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Challenges with carbon disulphide removal in petrochemical naphtha

Meeting new specifications for removing carbon disulphide in petrochemical naphtha using dividing wall column technology

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

- Focusing on refining and petrochemical integration
- Exploring feedstock flexibility options
- Exploring energy integration options
- Increasing petrochemical manufacturing capacity.

Decreasing conventional transportation fuel demand drives closer integration of refining and petrochemical assets, predicating minimal production of the naphtha-to-gasoline route in favour of higher value-addition strategies and instead upgrading naphtha to ethylene and other petrochemicals like benzene, toluene, and paraxylenes.

Global demand for ethylene, the most widely used monomer in the petrochemical industry, incentivises increased petrochemical naphtha production as an important ethylene feedstock. In parallel, many countries have seen their facilities invest heavily in new cracker projects.

Due to the expected growth in petrochemical demand, facilities are working on the integration of petrochemical assets in order to improve their refining margins and ensure participation in a growing market. Petrochemical naphtha can be converted into the following compounds with varied uses, including:

- 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 moulding and fibres and for manufacturing cumene.

Challenges

Shifting to petrochemicals not only requires changes to existing configurations along with challenges faced complying with strict petrochemical specifications. Crude oil refining processes cater to crude feedstock with lesser

impurities compared to petrochemical naphtha, so they are designed accordingly.

Petrochemical grade naphtha is typically composed of the lighter fraction of straight-run naphtha, wherein a cause of concern is the stringent compliance of carbon disulphide (CS₂) in the naphtha. It was quickly recognised that CS₂ is a potent poison to catalysts used in Ziegler-Natta petrochemical processes. CS₂ is also known to induce fragility and imperfections in the polymeric chain, primarily in isoprene, an intermediate to rubber production.

The lighter naphtha fractions carry most of the CS₂ due to the temperature range in which the CS₂ boiling point lies. Moreover, CS₂ remains chemically stable in the steam cracking process. Because of these negative consequences, controlling CS₂ in petrochemical grade naphtha is a cause of concern and needs to be managed very wisely. Sources contributing to the presence of CS₂ in petrochemical naphtha include:

- Crude oil reserves
- Natural gas liquids (NGLs)
- Refinery processes
- Shale fracking solvents.

There are multiple reasons for CS₂ entrainment in crude, including the use of formaldehyde additives to counter extraction difficulties caused by the presence of hydrogen sulphides and heavy metals amines. These bespoke additives tend to react with crude oil and form complex compounds, which eventually crack and release CS₂. The presence of CS₂ is sometimes directly related to the naphtha source.

Catalyst deactivation by CS₂

It has been observed that H₂S has the strongest catalyst poisoning effect and CS₂ has the second strongest. Reactor temperature must be increased in the presence of a few ppm of CS₂ in the feed to compensate for the catalyst deactivation. With CS₂ present in the feed above the defined specifications, the catalyst activity shifts from the top part of the catalyst bed to the bottom part. This is strong enough evidence to show CS₂'s harmful impact on catalyst activity when considering that the top bed deactivates at only a few parts per million of CS₂.

It is evident that CS₂ acts as a strong inhibitor for the palladium-based catalyst. Many pygas units operating with

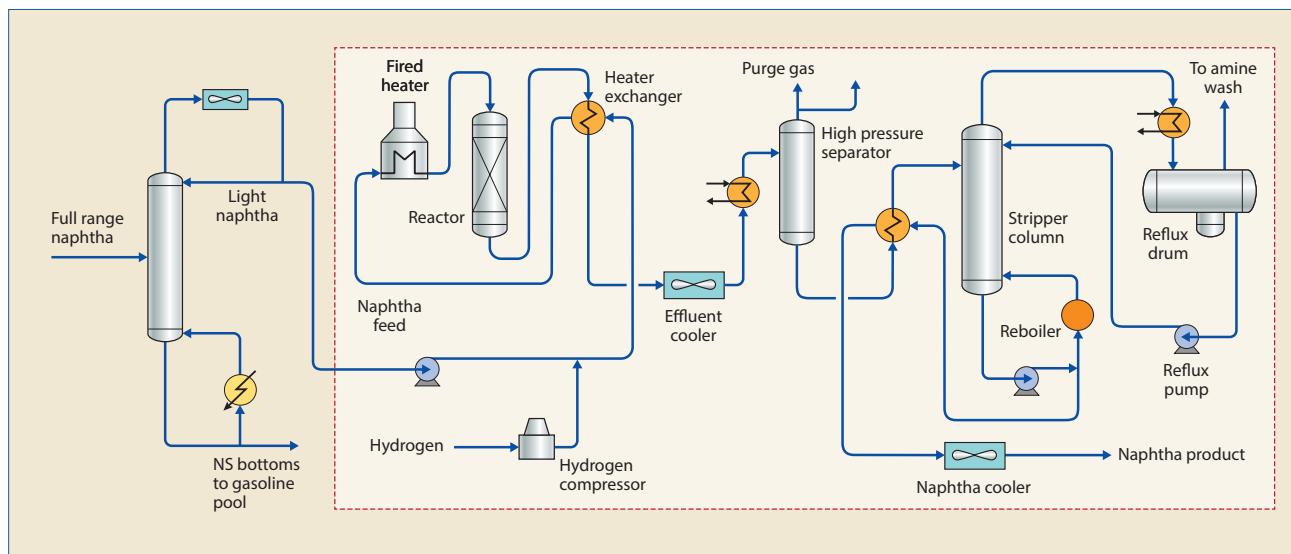


Figure 1 CS₂ removal by hydrotreating

a nickel-based catalyst have also observed that the catalyst is poisoned in the presence of CS₂. A specific catalyst treatment is required to recover activity.

It is observed that the nickel-based catalyst can tolerate CS₂ contamination in the range of 10-20 ppm with mild temperature elevation as compared to palladium (Pd) catalyst. But they tend to be poisoned with further increase in the CS₂ level. However, Pd-based catalyst is more active than a nickel (Ni) catalyst and recovers its activity more easily without any specific treatment once feed conditions come back to their initial level (with CS₂ in the specified range).

Moreover, Ni catalyst's residual activity is minimised with CS₂ poisoning, and it is impossible to recover the initial activity when operating with feed containing a high amount of CS₂. Thus, while keeping up with growing petrochemical demand, 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 in view of the declining fuel market, petrochemical naphtha (PCN)

production emerged as a lucrative option. PCN is light naphtha without CS₂. Considering that it tends to concentrate in the light fraction of naphtha, it must be treated for CS₂ removal.

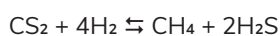
Mainly seen in the world's refineries, the naphtha splitter separates full-range naphtha into heavy naphtha which is routed to the CCR unit, while the light naphtha, primarily used as fuel, is mainly upgraded to a higher RON through the process of isomerisation. Chemically, light naphtha is the fraction 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 an FBP of 130°C. With light naphtha being converted to PCN by processes that remove CS₂, it caters to the making of ethylene. Steam cracking PCN converts to ethylene, the raw material for most plastics. Other ethylene feedstocks include ethane (C₂H₆) and propane (C₃H₈). **Table 1** shows typical petrochemical grade naphtha specifications where the CS₂ specification is as low as 1-2 ppm.

CS₂ removal by naphtha hydrotreating

Naphtha hydrotreating is an important unit in the refinery, performing hydro-desulphurisation (HDS) of hydrocarbon feed. It is used in petroleum refining to remove sulphur and nitrogen compounds from natural gas and other refined petroleum products like diesel, gasoline, and jet fuel.

HDS is the first choice of facilities when it comes to the 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 the presence of hydrogen, wherein CS₂ is converted into H₂S according to the following reaction. The effluent is routed to a stripper where the produced H₂S is recovered from the top product and sent to the sulphur recovery unit (SRU):



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°C, kg/m ³ , max	700	ASTM D 4052	690
3	Allowable CS ₂ , in ppm	1-2		1
4	Total paraffins, vol%, max	60-65	ASTM D 5134	65
5	Olefins, vol%, max	1.0	ASTM D 5134	<1.0
6	Aromatics, vol%	10-12	ASTM D 5134	10-12
7	Naphthenes, vol%, max	By Balance		Balance
8	ASTM distillation		ASTM D 86	
	IBP, °C	Report		40
	FBP, °C, Max	130		130

Table 1

Figure 1 shows the hydrotreating unit in operation, which typically receives feed from the top (overhead) 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, yielding product free from sulphur.

Though hydrotreating is the process of choice when it comes to attaining the desired specification with respect to the CS₂ content in the petrochemical naphtha, this only applies to cases 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 is because this stream is otherwise low in contaminants. For this reason, hydrotreating results in substantial increases in operating costs.

CS₂ removal by physical adsorption

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

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 behaviour of CS₂ in PCN, distillation is nonetheless another promising and interesting method for CS₂ removal from PCN.

As distillation takes advantage of the CS₂ boiling point lying between isopentane and hexane, it is possible to use distillation and obtain three cuts from the column. By this route, isopentanes and normal pentane carry most of the CS₂, while PCN, which is withdrawn as the bottom cut, will have minimal CS₂ content. **Table 2** provides the boiling points of components in a typical PCN mix.

Figure 2 shows PCN production using the distillation method. Though distillation is an effective way to reduce CS₂ content, employing conventional distillation methods has its own set of limitations:

- High energy consumption to get desired PCN specifications
- Overhead product is predominantly a mix of iC₅/NC₅
- Low RON, blending into the gasoline pool will lower the overall RON.

This bottleneck with conventional distillation schemes was addressed by technocrats, who developed new models, including hybrid schemes based on divided wall column (DWC) technology. DWC technology was successfully implemented in a Southeast Asia facility, to be discussed further.

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-Disulphide	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

Table 2

Why DWCs?

Process optimisation techniques of late, especially DWC technology, are for improving 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.

DWCs have provided an effective way to reinvent age-old distillation methods and offer the benefits of lower capital investment and lower operational costs compared to their conventional counterparts. It 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 summarised as follows:

- 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 footprint as equipment count is reduced by half
- Operational and capital expenditure are reduced by approximately 20-50%.

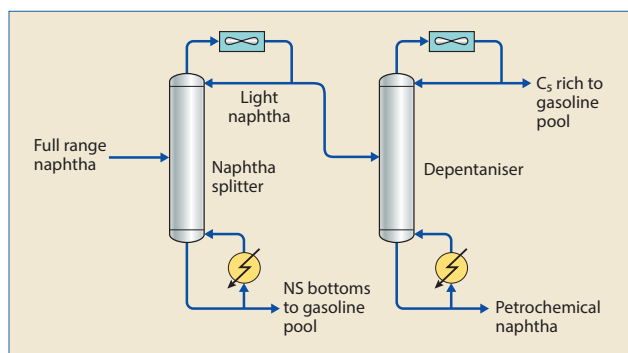


Figure 2 Conventional distillation scheme for obtaining PCN

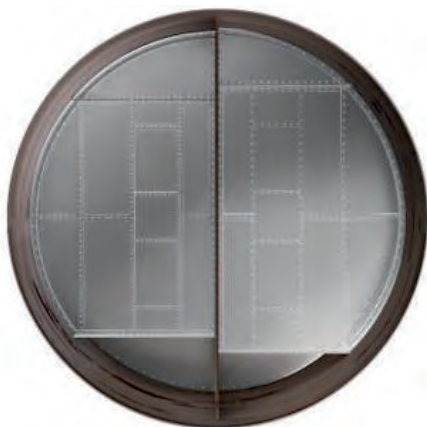


Figure 3A Top view of dividing wall column (Image courtesy of DWC Innovations).

It is interesting to see how divided wall columns overcome 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 in conventional columns, so higher thermodynamic efficiencies are achieved, as illustrated in **Figures 3a** and **3b**.

Use of DWCs to obtain PCN with iC_5 rich stream

Within the context of the bespoke discussed processes and their limitations, DWC technology is the process of choice because it is low in CAPEX and OPEX but can seamlessly obtain the desired PCN specifications and 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 the revamped DWC is diverted to naphtha for the gasoline pool.

The benefits of revamping the depentaniser column into a DWC can be summarised as follows:

- Meets CS_2 limit in PCN
- No additional load on the NHT unit
- Produces premium gasoline, improving profitability
- Energy consumption offset by an improved margin from producing premium gasoline
- Retrofits into existing columns.

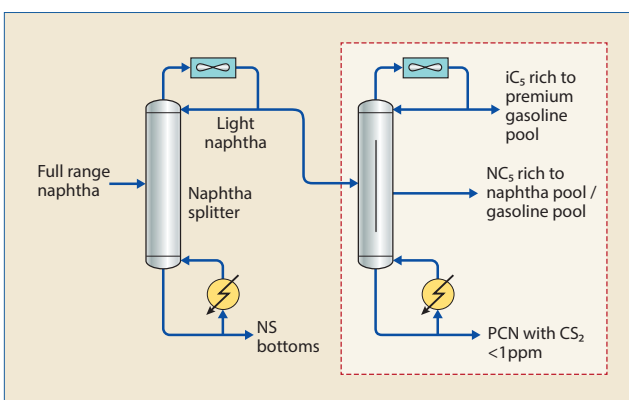


Figure 4 Flow scheme after revamp of depentaniser into a DWC. The C_5 rich side-cut with concentrated CS_2 is diverted to naphtha/gasoline pool



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

Case study: incorporating the hybrid model

A facility in Southeast Asia was looking forward to a major diversification. It was able to identify a huge demand for PCN, being mindful of a less than 1 ppm CS_2 specification. It could visualise the added benefit of this revamp by also producing premium gasoline. A stream of 90% iC_5 could be obtained as the top product from the depentaniser column.

As most of the CS_2 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 specification targets), which in turn would offload the NHT unit. The revamp objective included:

- Maximum iC_5 (>90 wt%) recovery in overhead product
- The nC_5 side-cut would contain most of the CS_2
- PCN bottom product with less than 1 ppm CS_2 in PCN.

In its existing configuration at the facility, the full-range naphtha was routed to a series of two columns that included a naphtha splitter and a depentaniser column to get C_5 rich and C_6 rich streams as top and bottom products. The C_5 rich stream was routed to the gasoline pool, while the C_6 rich was sent to the naphtha pool.

There was an option to proceed in a conventional way by installing a new column after the second column or convert the second column into a side-cut column. Both 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 using DWC technology. Any facility pursuing this route to obtaining PCN has two options:

- Route the midcut from the column, which is mainly NC_5 that carries the majority of the CS_2 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 (see **Figure 4**)
- The second option is to route the midcut to the NHT unit to strip off the CS_2 in the form of H_2S and mix this stream again with the PCN stream, the bottom product of the depentaniser column. This further increases PCN production (see **Figure 5**).

Engineers decided to revamp the depentaniser column to a DWC to produce three high-purity cuts, as discussed. It achieved the desired CS_2 specs for PCN, wherein the CS_2

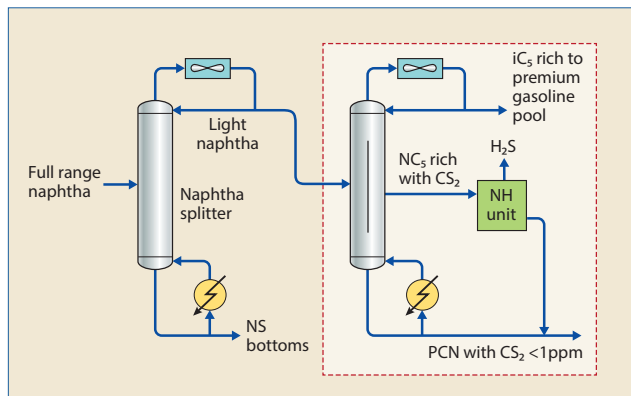


Figure 5 Flow diagram after revamp of depentaniser into divided wall column.

content remained between 1 and 2 ppm. The NHT unit was debottlenecked so that after the revamp only the midcut, which carried most of the CS₂, was routed to the NHT unit, as shown in **Figure 5**.

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

The product specifications after the revamp to DWC is summarised in **Table 3**.

Conclusion

In one of the many and varied applications of divided wall column technology, its use to obtain PCN with stringent CS₂ specifications is less tedious and an economically viable route than other conventional methods.

As DWCs are robust operationally and the revamps are easy to take up, this technology has seen a resurgence over

Product specifications after revamp to DWC				
Stream description	Feed	iC ₅ product	C ₅ sidecut mix	Bottoms petrochemical naphtha
Total flow, kg/hr	194,000	18,887	49,952	125,162
Composition, mass%				
C ₄ and lighter	0.45	4.60	0.01	0.00
iC ₅	13.97	90.00	19.88	0.13
NC ₅	15.59	5.24	55.56	1.21
Others	69.99	0.11	24.54	98.66
CS ₂ , ppm	70	100	200	<1

Table 3

the last decade. Not only has it paved the way to find areas in facilities where optimisation in terms of lowering CAPEX and OPEX is required, but it has also helped to obtain desired product specifications compared to other conventional ways employed in the facility.

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