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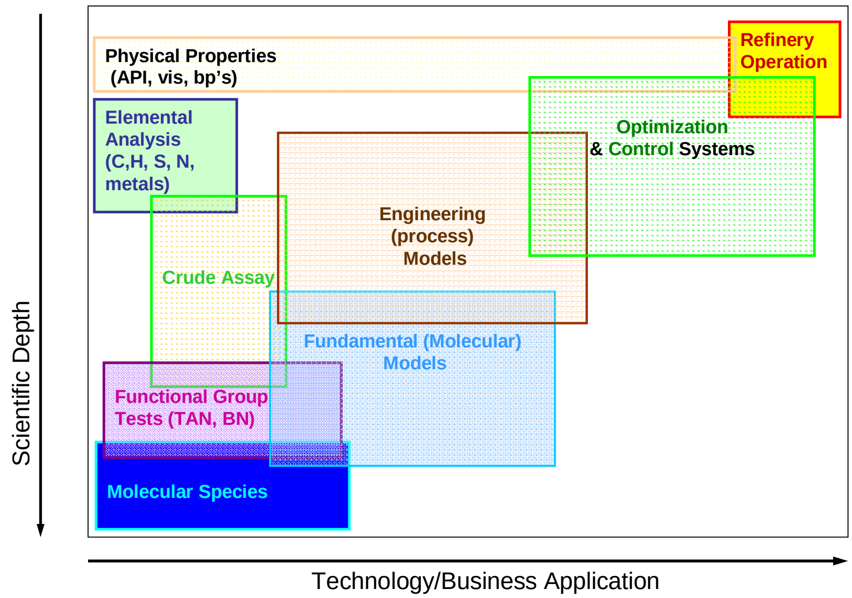
Applied Chemistry Spans Molecules, Models, and Refinery Reality

By Winston K. Robbins, Ph.D.

Modern refineries operate on the basis of complex optimization models that are derived from basic research. Optimization model inputs include refinery configuration, operating conditions, physical properties, and target product qualities. Process parameters are adjusted to maximize the return for a given blend of crudes and target products. The sophistication that has been reached in producing control models has made refinery practice distant from the chemical knowledge underlying the fundamental molecular models (Figure 1).

Figure 1. Refinery Operations are Distant from Molecular Chemistry



Operations run smoothly for conditions where the models adequately manipulate the molecular information with kinetic and thermodynamic conditions adapted for specific refinery hardware configurations.

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Refinery operation emphasizes process control parameters (e.g., heat, hydrogen, pressure, etc.); modeling combines engineering with high-level computation; molecular characterization draws on research analytical methods. Success continues as long as the integrity of the molecular data and assumptions of the models are maintained. That is, knowledge flows along the diagonal from molecules to refinery.

Refinery operators, model builders, and research analysts often apply chemistry to a narrow task; while each uses chemistry, none may have a broad enough chemical knowledge to troubleshoot upsets. When upsets occur, help from an applied chemist with practical knowledge of the underlying petroleum chemistry may be needed. Drawing on experience, broad chemical knowledge, an understanding of processes, and the assumptions underlying the model development, the applied chemist provides molecular insights to a real refinery problem. In troubleshooting teams, the applied chemist may suggest analyses, question assumptions, and propose solutions that might be overlooked by the specialist.

Contributions of applied chemists are often overlooked, but can be found throughout the industry.

For example, consider the following incident:

A refinery hydro-finishing wax for food-related applications, routinely sent samples to an analytical lab for FDA compliance testing. Although this product had a long history of complying easily, a sample failed. Requests for additional tests confirmed that the product was off-spec and the product was diverted to other applications. An applied chemist was asked to determine the cause of the failure.

The FDA test, developed for screening products for polynuclear aromatic hydrocarbons (PAH), combined DMSO extractions with pass/fail UV measurements at four wavelengths. The applied chemist reviewed previous compliance tests at the lab and found that while most samples had passed easily, the batch prior to the rejected lot exhibited a marginal pass. When asked about this, the refinery responded that there had been no apparent change in the hydroprocessing conditions that might coincide with the change in UV performance.

At the applied chemist's request, additional tests were run on retains of the "easy," "marginal," and "rejected" lots. These tests replicated the earlier data, confirming that the analytical procedure was being performed properly. In observing the analytical test, the applied chemist used a "black-light" to examine the extracts from each test type as a quick check for PAH (many fluoresce under black light excitation). The "reject" sample glowed brightly, the "marginal" glowed dimly and the "pass" sample remained dark. With this observation, he returned to the lab and inspected the spectra of the "rejected" and "marginal" tests. These spectra exhibited sharp peaks characteristic of individual PAH. Upon his request, more sophisticated analytical procedures were used to isolate and identify perylene as the PAH responsible for the rejection.

The applied chemist recognized perylene as a PAH that can be formed in hydroprocessing when operated under hydrogen starvation conditions. With perylene identified, the refinery again checked its records on operations. This investigation revealed that just prior to sampling of the "marginal" batch, the wax had gone "off-color." Suspecting a pin-hole leak in the feed heat exchanger, the operator had increased the hydroprocessing temperature from 550°F to 575°F and brought the color back in spec. Over time, temperature was increased further to hold color, but according to the readings, the

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Controlling Piping System Vibration

By Vincent A. Carucci

The method used to solve a particular vibration problem depends on the type of vibration and the type of piping system. For example, adding restraints to a piping system will not solve a vibration problem caused by high acoustic energy.

It is not always possible to eliminate or isolate the source of vibration in many piping systems. Therefore, other means must be used to control vibration. Some common methods for doing this are briefly described below.

Bracing

One way to control piping vibration is by adding bracing (i.e., restraints) to the system. This increases the mechanical natural frequency of the piping, thus ensuring that resonance due to low frequency excitation will not occur. It also limits large deflections that could be caused by slug flow, water hammer, etc.

When bracing addition is being considered, it must be confirmed that this will not adversely affect the thermal flexibility of the piping system. Adding restraints increases the system stiffness and can cause higher pipe thermal stresses and end-point reaction loads. New thermal flexibility calculations may be required to confirm that the design is acceptable after adding the restraints.

Snubbers

Vibration amplitudes can be decreased by installing hydraulic or mechanical snubbers. These devices (e.g., dashpots or other frictional devices) increase the system damping by resisting rapid displacements, such as that resulting from vibration. However, they permit movement resulting from slow displacements, such as those from thermal movement. Thus, snubbers may be used in situations where bracing must be added to reduce or prevent vibration movements, but rigid restraints would cause unacceptable thermal displacement stresses or loads.

Surge Suppressers

Surge suppressers may be used to control surge or pulsation-induced vibration. A typical surge suppresser consists of a pilot operated valve which quickly opens after a power failure through the loss of power to a solenoid, or by a sudden large pressure reduction or increase at the surge suppresser. The open valve releases liquid from the line being protected, thus smoothing and reducing the pressure fluctuation. The valve is closed at a slower rate by using a dashpot in order to limit the pressure rise as the liquid flow is shut off.

Accumulators

An accumulator is a pressure vessel that is partially or completely filled with a gas (usually inert). This vessel is then connected by pipe to the main line being protected. In the simplest case, the liquid in the pipe is in direct contact with the gas. In some cases, an elastomer membrane separates the liquid from the gas but transmits pressure between them. In other cases, a rupture disk forms a more rigid barrier between the gas in the accumulator and the liquid in the pipe. For the first two configurations, the device acts instantaneously to a rise in pressure at the gas/liquid interface. In the last configuration, the rupture disk delays the reaction time from 0.2 to 2.0 milliseconds since it must rupture before pressure is transmitted between the two fluids.

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temperature never exceeded 650°F (a temperature where hydrogen starvation would begin). Because the applied chemist had provided such strong evidence of over-temperature, the thermocouples were checked and the controlling thermocouple was found to be 50°F out of calibration.

As a result of this work, the wax hydroprocessing unit was shut down, the pin-hole fixed, and all thermocouples recalibrated. Once lined out, the unit was back on stream producing food-grade wax that easily met the FDA requirements.

In this case, the applied chemist provided the link between the hydroprocessing process and the analytical laboratory. His knowledge of PAH, the choice of analyses, and the effect of process conditions on hydroprocessing chemistry, allowed him to guide the refinery to a successful solution of its upset.

In many cases, the input of the applied chemist is overlooked because his skill doesn't fit into a "routine" job description. In a refinery, an experienced person (senior engineer, lab head, etc.) may serve as an applied chemist when needed, as in troubleshooting. At other locations, outside resources (e.g., company research group, engineering service provider, or consultant) may also be called upon to provide this capability. Ideally, every refiner should have a network of applied chemists identified for their specific operations. Do you know who your applied chemists are?

Future articles will provide additional examples of the applied chemist at work.

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Temporary Restraints

Cables or chains can be used to temporarily control large deflections caused by vibration in piping systems. The cable or chain is attached to the pipe, connected back to nearby structure, and tightened to stop the pipe movement. Quite often, even blocks of wood or scrap steel are used as wedges between the pipe or its supports and nearby structure to stop pipe movement. This approach is useful in stopping large amplitude vibration before it can damage the pipe, and to determine the best locations to place permanent bracing. This technique is not a permanent solution to a piping vibration problem.

Since the temporary restraints are installed while the system is in operation (and hot), their presence could restrict pipe thermal movement when the system is shut down. This should be considered when locating the restraints to determine if they would cause excessive thermal stresses or loads when the system is shut down. In extreme cases, it might be necessary to remove the restraints before or as the system is shutting down in order to permit free thermal movement.

Hot Tap Guidelines

By Vincent A. Carucci

Hot tapping is the technique used to attach a branch connection to a pipe while the system is in service, and then creating an opening in that pipe by drilling or cutting. While hot taps are most often done on pipe, they may also be done on pressure vessels and storage tanks. The figure illustrates a typical hot tap installation.

As an example, Carmagen engineers developed the design details and procedures that were used to hot tap two nozzles into a crude tower. In this case, the nozzles were needed to install bypass lines around plugged distributor trays, and were located about 150 ft. above grade.

Hot taps permit adding connections without depressurization or disruption of process operations. They may also be used to make piping connections where it would be inconvenient to prepare the system for hot work. Hot tapping is also used to isolate pipe sections for maintenance by plugging or stoppling the line.

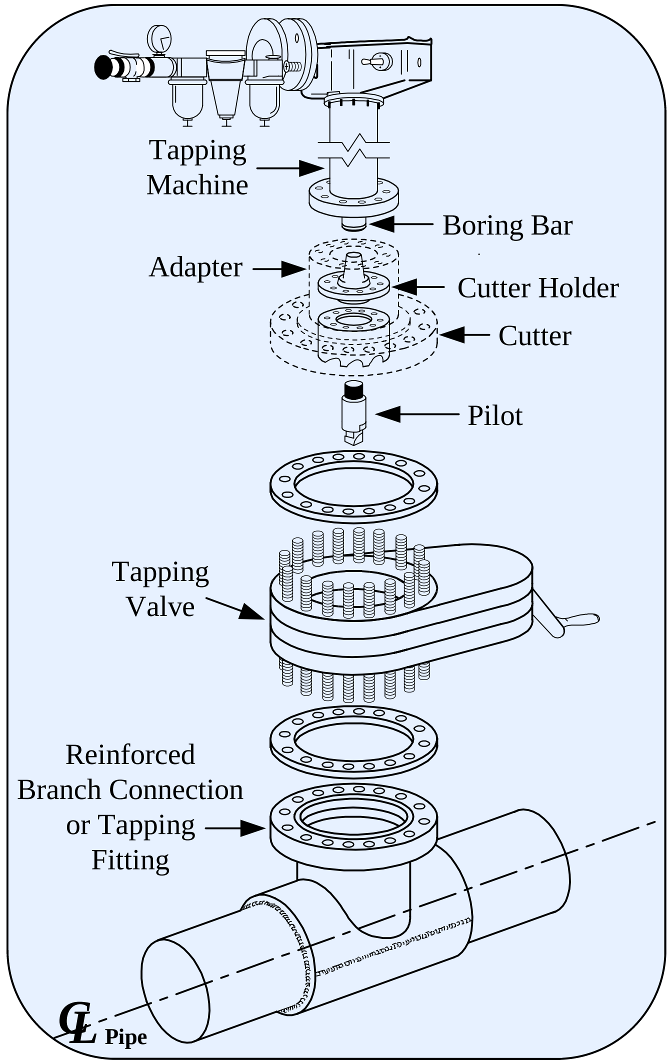
Hot taps are successfully completed every day. However, remember that a hot tap is an inherently dangerous operation. Therefore, hot taps should generally be used only when it is impractical to take the system out of service. When specifying hot taps, care is required in inspection, design, and testing to ensure that this operation is done in a safe and reliable manner. Therefore, a hot tap should be considered only after other options are evaluated and rejected. Each hot tap should be properly designed, the hot tap location thoroughly inspected, and the installation procedures reviewed.

Sometimes A Hot Tap Should Not Be Done

Hot taps may be made in most cases without difficulty. However, hot tapping is not recommended in some cases and requires extra precautions in others. Each case must be evaluated based on the particular service, pipe material, and hot tap location.

Hot tapping is not recommended under any of the following conditions:

- Piping containing a combustible or flammable mixture.



Typical Hot Tap Installation

- Piping containing acids, chlorides, peroxides, or other chemicals that are likely to decompose or become hazardous from the heat of welding (e.g., sulfuric acid or acetylene).
- Piping containing caustic.
- Piping that contains pure oxygen or chlorine.
- Air lines where the absence of hydrocarbon cannot be assured.
- Monel piping handling sulfur compounds.
- Stainless steel piping containing catacarb solution.

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You Can Hot Tap, But ...

Services or conditions where hot tapping may be permitted, but where special precautions are necessary, are listed below.

- Systems with no flow, unless the fluid is not dangerous (e.g., cooling water) or the pipe is open to another system or equipment item.
- Hydrogen service. It should first be confirmed that the pipe has not experienced hydrogen attack (e.g., by confirming that it has not operated above the Nelson Curve limits).
- Flammable or combustible liquid below atmospheric pressure. The concern here is that a flammable or combustible mixture may form if air enters the system during the hot tap.
- H_2S or other toxic materials. Additional safety precautions may be needed.
- Air lines that are free of hydrocarbon, but with greater than 23.5% oxygen.
- Butadiene, ethylene, or wet H_2S services.
- Piping operating at a process temperature above 750°F (400°C), due to potential concerns with creep cracking at attachment welds.
- Equipment that meets a Level 3 brittle fracture assessment per API RP 579 (i.e., grandfathered) requires special welding precautions to prevent brittle fracture.
- Stainless steel systems subject to chloride stress corrosion cracking should be inspected first to confirm that cracking is not already present.
- Hot taps that will be made at low temperatures [e.g., carbon steel below 40°F (4°C)]. Special welding procedures will be required to prevent moisture.
- Services that may produce carburization, nitriding, or other forms of embrittlement of the material to be welded. Special welding procedures may be needed to avoid embrittlement. In addition, confirm that there is adequate remaining thickness of unembrittled material.
- Services in which aqueous or room temperature hydrogen fissuring may occur. Perform NDE to confirm that the material is sound.
- Piping requiring PWHT. However, it may still be possible to hot tap, depending on the material involved and the reason for the PWHT.
- For piping with internal linings, cladding or weld overlay. The internal material will be damaged by the hot tap, and the potential consequences of this must be evaluated.
- Concrete or refractory lined pipe. The consequences of potential lining damage or detachment must be evaluated.
- Underground pipe.
- Large diameter lines where it might be necessary to reinforce the coupon to prevent it from becoming flat and causing the cutter to bind.

This article provided an introduction to what a hot tap is, when it should not be done, and when it may be done with special precautions. Other articles will discuss hot tap location, design, installation, inspection, and safety considerations.

HIGHLIGHTS

- Assisted a technology developer in a conceptual design for a novel reactor system.
- Completed a Hydroprocessing reactor design for a technology licensor.
- Provided troubleshooting support on a Cracked Naphtha Hydrotreating unit at a US-based refiner.
- Provided specialized equipment layout consulting for a large, grassroots facility in the Middle East.
- Performed or participated in several HAZOP reviews.
- Provided specialized coking/incompatibility consulting to several clients.
- Providing ongoing Process and Offsites/ Utilities support in connection with the expansion of Middle East gas facilities.
- Assisting a European client in Energy Management optimization for a designated refinery unit.
- Providing specialized support to a major novel technology-based project.
- Conducted a "Cold Eyes Review" for a modification to a fired heater for a client in the Far East.
- Provided Reliability and Maintenance program recommendations for a European client. When implemented, these will achieve at least 25 M$ annual credits through a combination of reduced costs and improved mechanical availability.
- Conducted a scoping study for a major Reliability and Maintenance review effort for an upstream client in Canada.
- Carried out a Marine Terminal Technical Assessment to allow the handling of larger crude tankers at a domestic refinery.
- Provided Materials Engineering Consulting advice regarding a waste heat boiler tube failure problem for a domestic refiner.
- Provided shutdown planning assistance for refractory lined units for a refining client in Canada.
- Completed multiple pressure vessel, storage tank, and piping system evaluations.