the many and varied applications of dividing wall column technology, its use to obtain PCN with stringent CS2 specifications is less tedious as well as an economically viable route as compared to the other conventional existing ways. As dividing wall columns are robust operationally and the revamps are easy to take up, this technology has shown resurgence during the last decade. As this technology has not only paved way for finding out areas in facilities where optimisation in terms lowering capex and opex is required but has also helped in getting desired product specifications as compared to other conventional ways employed in the facility.