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Research Reality

By Winston K. Robbins, Ph.D.

Most modern refineries are run based on process models. However, underlying these engineering models are laboratory research studies. Between the lab and the refinery, "unit factors" are often applied to make research findings fit the real world. In some cases, the "unit factors" are due to local engineering requirements; however, in others, they arise from chemical limitations inherent in the research. In general, the engineering factors that are required to scale-up lab research are well recognized. On the other hand, the chemical limitations are often overlooked.

Ideally, research would be carried out by following the effects of a process on all components in a refinery stream using multiple analytical tools. Unfortunately, studies that are carried out on whole feeds can quickly degrade into analytical method development projects. As an alternative, research often turns to using "representative" model compounds, synthetic matrix oils, and established detection methods. The limitations of this approach are illustrated in the following examples that include a reality check and potential improvements that are available by using advanced characterization methods.

Lubes processing

- Background: Solvent extraction of heavy vacuum gas oils (HVGO) is used to remove multi-ring aromatics that degrade lube performance while retaining saturates and mono-aromatics.
- Model Study: Fluorescence measurements of anthracene and pyrene have been studied for the partitioning between iso-octane and polar solvents.
- Reality Check:
  - Model compounds
    - Neither anthracene nor pyrene are found in petroleum HVGO
    - Anthracene and pyrene do not boil in the HVGO temperature range (i.e., 850-1050°F)
    - Most 3+ ring aromatics in HVGO have 2+ sides
    - Some 3+ ring aromatics include fused naphthene rings
    - 3+ ring aromatics in the 850-1050°F range have molecular weights that are equivalent to C25 - C32
  - Matrix oil
    - Iso-octane is immiscible with extraction solvents; HVGO less so
    - Iso-octane has no aromaticity, vs. >20% in HVGO

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- Measurement
  - Fluorescence is sensitive to self-quenching; ppb levels are used for testing
  - Fluorescence is color quenched; so, only pure solvent can be applied
- Advanced characterization: Various methods have shown that HVGO may contain 5 to 20% compounds with three or more fused rings and total aromaticity of over 30%.
  - Appropriate 3-ring structures are phenanthrene and chrysene
  - Appropriate structures are alkylated with two short and one long side chain
  - Extraction evaluation requires wet extraction solvents

Shale Oil Hydro-processing

- Background: Shale oils that are produced as pyrolysis oils from resources located in Colorado and Australia resemble coker liquids but are much richer in N and lower in S.
- Model Study: Shale oil fractions were hydro-treated to reduce olefins under conditions that were developed for coker liquids. Excessive amounts of water and ammonia were detected. Pyrolysis of model amides yields ketones and nitriles.
- Reality Check:
  - Model compounds:
    - Functional groups only identified after the fact
  - Matrix Oil - OK
  - Measurement:
    - Too simplistic; based on elemental analysis, tests for olefins
- Advanced Characterization: HPLC, MS and FTIR demonstrated the presence of ketones, nitriles, and amides in addition to the pyrrole and pyridine benzo-logs normally found in coker liquids.
  - Appropriate model compounds identified
  - HPLC can separate fractions by functional groups
    - Ring types
    - C13 NMR indicates alkylation
  - FTIR can monitor functional groups
  - MS (GC/MS) defines MW

Non-Porphyrin Ni &V Compounds in Vacuum Resid

- Background: Refinery vacuum resid contains varying amounts of Ni & V that is identified as non-porphyrin metal compounds on the basis of Soret and elemental analyses.
- Model Study: Model Ni & V model pophyrins were well resolved from Ni & V compounds in vacuum resid and a variety of other model organometallic Ni & V compounds in toluene by HPLC or GPC techniques.
- Reality Check:
  - Model Compounds:
    - Commercially available Ni & V etio-porphyrins do not resemble native porphyrins
    - No basis for alternative organo-metallics beyond availability
  - Matrix Oil
    - Toluene adequate for dissolving resid
    - Toluene inadequate for dissociating asphaltenes
  - Measurement
    - Soret bands (porphyrin colors) are structure dependent
    - Ni & V porphyrins as pure compounds yield Soret bands
    - Ni & V mixtures of porphyrins overlap Soret bands
    - Vacuum resid color overlaps Soret bands
    - HPLC & GPC not run at sufficient temperature to dissociate asphaltenes (~180°C)

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- Advanced Characterization
  - XPS and related techniques demonstrate that <u>all</u> Ni & V are in a tetra-N environment (i.e., in porphyrin-like complexes)
  - Some commercial model compounds are substituted in bridgehead positions, not seen in petroleum
  - Modern MS techniques have identified a large variety of C28 to C32 (i.e., alkyl isomers) of the Ni & V porphyrins

The limitations of a research study can be determined by how adequately the choice of model compounds, matrix material, and methods of detection probe the chemical reaction space. The chemical research space can be envisioned as a balance of three contributing factors (Figure 1).

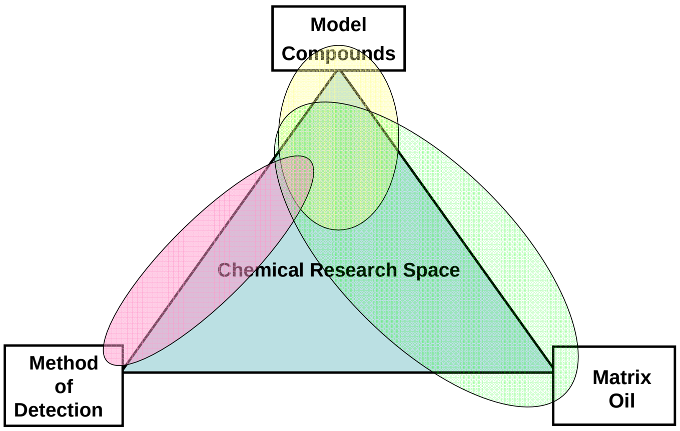

Figure 1 - Chemical Factors in Research Studies

As shown, each of the factors may cover only a portion of the research space, and a given combination may only represent a small portion of the area of interest. It is important to recognize that all three factors bound the results. A combination of two factors may dictate the choice of the third. As a trivial example, if color is to follow a reaction of a model compound, then the matrix oil should dissolve the compound and have no color of its own.

Some of the parameters for each factor are listed below.

Model Compound	Matrix Oil	Detection Method
Functional group	Boiling Range	MW range
Molecular weight	Aromaticity	Ionization
Core Ring Structure	Purity	Sensitivity
Side chain(s)	Compatibility	Interferences
Steric Hindrance	Transparency	
Purity	Viscosity	
Availability	Solvency	

This list is far from complete. However, it provides a framework for designing or evaluating research studies. As seen in the examples, a poor choice of model compounds, matrix oil, or detection method limits the relevance of the research.

Advanced characterization methods play a vital role in maximizing the benefit of research studies. A thorough characterization of a target process stream defines the range of molecules that must be included as model compounds. The same characterization can identify a composition that meets the solvency of the matrix oil and compatibility with analytical measurement methods. Future articles will expand on the framework described above.

Win Robbins has extensive analytical expertise in the areas of reactive sulfur/naphthenic acids characterization, HPLC-2 ring type definition technology, and polynuclear aromatic hydrocarbons (PNA) characterization. Please contact Jerry Lacatena if you'd like more information on Carmagen's expertise in this area.

Article 2 - API RP 579 Fitness-for-Service

By Stephen J. Gliebe, P.E.

The first installment of the Fitness-For-Service (FFS) series of articles introduced the concepts contained in API RP 579. The types of assessments (i.e., Level 1, Level 2, Level 3) and degradation mechanisms (e.g., general metal loss, pitting) were described, and plants were encouraged to consider how FFS assessments could be used to reduce maintenance expenditures in their facility.

The discussion was limited to assessing general metal loss using individual point thickness readings applied to components subjected to pressure loading ONLY. The procedures and limitations for assessing general metal loss under pressure loading conditions were provided.

In this second installment, we will take a look at a general metal loss (GML) Level 2 assessment in a region located away from structural discontinuities, but where supplemental loads must be considered.

GML Level 2 Limitations

GML Level 2 assessments are permitted only if certain conditions are satisfied. The complete list of limitations in Section 4 of API RP 579 should be reviewed before proceeding with a GML Level 2 FFS assessment. Some of the limitations are:

- The original design criteria must be in accordance with a recognized code or standard (e.g., ASME Code Section VIII or ASME B31.3).
- The component must have either a design equation that specifically relates pressure (or liquid fill height for tanks) and/or other loads, as applicable, to a required wall thickness (e.g., pressure vessel or storage tank cylinder), OR must be one of the following components:
  - Pressure vessel nozzle, tank nozzle, or piping branch connection
  - Reinforcement zone of conical transitions
  - Cylinder-to-flat head junctions
  - Integral tubesheet connections
  - Flanges
  - Piping systems
- Supplemental loads that impact the thickness of the component being evaluated must be considered. Some examples include loads due to:
  - Weight of the component including contained fluid, insulation, or refractory
  - Wind, earthquake, snow and ice
  - Constraint of free thermal expansion
  - Process upset conditions

GML Level 2 Methodology

A Level 2 GML assessment may be performed using individual point thickness data or thickness profiles as described in Article 1. Thickness profiles are required if there is too much variation in the individual point thickness readings. Below is a summary of the Level 2 GML assessment methodology using thickness profiles where supplemental loading must be considered. Guidance on the use of thickness profiles can be found in API RP 579 Section 4.

GML Level 2 Assessment Summary For Cylindrical Components:

- Review the inspection history of the equipment.
- Calculate the required minimum thickness due to circumferential stress (e.g., caused by internal pressure or liquid fill height).
- Determine the supplemental loads (e.g., weight of the component and insulation, wind, earthquake). Refer to API 579 Appendix A for additional details on loads.
- Calculate the required thickness due to supplemental loads.
- Calculate the required minimum thickness due to longitudinal stress (e.g., consider thickness required for internal pressure, external pressure, and weight loads).
- Obtain the thickness profiles for the thin areas.
- Determine the critical thickness profiles for the circumferential and longitudinal directions (CTPC and CTPL).
- Select the minimum measured metal thickness from the lower of CTPC or CTPL.
- Specify the Future Corrosion Allowance (FCA). The FCA is the amount of metal loss anticipated before the next scheduled inspection.
- Compute the remaining thickness ratio. The remaining thickness ratio is based on the minimum measured thickness, the FCA, and the minimum required thickness as noted below. It is one of the inputs needed to establish the length over which the thickness data may be averaged.

$$R_t = \frac{t_{min\_measured} - FCA}{t_{min\_required}}$$

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- Compute the maximum length that may be used for thickness averaging.
- Determine the axial and circumferential extent of the flaws using the tables and equations in API RP 579 Section 4.
- Measure the distance from a major structural discontinuity (e.g., nozzle, support skirt).
- Determine the average and minimum thicknesses by numerically averaging over the length of the flaw. For cylinders, this must be done in both the longitudinal and circumferential directions.
- Compare the calculations for the remaining thickness ratio, minimum measured thickness minus the FCA, average measured wall thickness, circumferential extent of the flaw, and the distance from a major structural discontinuity, to the API RP 579 acceptance criteria.
- If the flaw is acceptable, develop an inspection strategy for the equipment.
- If the flaw is unacceptable:
  – Repair the flaw, rerate or replace the component
  – Lower the FCA (e.g., by reducing the inspection interval or mitigating the corrosion)
  – Conduct a Level 3 FFS assessment. Note that a Level 3 assessment is not required in most situations, and it requires more data and more time to conduct.

Article 3:

Article 3 in this series will cover API RP 579 General Metal Loss Level 2 assessments for reinforced nozzles in a cylindrical shell using the area replacement method.

Steve Gliebe is a Professional Engineer with 30 years experience in the refining and chemical industries. He is well-versed in both engineering and supervision including hands-on experience managing maintenance and capital projects, training union and management colleagues, supervising maintenance/inspection organizations, developing programs for preventative maintenance of fixed equipment and piping per industry standards, and performing root-cause analyses to improve equipment reliability. Please contact Vince Carucci if you'd like more information on Carmagen's expertise in these areas.

Process Plant Bad Actor Program

By Walter Lambertin

Any process plant that wishes to have a cost-effective maintenance program and maximize unit run lengths must have an effective equipment Bad Actor Program. Such a program will systematically minimize repetitive or costly repairs, extend run lengths, and focus maintenance expenditures on those items that impact on plant reliability. This will contribute to increasing profits through longer unit run lengths and reduced maintenance expenditures in the long run.

The first step in starting a general equipment Bad Actor Program is to define what a "Bad Actor" is. Each plant must develop a definition that suits their particular situation. We offer the following proposed definitions as guidance.

Static Equipment – Piping, Drums, Pressure Vessels, Heat Exchangers

- Any equipment tag or line number with one or more interventions per year
- Any equipment tag or line number with a repair in excess of $75,000
- Any equipment tag or line number that has a repair cost/year in excess of the average for its class
- Any equipment tag or line number that contributed to a planned shutdown, or an unplanned shutdown or slowdown
- Any equipment tag or line number that did not reach its expected life
- Any equipment tag or line number that experienced a problem within two months after being repaired

Fired Equipment – Furnaces & Boilers

- Any equipment tag with a repair cost in excess of $150,000
- Any equipment tag that contributed to a planned shutdown, or an unplanned shutdown or slowdown
- Any equipment tag or component that did not reach its expected life
- Any equipment tag that experienced a problem within two months after being repaired

Other Equipment – Machinery, Instrumentation, Analyzers & Electrical

- Any equipment tag that has a Mean Time Between Repair (MTBR) lower than the average for its generic class
- Any equipment tag with one or more interventions per year
- Any equipment tag with a repair in excess of $15,000
- Any equipment tag that has a repair cost/year in excess of the average for its class
- Any equipment tag that contributed to a planned shutdown, or an unplanned shutdown or slowdown
- Any equipment tag that experienced a problem within two weeks after being repaired

Prioritization of Bad Actors

- Calculate the margin losses and maintenance costs for each bad actor
- Rank in order of highest total cost
- Evaluate the resources available to study these issues
- Estimate the probability of success in finding a cost-effective solution
- Select the bad actors to be evaluated

Having a Bad Actor Program in place is not the only thing needed to have a cost-effective, process plant reliability and maintenance program. But without one, plant management cannot hope to achieve "world class" results.

Walter Lambertin has over 33 years experience in refinery technical support positions in the maintenance, mechanical, and materials engineering areas. Extensive experience in refinery technical organization, mechanical and technical procedures, and cost effective work practices. Please contact Vince Carucci if you'd like more information on Carmagen's expertise in this area.

HIGHLIGHTS

Training

- Presented a training course covering "Safety in Process Design" for a Canadian process plant. The course was very well received and we anticipate doing it again for the same client in the near future.
- Presented a training course covering "Design and Maintenance of Aboveground Atmospheric Storage Tanks" at a Canadian location. The course was attended by individuals from several local companies and was very well received.
- Presented a training course covering "Design and Inspection of Refractory Materials for Refineries" for a US refining company. This course has been presented at several refineries owned by the same company and is always very well received. Information discussed has typically assisted the refinery improve the overall reliability of their refractory systems and identify preferred methods for its installation and repair.
- Providing global manufacturing training course development support for a major refiner.

Heat Transfer Equipment

- The performance of a revamped refinery fluid coker CO boiler was examined. Its predicted performance with increased CO fuel gas availability and a new clean economizer with a fraction of total available tube passes blocked was assessed and found to be acceptable.
- After the operational and design review of eleven (11) critical heaters for a Western European refinery, valuable assistance was provided relating to materials and study of hot spots in radiant section tubes of crude vacuum distillation unit heater.
- Assisted a major European refiner with a study of a mild Hydrocracker preheat furnace for revamped conditions related to a local expansion project at the refinery. The study involved modeling the heater based on the existing plant data and testing the modifications to a validated model to determine the required changes in the basic design of the heater.
- Continued to provide resident, heat transfer related consulting to the central engineering division of a major oil company in the areas of fired as well as non-fired heat transfer equipment.
- Continuing to provide a furnace modeling and evaluation service for a major revamp project for a Canadian refiner – this time involving a hydrogen plant reformer furnace.

Process, Operations, and Safety

- For a European refiner, a study was concluded to determine the additional cooling water tower capacity that can be attained with possible modifications such as inclusion of a new high performance fill and/or upgrading of the air handling mechanical equipment (fan, motor, switchgear, etc.), and/or improving the design of the drift eliminators.
- Continuing to provide plot layout support for domestic and international refiners.
- Performing strategic reliability initiatives for an international refiner, including a hydrocracker catalyst evaluation and reactor loading plan to maintain conversion, increase run length, and also produce a 10 ppm sulfur diesel plus assessment of unit performance.
- Performing review of vacuum tower performance test run data, and evaluation of wash zone internals to assess if modifications are required. Review of tower simulations and recommendation to modify tower internals is anticipated.
- Performed scoping study of overseas refinery to identify areas recommended for further optimization of plant operations management. Identified a significant number of areas where more detailed study is warranted.
- Continuing support on developing LOPA standards for a domestic refiner.
- Providing ongoing process design support in a major technology provider's offices.
- Providing on-going technical process and heat transfer support in an expanding role to a major domestic client for "first-of-a-kind" Biomass process development for ethanol production, Devol and CO_2 removal technology evaluation are included in this activity.
- Performing PIMS modeling and refinery planning support.
- Provided process design consultation on refinery planning for a Northwest refiner anticipating expansion to handle oil sands.
- Providing ongoing mogas blending consultation to seven domestic refineries regarding optimization, equipment and controls assessment, and certification.
- Performing Hazop support at multiple locations for a domestic refiner.
- Providing extended onsite process engineering support to a US refiner's expansion program, including support in the contractor's office to assist in engineering program execution work.

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- Supporting client's work for a US refiner's expansion program to investigate broad process opportunities, including fuel gas balance improvement, H_2 management and reformer octane optimization, review of tower internal modifications, and other miscellaneous support.
- Conducting revamp studies for US refiner's multiple trains of crude and vacuum unit fractionation, with the objective of identifying profit improvement opportunities.
- Supporting an Indian refiner in hydrocracking operations.
- Providing analytical chemistry and materials engineering support to a corrosion inhibitor vendor for a client intending to process high acid crudes.
- Conducting scoping review of overseas client's wastewater treatment and cooling tower facilities.
- Providing pilot plant and brainstorming support to domestic refiner's process research entity.

Reliability and Maintenance

- Provided follow-up, onsites Cold Eyes Review of the plans being developed for a refinery-wide turnaround for a major refinery in Western Europe. Several improvements were made as a result of recommendations provided during an earlier visit, which resulted in a cost saving of at least $1M. Additional recommendations were made during this visit which, if implemented, could yield additional time and cost savings. Among these are reductions in the planned time to shut down the units, improvements in contract strategies and scheduling, increase in turnaround committee review meetings and oversight, etc.
- Developed a process plant Turnaround Resource Guide for a major international oil company. The Guide provides recommendations for the best ways to plan for and organize turnarounds, especially those that are being done in conjunction with capital projects, in order to avoid schedule and/or cost issues that have resulted in increased cost in the past.

Materials, Refractory, and Corrosion

- Consulting on numerous refractory related issues in both fluidized cat crackers (FCC's) and sulfur plants (SRU's) continued since the last newsletter issue. In addition to normal evaluations and consulting of the refractory systems, three US refineries were also assisted by providing laboratory testing and analysis of their refractory samples (bricks and lining) to provide an insight into the maintenance requirements for their units.
- Provided technical assistance in re-writing an existing refractory engineering specification via updates to the knowledge base and incorporating feedback from different operating and engineering locations of the client organization.
- Corrosion Mitigation Guidelines were developed for a domestic oil company for their FCC units and crude units at multiple locations. The work involved complete investigation of the plant inspection reports and plant geometry to determine the state of corrosion in various process areas of the plant in detail.
- Provided materials engineering assistance to a US refiner during a failure analysis of a critical refinery gas turbine. The services included a thorough investigation of the work being carried out by the manufacturer of the turbine in analyzing potential causes of failure.

Project Management

- Continued to provide significant project management and cost engineering consulting support for multiple clients in the US and overseas.
- Continued to provide long term resident engineering support in the areas of cost estimation, procurement, and construction management to a major grassroots petrochemical undertaking in the Far East.

Mechanical Equipment

- Fitness for Service (FFS) evaluations were concluded for several pressure vessels and one crude preheat furnace for (a) a major chemical plant in the US and (b) a key refiner in Europe. An FFS course is now planned for the European client in Spring of 2008 when the actual FFS work done will be utilized as one of several case studies.
- Provided mechanical engineering assistance to an EPC company during their detailed engineering related to a major revamp of a refinery fluid coker unit.
- Continuing to provide consulting services to the Biomass fuel technology developers within the US. Mechanical engineering analysis and review of alcohol reactors from the point of view of mechanical engineering quality control (MEQC) was provided for a biomass conversion process developer in the US.

Miscellaneous

- Continued to provide welding, materials, and process engineering litigation consulting support for multiple major cases.
- Assisted a domestic refinery for a major oil company in reviewing crane usage procedures for three different cranes in three different services during a turnaround and revamp project construction.
- Providing technical litigation support in analytical chemistry, process and metallurgical areas to defend major refiner in a class action suit.
- Providing technical consultation regarding client's review of third party intellectual property and proprietary catalyst benefits.