Economics of ammonia production from off-gases

VK Arora of Kinetics Process Improvements, Inc. examines various process options to produce ammonia from off-gases along with case study economics for the US Gulf Coast and Middle East for different sourcing and process options.

Fig 1a: **Excess ethane availability**

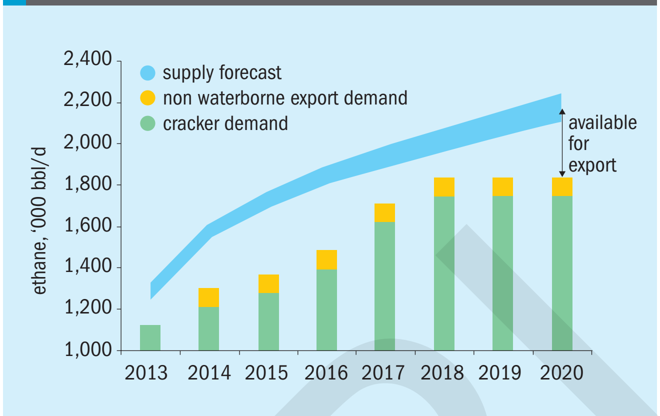
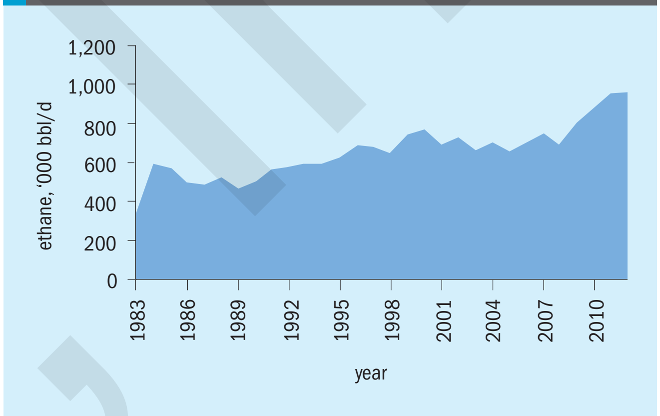


Fig 1b: **US demand growth for ethane crackers**



Ammonia production using hydrogen rich off-gases has been well known for a long time but practiced only in a handful of plants. The dynamics of a new feedstock trend in the petrochemicals industry coupled with several new process options provide opportunities to source larger volumes of hydrogen rich off-gas streams to produce low cost ammonia. The new sources of hydrogen rich off-gases are large enough to integrate and support a typical world scale ammonia plant to provide an economy of scale even in smaller sizes with an added environmental benefit. However, sourcing those off-gas streams will pose its own challenges.

Feedstock dynamics

The abundant supplies of ethane from the shale gas boom has positioned the US as the most competitive, low-cost ethylene producer, resulting in increased investments in ethane recovery, pipelines and ethane crackers. Figures 1a and 1b are indicative of the excess ethane availability along with its demand growth for the crackers in the US.

As a result, most ethylene producers in the US have switched to low cost ethane to the extent possible and several companies are already progressing with their plans to build mega ethylene crackers using ethane.

The ethane cracker produces a large amount of hydrogen rich stream, which is conventionally combusted in the cracking furnaces to provide the required heat of cracking. This large source of hydrogen rich stream provides a potential opportunity for ammonia producers to explore this alternative feedstock option to build world scale ammonia plants with the benefit of lower capital and energy costs with better return on their investments.

The new ethane based steam crackers announced in the US with an ethylene capacity totalling in excess of 7 million t/a are listed in Table 1.

The total planned new ethylene capacity is ~9.8 million t/a, which is 37% of the

Table 1: **New ethane based steam crackers announced in the US**

Company	Capacity, million t/a	Location	Start-up date
Chevron	1.5	Texas	2017
Dow	1.5	Texas	2017
Exxon-Mobil	1.5	Texas	2016
Formosa	1.2	Texas	2017
OxyChem	0.5	Texas	2017
Sasol	1.5	Louisiana	2017

Table 2: **Announced propane dehydrogenation (PDH) capacity in North America**

Company	Capacity, '000 t/a	Location	Start-up date
Ascend	>750	Texas	2016
Enterprise	750	Texas	2015
Dow	750	Texas	2015
Formosa	600	Louisiana	2016
PetroLogistics	Expansion	Texas	2016
Williams	500	Canada	2016

Table 3: **Hydrogen rich stream sources**

H_2 rich stream source	H_2, vol-%	Other components
Steam cracker	80% to 95%	CH_4, CO, N_2
PDH	80%+ typical	CH_4, C_2H_6,CO, CO_2, N_2, light olefins
Methanol Plant	75% typical	CH_4, CO, CO_2, N_2, methanol, waxes
CO plant	90%+ typical	CH_4, CO, N_2
Caustic soda	99%+ typical	CO_2, N_2, O_2, trace Cl_2
Styrene plant	< 50%	CO, CO_2, EB, styrene, etc.*
Coke oven	60% typical	CH_4, CO, CO_2, HCs**

** Recovery uneconomical ** Obsolete*

existing ethylene capacity, and nearly two-thirds of all ethylene capacity uses ethane as its feedstock. Nearly 70% of ethylene in the US is produced from ethane as opposed to 45% just six years ago. Globally, ethane represents 36% of ethylene production compared to 26% just 10 years ago.

By the same token, a large number of existing steam crackers in the Middle East use associated gas (ethane and ethane/propane) and provide a similar opportunity for ammonia producers.

In Europe, 90% of ethylene is produced from cracking naphtha, gas oil and condensates while cracking of ethane is primarily carried out in the US, Canada and Middle East.

Shrinkage of product slate

A larger shift to ethane-based olefins production in the US has also taken a toll on propylene, higher olefins, aromatics as well as other co-products made with heavier-feed cracking. The propylene supply from refineries has also been curtailed due to sluggish demand of gasoline.

A huge shortfall in propylene is being made up by on-purpose propane dehydrogenation (PDH) units - another source of hydrogen rich stream. PDH capacity of over 3 million t/a of propylene in the US has already been announced (see Table 2).

Excess propane supplies coupled with high oil price relative to natural gas price, has driven the demand for PDH units as the main growth engine for propylene supply. The North American shale gas and tight oil revolution shifts the US to a net large exporter of propane even after addition of all the above PDH units.

Propylene shortage and its demand growth in China has driven a massive wave of new PDH units with imported propane mostly from the Middle East and some from North America. Nearly 6 million t/a of PDH capacities is already in the engineering and construction phase in China for nine different projects and another 2 million t/a PDH capacity is in planning. This also provides opportunities for ammonia producers in China.

The Middle East was the first region to build several PDH units with currently operating PDH capacity of nearly 3 million t/a and also provides similar opportunities for ammonia producers in the Middle East.

Hydrogen rich stream sources

Table 3 lists the potential sources of hydrogen rich streams from various processes. The impurities contained in those streams needs to be removed if used for ammonia production. The purification steps to remove the impurities depend on the nature and amount of impurities present along with the selected scheme.

Process options

The following process options are reviewed for hydrogen recovery and syngas generation in combination with additional natural gas for the ammonia production:

- PSA;
- secondary reforming with air;

Fig 2: **PSA option**

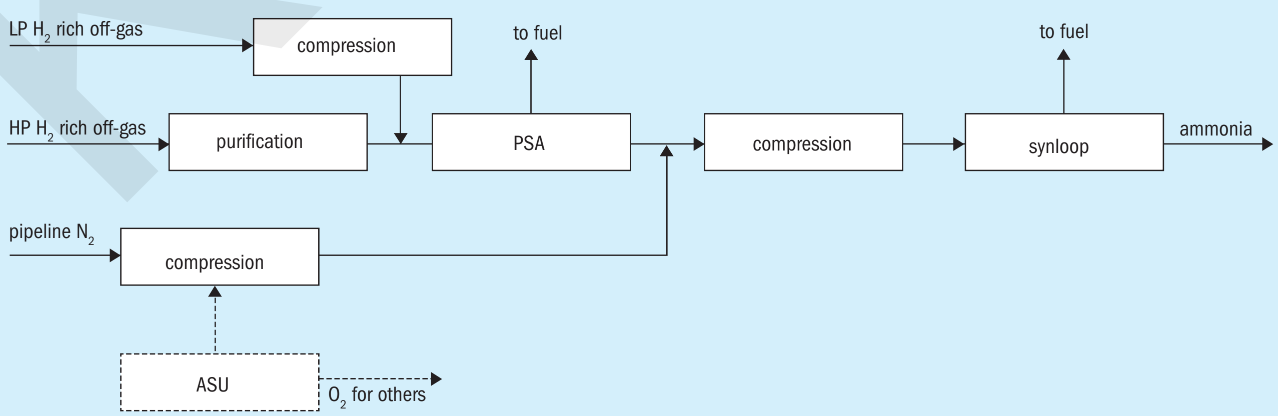


Fig 3: **Nitrogen wash option**

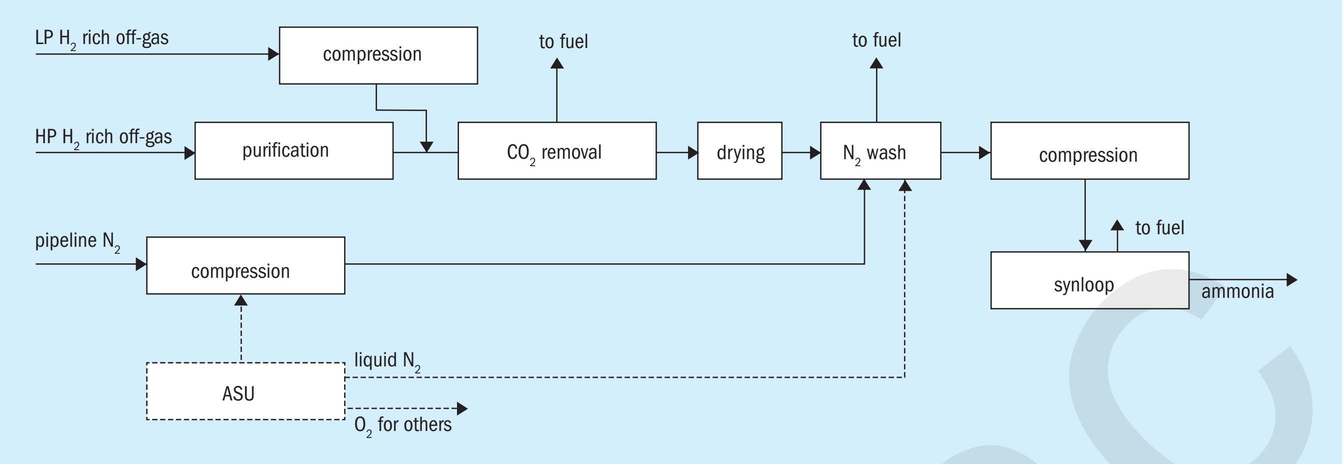
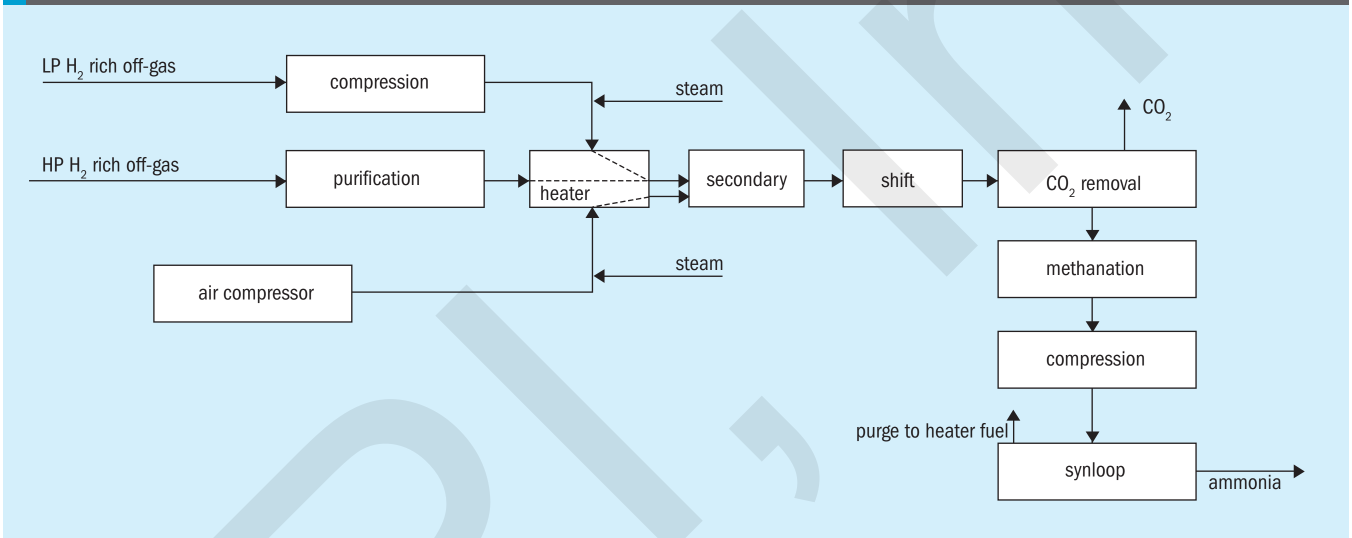


Fig 4: **Secondary reforming with air option**



- secondary reforming with enriched air;
- secondary reforming with GHR.

For all the listed process options, there is no need for an expensive and energy intensive primary reformer which helps to reduce both capex and opex for the ammonia plant. The choice of the process option will depend on the site specific constraints and resulting economics.

PSA option

The PSA option schematic as shown in Fig. 2 is the simplest option with a relatively lower capital cost and the least ammonia production. In this option, full recovery of hydrogen is not possible due to the very nature of PSA system. The high purity nitrogen required for the process can be provided through a pipeline or an ASU. Using pipeline nitrogen at a competitive price is usually a better economic option.

The make-up syngas produced in this scheme is very clean with practically no inerts. This allows the ammonia synloop to operate efficiently at a lower pressure and lower refrigeration duty for the same ammonia conversion with the least amount of purge gas, resulting in savings in both the capital and operating costs of the ammonia plant.

Nitrogen wash option

The nitrogen wash schematic as shown in Fig. 3 provides a relatively higher ammonia production than PSA because of nearly full recovery of hydrogen present in the off-gas. This option, however, requires extra nitrogen to provide the needed cryogenic cooling for the condensing and separation of impurities and inerts through the nitrogen wash system. The extra nitrogen lands up in the reject fuel stream and its requirement depends on various factors including the level of CO in the feed. HP nitrogen can be used but liquid nitrogen, if available, is preferred.

Similar to the PSA option, the make up syngas produced in this scheme is also very clean with practically no inerts. This allows the ammonia synloop to operate efficiently at a lower pressure and lower refrigeration duty for the same ammonia conversion with the least amount of purge gas, resulting in savings in both the capital and operating costs of the ammonia plant.

Secondary reforming with air option

The secondary reforming schematic as shown in Fig. 4 provides slightly higher ammonia production than nitrogen wash as the methane present in the off-gases is nearly completely converted into syngas. Also, this option does not require any external nitrogen unlike the PSA and nitrogen wash options. However, this option does require much more equipment and a larger

Fig 5: **Secondary reforming with enriched air option**

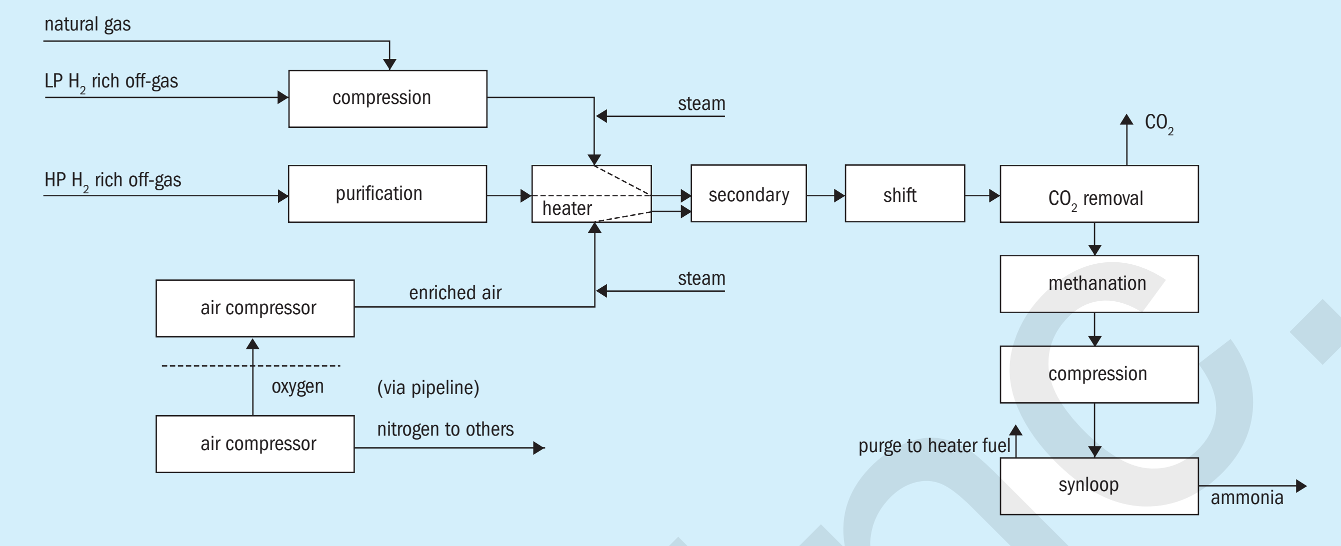
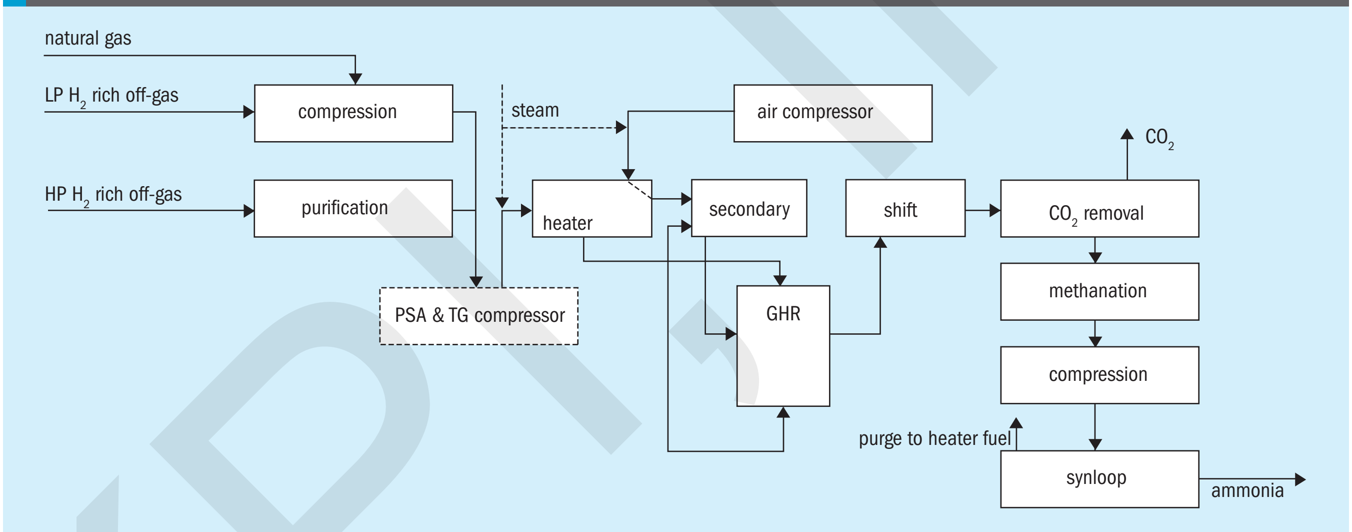


Fig 6: **Secondary reforming with GHR option**



capital for a small incremental ammonia capacity which may be hard to justify economically. Further, this scheme results in higher methane slip from the secondary reformer (than typical) due to heat input limitations and results in a much higher level of inerts. This means, a relatively inefficient synloop which needs to be operated at a higher pressure with larger size equipment for the same ammonia conversion and also results in a large purge rate.

Secondary reforming with enriched air option

To overcome the process limitations of the secondary reforming scheme, air enrichment with an external source of oxygen is reviewed in this option as shown in Fig. 5. This option permits a significant increase in ammonia production to provide the economic benefit of scale with additional natural gas and can also achieve a typical low methane slip without any heat input limitations in the secondary reformer. However, this scheme requires a source of oxygen which can be sourced either from a pipeline or from a dedicated ASU, depending on the site specific situation and economics.

Secondary reforming with GHR option

The previous option of secondary reforming with enriched air requires oxygen, which could be a limiting factor at some locations. To overcome this, an alternative scheme using a combination of secondary and gas heated reforming (GHR) is reviewed as shown in Fig. 6. This option does not require any oxygen and can achieve a significantly higher ammonia capacity similar to the secondary reforming with enriched air option, with an additional natural gas. This comes at the expense of reduced HP steam production which has to be made up externally depending on the drivers used and overall steam balance

Ammonia production potential

Ammonia production using the hydrogen rich stream from a world scale steam cracker (typical 1.5 million t/a ethylene capacity) for various feedstocks (ethane to AGO) with different process options is summarised in Fig. 7a.

Ammonia production using the off-gases from world scale PDH and methanol/CO plants with different process options is summarised below in Fig. 7b.

Fig 7a: **Ammonia production from a world scale-cracker**

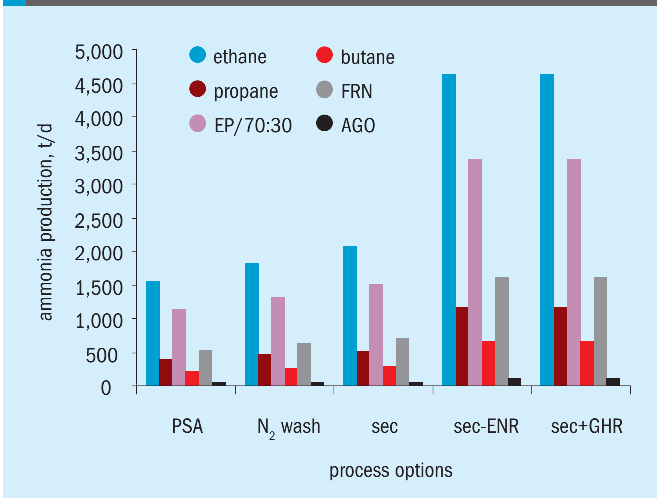
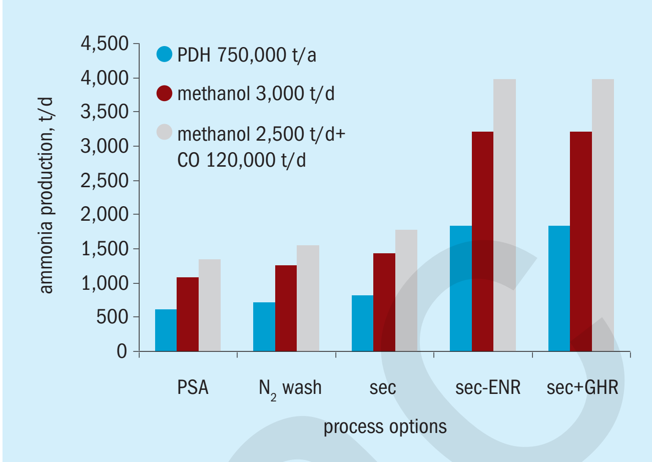


Fig 7b: **Ammonia production from methanol, CO and PDH plants**



Environmental benefit

Ammonia production using hydrogen rich streams will replace the Hydrogen rich firing with natural gas in the ethylene and reforming furnaces, which provides an added benefit of NOx reduction as shown in Fig. 8.

Impact on the source plant

No process modifications of the source plant are required. The combustion related components and associated combustion control system of the source plant may require nominal modifications depending on the original design basis and margins for specific plants.

Economic evaluation: A case study

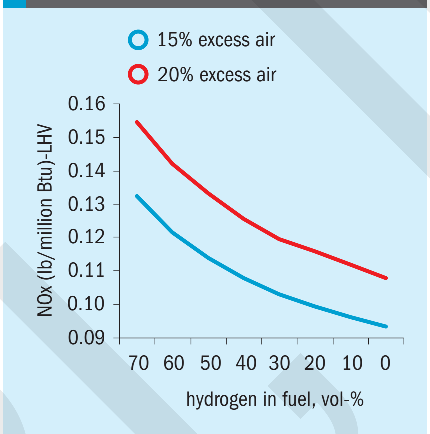
The presented case study examines the economics of producing ammonia using the hydrogen rich streams available from the following typical world scale and large/mid size process units for two locations (USGC and Middle East) using the least ammonia production option with PSA.

- 1.5 million t/a ethane cracker
- 1.5 million t/a E/P cracker
- 750,000 t/a PDH unit
- 3,000 t/d methanol plant
- 2,500 t/d methanol together with 120,000 t/a CO plant

The following assumptions are used in the economic evaluation:

- Capex includes
  - Both ISBL and OSBL with Storage
  - OTF Off-gas piping cost with compressors
  - Working capital
  - Owner's cost

Fig 8: **H_2 concentration vs NOx**



- Project completion – 40 months
- 90% operating rate in the first year
- Pipeline nitrogen
- Off-gas premium – 50% over the Btu cost to the supplier
- Utilities rates – typical of USGC and Middle East location
- Debt: equity 70:30
- Discount rate 10%
- Loan interest 8%
- Tax rate 35% (USGC) and Zakat (2.5%) for Middle East location
- Ammonia Prices of 400 \$/t and 500 \$/t with 1% increase each year

Figures 9 and 10 summarise the returns on the capital (as %IRR) to produce ammonia for each location using two different ammonia prices – \$400/t and \$500/t. KPI estimates of returns on capital for both locations are quite attractive for higher ammonia pricing of \$500/t. However, a typical Middle East location should provide even better returns than USGC for lower gas pricing and lower tax rates. Obviously, the overall economics for each site will much depend on various specifics.

Challenges

Despite the attractive economics, there are always going to be some challenges and considerations before concluding the overall viability of such projects. Some of the key challenges and potential risks are listed below and will depend on the specifics of each site:

- sourcing of the off-gas stream;
- incentive for the source plant;
- long term supply contract;
- reliability – an interdependence with the source plant;
- proximity with the source plant;
- availability of N_2 and O_2 at a competitive price
- market dynamics of the petrochemical products and impact on feed-slate.

Will it provide an attractive incentive for the source plant operator, especially for the ethane cracker operators who are making substantial profit margins (in excess of \$800/t ethylene)?

Although there is little expectation that the major source of feed will go heavy again "for the foreseeable future" there is always a potential depending on the market dynamics of the petrochemical products.

The additional incentives for the operators of ethane crackers may be captive demand for ammonia or its derivatives for their own petrochemical derivatives, like acrylonitrile etc. besides some environmental benefit of reduced NOx.

Fig 9: **IRR of ammonia production from different hydrogen sources** (PSA option, US Gulf Coast location)

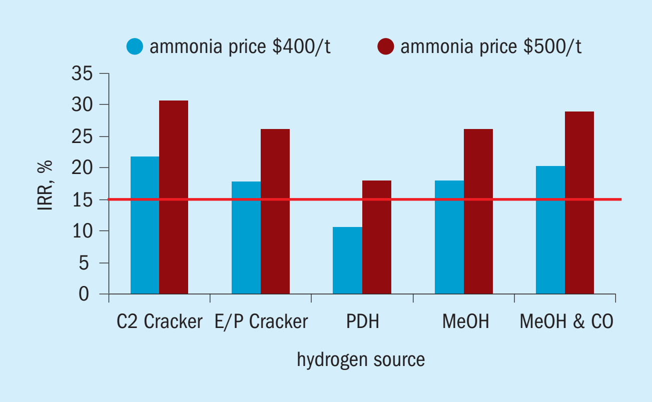
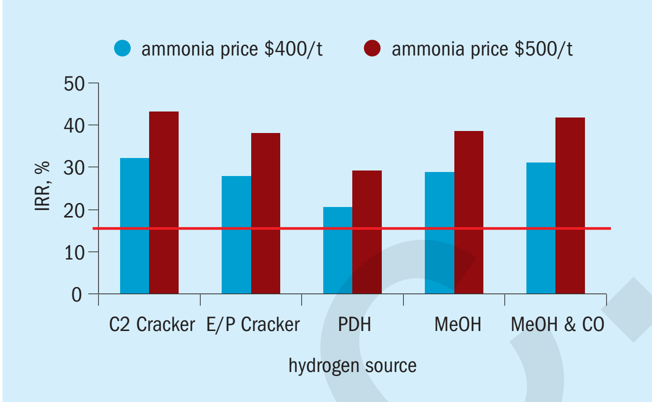


Fig 10: **IRR of ammonia production from different hydrogen sources** (PSA option, Middle East location)



Conclusion

The dynamics of feedstock trends in the petrochemical industry has opened up additional and large volumes of hydrogen rich streams especially in North America, China and the Middle East. This provides additional opportunities for ammonia production.

New process options coupled with additional sources of large volumes of hydrogen rich streams from light crackers and PDH units can provide substantial capital and energy savings for ammonia production with attractive returns besides the large methanol facilities operating with hydrogen rich loop.

Of course, there are going be challenges in sourcing the hydrogen rich off-gases, especially from E/P cracker operators who have been enjoying exceptionally high profit margins. They will need to have substantial and sustainable incentives to consider this. ■

References

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