Contaminant Removal for Improved NGL Quality

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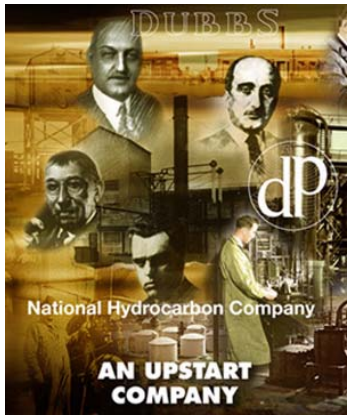
Introduction

- **UOP:**
  - Universal Oil Products (est. 1914)
  - Oil and Gas Treating Licensed Technologies
  - McCook Chicago (historic site - Oil Cracking pilate plant)



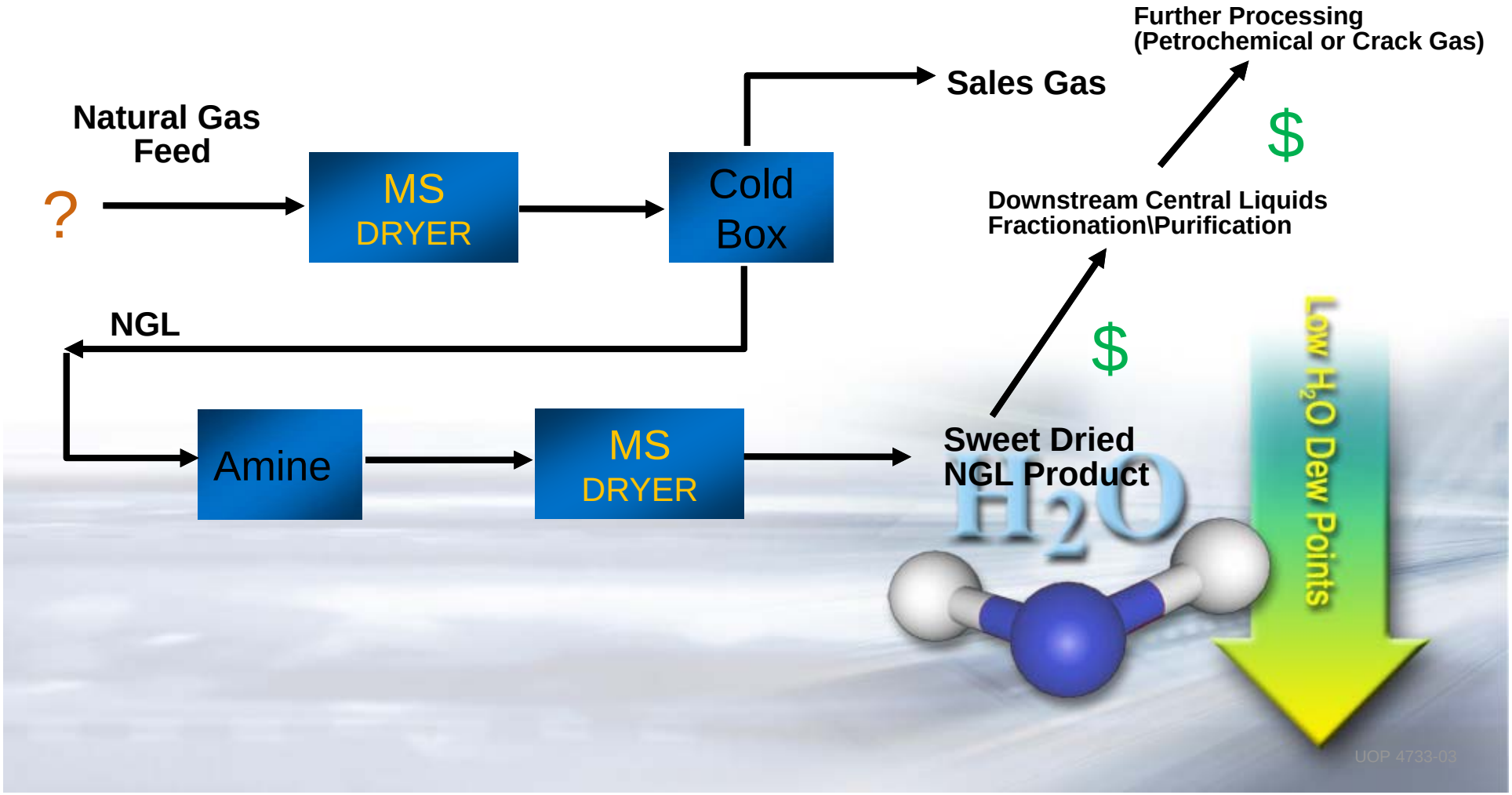
- **UOP Adsorbents:**
  - 1949 Union Carbide Adsorbents\Molecular Sieves established
  - Focus on Natural Gas + Liquids Based Purification from Wellhead, through Fractionation, LNG, Refinery and Petrochemical applications
- **UOP Capabilities:**
  - Adsorbent Unit Design, Start-up Assistance, Optimization and Troubleshooting
  - UOP Technical Team provides "**Customer Focused Solutions**" via worldwide Technical team

Outline

- **Introduction**
  - Historical use of molecular sieve in natural gas dehydration
  - What are Oxygenates?
  - What is the source of Oxygenates?
  - Why should we remove Oxygenates?
- **Discussion**
  - Challenges in using Adsorption Technology for Oxygenates removal
  - Adsorbent Products (UOP oxygenate removal since early 1980's)
  - Mole Sieve Unit Process Design
  - UOP's Analytical Capabilities
- **Case Histories**
  - Design Consultation
  - Field Measurements
  - Troubleshooting

Introduction

- **Molecular sieves units have historically been used for dehydration of upstream Natural Gas and also downstream of cryogenic Hydrocarbon Liquid recovery and purification systems.**



Introduction

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- There is a need to quantify all processing plant inlet\carrier stream contaminants!
- There is now an increased industry awareness on inlet oxygenate levels at natural gas plants
- Oxygenate removal is considered critical for protecting downstream processes:
  - What are oxygenates?
  - alchohols, aldehydes, ketones (contain –OH or Oxygen as part of chemical structure)
  - Some commonly found oxygenates in Natural Gas Streams are:

OXYGENATES	MOLECULAR WEIGHT	BP('F) @14.7psi	VP (psi) @ 110'F
METHANOL	32	149	6
ETHANOL	46	172	3.11
ISO-PROPANOL	60	180	2.5
ACETONE	58	133	9.3
DI-METHYL-ETHER (DME)	46	-13	141.8
TERT-BUTYL-ALCOHOL (TBA)	74	180	2.4

Table 1

Introduction

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- **Source of Oxygenates in Natural Gas:**
  - Oxygenates mostly originate from upstream wellhead or flow line methanol injection programs (used for hydrate control)
  - Other sources include upstream Production injection programs such as corrosion, or scale inhibitors
  - Injection Chemistries require freeze protection or chemical carriers
  - Other sources may yet to be identified?

- **Oxygenates can be potential poisons for downstream catalysis units using fractionated NGL as feed because:**

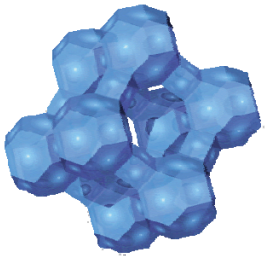
  1. Loss of downstream catalyst conversion efficiency and reduced life
  2. Oxygenates in NGLs to steam crackers cause excess CO_2 in the reaction furnace thus increasing downstream purification requirements

- **UOP's design ability enables oxygenate free NGL systems**
  - By upgrading exiting upstream mole sieve dehydration systems

  or
  - By adding customized downstream oxygenate removal systems

Discussion

- **Molecular sieves provide adsorption capacity as a consequence of:**
  - Electrically charged cationic crystal structure
  - Controlled pore opening size which allows for selective adsorption of smaller and more polar contaminant molecules



- **Oxygenates are challenging to remove due to:**
  - A Wide range of molecular sizes
  - Size distribution (small Methanol vs larger heavier alchohols + Ethers)
  - Range of Different Molecule Polarities
  - Mole Sieve units are a Non Steady-State with many potential Mass Transfer Zones during Adsorption
  - Oxygenates can react (during the cyclic regenerative Heat Cycle)
    - Can form coke (pore closure = loss of capacity) or generate H2O

Dehy Unit Upgrades for Oxygenates Removal?

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Process Design:

- Existing system evaluation is critical to determine if the upstream gas dryers or the downstream liquid dryer, or a combination of both would be a best solution for removal of oxygenates.
- Two critical aspects are firstly the size of existing vessels and secondly the operation mode\capabilities of regeneration system.

Product Selection:

- UOP MOLSIV™ UI Series Adsorbents offer effective oxygenate removal from natural gas streams.
  - UI-94 adsorbent, an industry favorite for severe natural gas drying systems, is also an excellent choice for removing methanol and smaller oxygenates due to its lower reactivity in the presence of oxygenates.
  - UI-710 (for natural gas streams) and UI-750 (for product NGL streams) adsorbents are the products of choice for broad range oxygenates removal.

Analytical Ability for Oxygenates Measurement

- UOP's Field Technical Service teams are equipped for *analyzing, measuring, and differentiating* oxygenates in various hydrocarbon streams
- "Any contaminant UOP can measure we can remove"
- UOP utilizes a proprietary gas chromatograph analyzer customized for measuring oxygenate levels down to 0.5ppm
  - *This type analyzer produces reliable field data both in vapor phase and liquid phase hydrocarbon applications for onsite assistance and troubleshooting services at customer plants.*

Onsite test facility

Case Study 1 (NGL Facility)

- Plant was providing a satisfactory level of water removal at both dehydrators in gas and liquid phase using UOP 4A-DG Adsorbent.
- When methanol and other oxygenates showed up in the inlet gas composition, the plant's moisture analyzer started showing moisture breakthrough. Moreover, increased oxygenates concentration was detected in the NGL product stream.

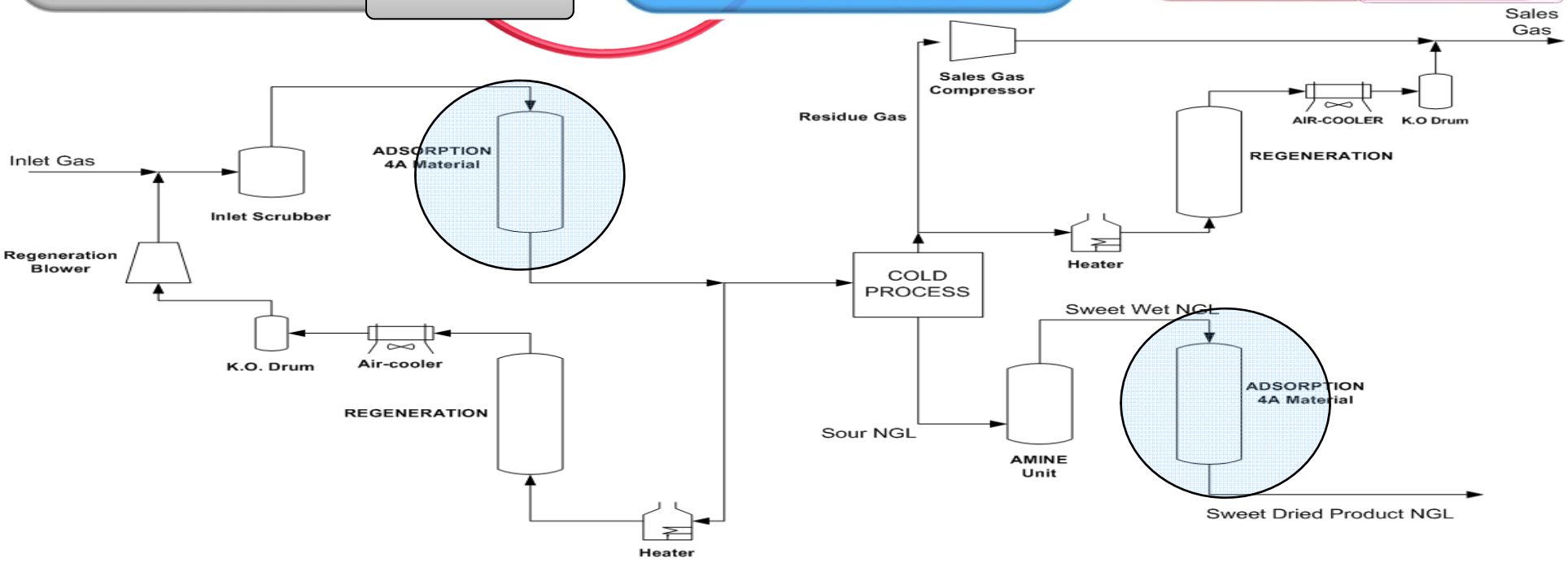
Critical business issue for user

UOP Support

- UOP R&D conducted analysis of the UOP 4A DG adsorbent which showed high levels of coke formation consistent with reduced adsorption capacity
- Plant existing flow scheme was reviewed before recommending a treatment scheme.

- UOP provided a charge of UOP MOLSIV™ UI-94 Adsorbent, for dehydration with partial oxygenate removal
- UI-750 adsorbent was installed in the NGL treaters for moisture and oxygenate removal
- Plant now makes on-spec product with no moisture slippage concerns

Product recommendation



Case History 2

- Both the gas dryer and NGL dryer were meeting moisture specification performance using 4A-DG product
- Due to seasonal methanol injection in the production fields, methanol was getting concentrated in the NGL product leading to failure of oxygenates sales specifications

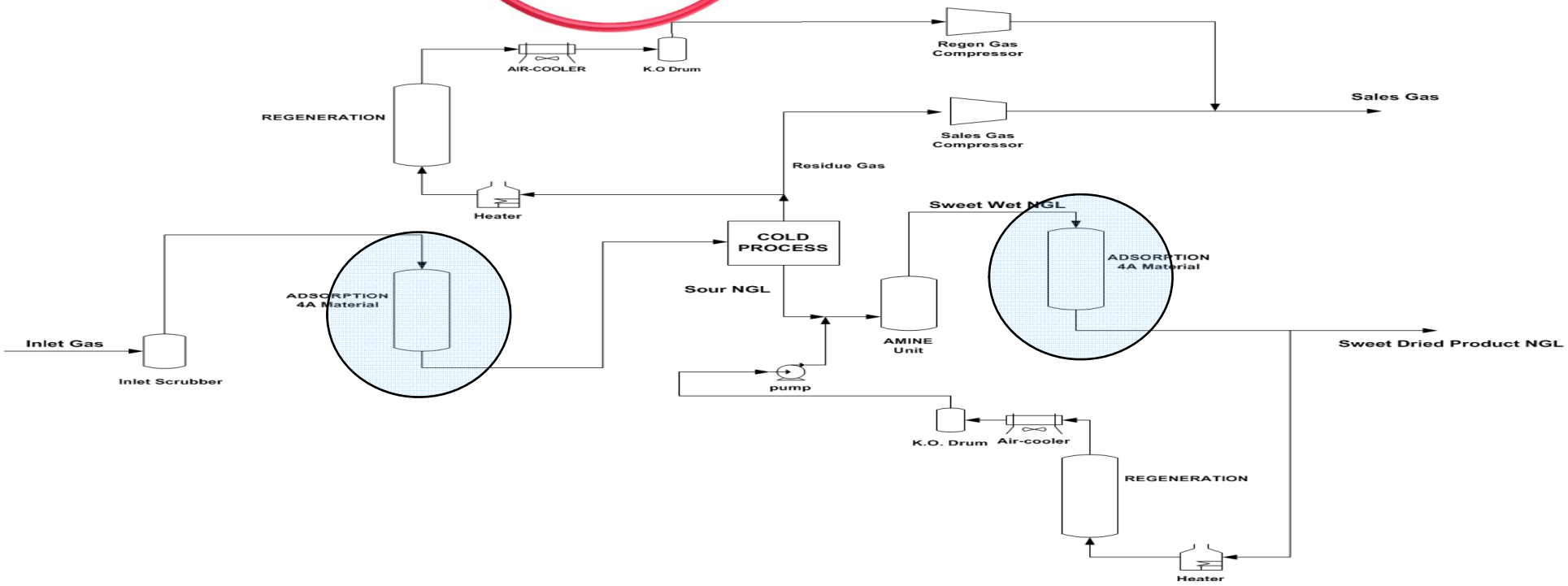
Critical business issue for user

UOP Support

- Plant existing flow scheme was reviewed before recommending a treatment scheme
- Recharge of the inlet gas dryers with UOP MOLSIV™ UI-710 adsorbent was suggested to remove all the water and methanol upfront in the gas phase

- UOP's recommendation was implemented and the plant saw immediate improvement in the dryers as well as NGL product with on-spec oxygenates content achieved

Product recommendation



Case History 3: Multiple Oxygenate Species

- Plant C was in operation as illustrated in Figure 5. A new feed gas to this cryogenic NGL facility contained a multiple oxygenates species including methanol, acetone, MEK, iso-propanol, and TBA.
- An upgrade of this inlet gas drying system to a compound bed of UI-94 and UI-710 adsorbents was implemented to provide more effective removal of both water and oxygenates.
- Although the bed appeared to be removing all the methanol and MEK, the customer reported that some oxygenates (acetone, TBA and DME) apparently had managed to slip through the bed causing total ether and total oxygenates in NGL stream to be above specified level.
- UOP Field Technical Service personnel did onsite performance evaluation to provide any necessary troubleshooting.

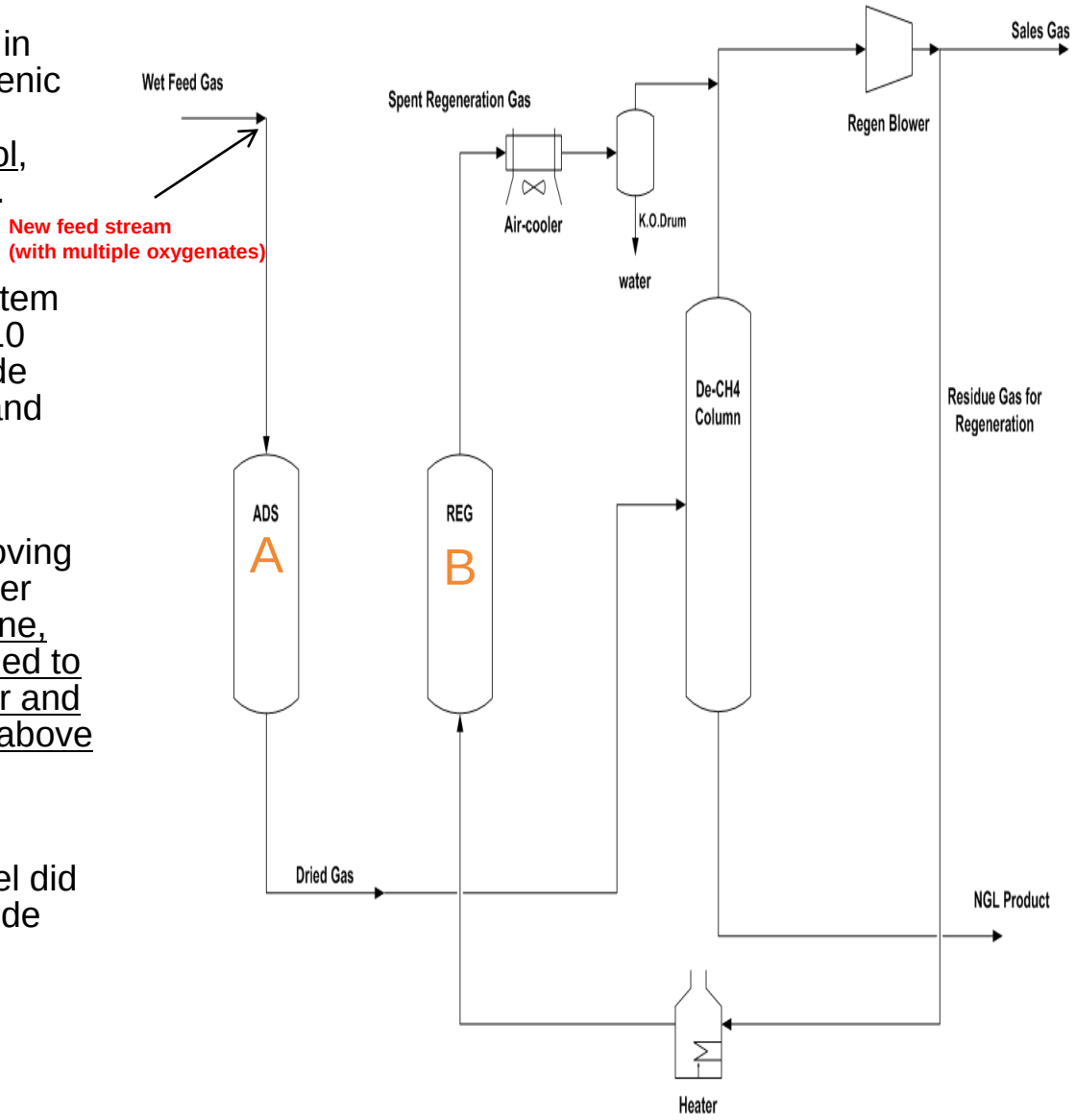
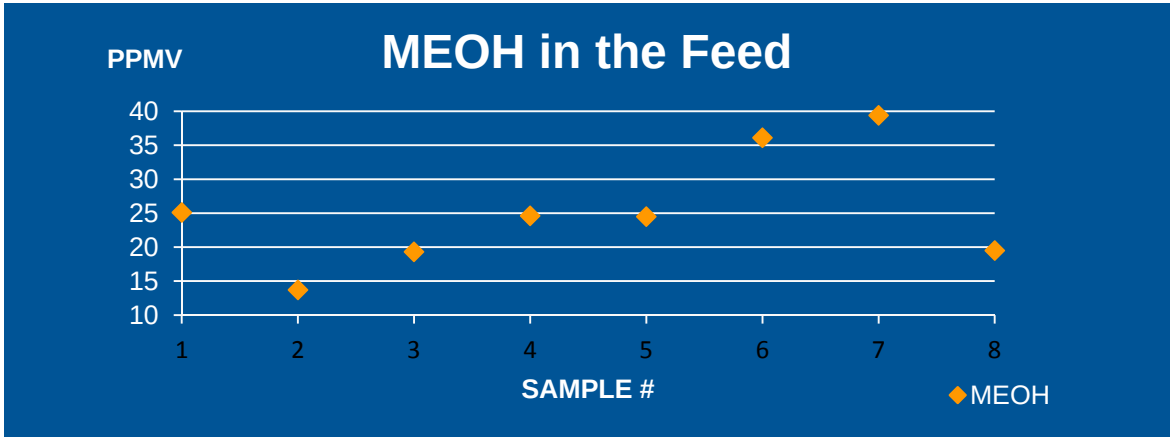


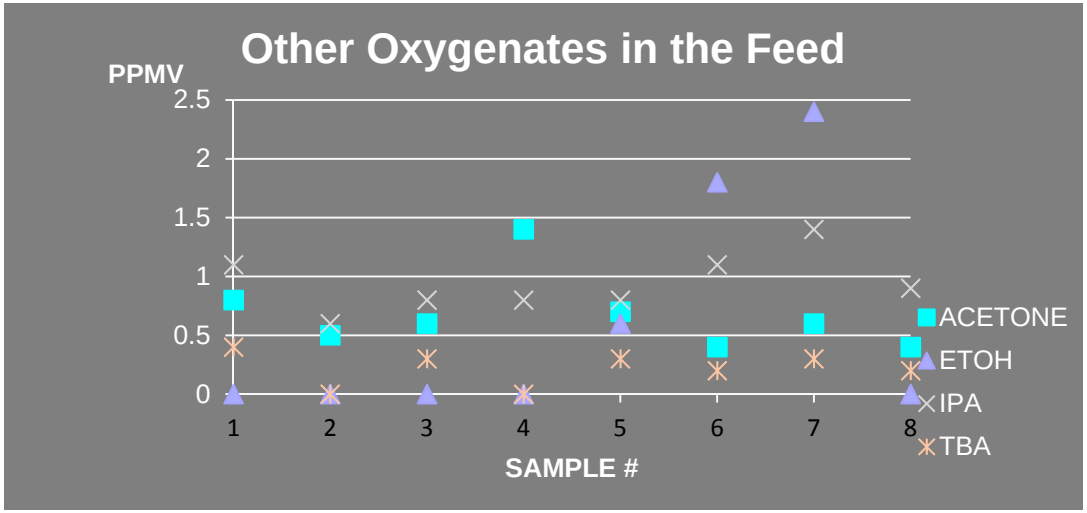
FIGURE 5: PLANT "C"

Case History 3

- **Figure 6: Plant Inlet Feed Stream (12-40 ppmv)**

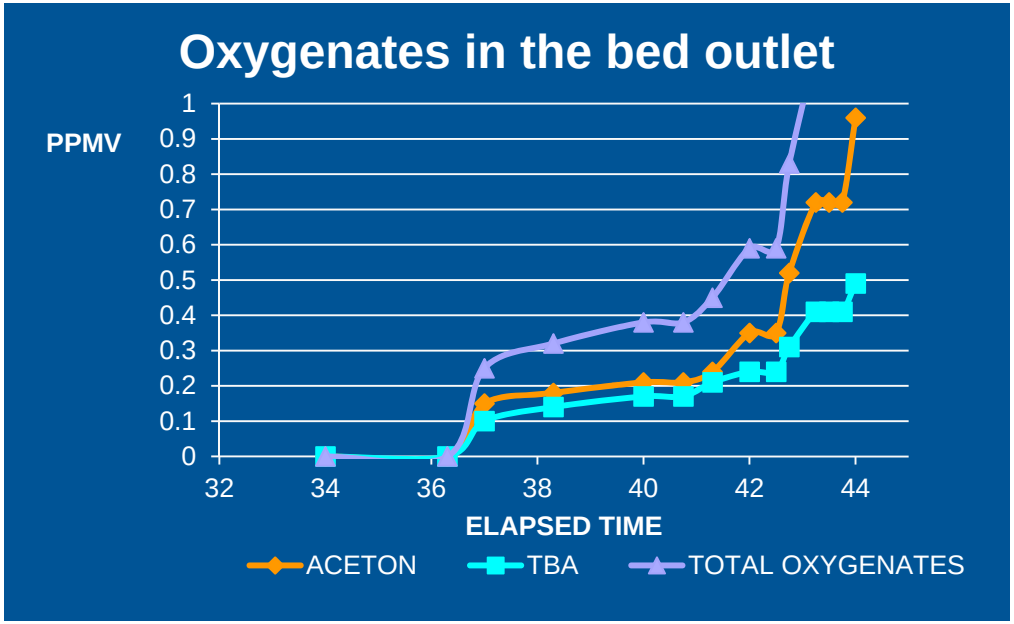


- **Figure 7: Plant Inlet (other measured Oxygenates)**



Case History 3

- UOP Field Technical Services measured the bed outlet Oxygenate breakthrough contaminant matrix as a function of the cycle time
- No Methanol breakthrough was detected (<44 hrs)
- As a result of this onsite testing, the customer reduced the cycle time to a recommended (<36 hrs) to achieve the overall oxygenate specification in the NGL product.



Conclusion

- **Evaluation of existing units and upgrading them from a simpler dehydrator to a more complex oxygenate removal unit can be a challenging task.**
- **UOP's commercial experience with oxygenate removal units with Technical Service and field analytical capability have proven to be very helpful in assisting cryogenic plant operators in retrofitting their units for oxygenate removal.**

UOP = Customer Focused Solution Provider


Q&A