

'Green up' air and water pollutant control

Recycling spent activated carbon can offer economic benefits and environmental credits

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Petroleum refineries are faced with a number of purification needs, driven by increasingly stringent regulatory requirements as well as improving product quality. One traditional technology, activated carbon, remains a cost-effective method for refineries to comply with federal, state and local regulations, and handle product purification needs.

Activated carbon is successfully used in many "clean up" applications in a typical refinery. Recent cost increases for virgin activated carbons, however, have created a renewed interest for "green" solutions for many carbon applications, such as substituting virgin activated carbons with reactivated carbons.

Reactivated carbon is spent carbon that is recycled by being regenerated at very high temperatures. In refineries, reactivated carbons can be used for volatile organic compounds (VOCs) abatement in vapor-phase applications, wastewater treatment and groundwater remediation.

Green benefits. The most important benefit of using reactivated carbon is cost savings. Recycling carbon reduces operating costs since the expense for reactivated carbon is typically 20%–40% less than the cost of virgin carbon. In addition, some facilities also receive environmental credits issued by regulatory agencies for waste minimization. The reactivation process ends the chain of custody for adsorbed contaminants, thereby eliminating liabilities associated with handling and disposal of spent carbons. Reactivated carbon is considered a recovered resource.

Reactivation process. Thermal reactivation uses steam and high temperatures to remove and to destroy the organic compounds that have been adsorbed onto the carbon. Fig. 1 shows a typical reactivation unit. The reactivation process has three goals:

- Restore the spent carbon's activity level to as near as original as possible
- Maintain the internal pore structure of the media
- Minimize product losses due to gasification and attrition.

During reactivation, residence time in the furnace, reactivation temperature and gas composition must be carefully controlled to obtain the desired reactivated carbon quality. The reactivation process typically has three stages:

- **Stage 1** (furnace temperatures of 200°F–500°F)—The carbon is dried, and more volatile/low-boiling point organics are volatilized off the spent carbon.

- **Stage 2** (furnace temperature of 400°F–1,200°F)—Pyrolysis of higher boiling point organics occurs on the carbon surface.
- **Stage 3** (furnace temperature of 1,350°F–1,800°F)—Gasification of the pyrolysis residues occurs.

Reactivation gases containing volatilized organics and residues, exit the furnace, where they pass through an afterburner to mineralize any remaining organic compounds. Inorganic gases are removed via a wet scrubber.

Two furnace types are used to thermally reactivate carbon: multiple hearth furnaces and rotary kilns. Each has distinct advantages and disadvantages:

Multiple hearth furnace (MHF):

- High degree of control over reactivation process, especially the furnace atmosphere for steam ratio as well as gas use



FIG. 1 Multiple Hearth furnace plant in Parker, Arizona.

APPLICATIONS TO USE ACTIVATED CARBON IN REFINERIES

Activated carbon is a versatile adsorbent material that has several common applications within a typical petroleum refinery. Regulatory compliance and improvement in product quality are the two main drivers for using activated carbon. Common applications include:

- **Vapor-phase VOC treatment and control.** Compliance with the Benzene NESHAP or local air emission regulations drives the need for VOC control at sewer sumps, covered API separators and DAF units, storage tanks, and other sources. Adsorbents using either virgin (pelletized coal-based or granular coconut shell-based) or reactivated carbons can be applied.

- **Vapor/solvent recovery.** Economically valuable products at refineries and terminals can be recovered via pressure swing or temperature swing systems that use activated carbon. Carbon type is driven by the boiling point of the solvent; volatile solvents often require microporous carbons (e.g., coconut shell-based), while higher boiling point solvents require macroporous (coal-based) carbons. Carbons with high working capacities (allowing for effective adsorption/desorption cycles) are desired.

- **Hydrogen sulfide removal.** Sour crude oils are often the source of hydrogen sulfide (H₂S) emissions. Specialty grades of carbon (impregnated or catalytic grades) can remove H₂S.

- **Wastewater treatment.** Activated carbon can help refineries meet wastewater discharge permits (COD, BOD, TOC and

biotoxicity). Reactivated carbons are most commonly used in this application that often requires upfront testing or piloting to properly size the system.

- **Groundwater remediation.** Organic compounds (BTEX, MTBE) often migrate into groundwater supplies from leaking underground storage tanks or holding ponds. Reactivated or virgin coal-based carbons are often used to remediate BTEX, while coconut shell-based carbons (with higher adsorptive capacity for trace removal) are often selected for MTBE removal.

- **Boiler feedwater treatment.** Organic impurities in boiler feedwater can cause scaling, corrosion, foaming or other problems. A low-silica coconut shell-based carbon (to prevent silica leaching into the feedwater stream) can successfully adsorb organic contaminants.

- **Amine purification.** Various alkanolamines are used in refineries to purify gas streams. The amine solution picks up hydrocarbons and organic acids. A slipstream of the amine solution is passed through a carbon adsorption system to prevent a buildup of these hydrocarbons. Virgin coal-based carbons are the best fit for this application.

- **Decolorization.** Activated carbon can be used for color, odor or contaminant removal from desired end products such as jet fuel, kerosine, gasoline and lube oil. Powdered carbons can be used in batch treatment processes, or granular carbons can be applied in continuous processes.

- Reduces losses due to gasification
- Less physical attrition losses
- More energy efficient on energy consumption per unit of product
- Offers better carbon/gas contact.

Rotary kiln:

- Provides flexible operation
- Creates clean breaks between product runs
- Operation and maintenance require less operator skill than MHFs
- Lower labor and equipment maintenance costs than MHFs.

The decision about which furnace type to use is determined by such factors as fuel sources, requirements for operating flexibility, local technology sources and emission constraints.

Evaluating reactivated carbon performance. The performance of reactivated carbon can be measured by several methods including Iodine and Butane Numbers. These ASTM and AWWA standard adsorption capacity tests are used as an initial basis for comparing reactivated carbon with virgin carbon. While these tests are sufficient for most applications, some applications require comparing the removal efficiency of targeted compounds. For these applications, bottle point isotherms or the Rapid Small Scale Column Test (RSSCT) should be used, which compares the adsorption performance of reactivated vs. virgin carbons with a sample of the influent water stream.

Reactivation services. A number of vendors provide reactivation services. Different programs are available to suit the users' application. These include:

React and return is a highly controlled program in which activated carbons are removed, reactivated and returned for reuse to the same client. It is most commonly applied to potable water

applications. The carbon is segregated from other spent carbons during reactivation and storage. Virgin carbon is used to offset normal losses that occur during handling and reactivation to ensure 100% of the original carbon is returned to the customer.

Pool reactivation is a program whereby spent carbons are segregated and then pooled according to application type (vapor phase/liquid phase) and mesh size. These pooled carbons can then be sold into many applications as a substitute for virgin carbon to lower the operating costs.

Field services associated with reactivation programs include spent carbon profiling, spent carbon removal and packaging, non-hazardous and/or hazardous waste handling and transportation to the reactivation plant or hazardous waste reactivation plant, carbon vessel inspection with minor repair and vessel reloading with reactivated carbon. Vendors performing reactivation services can offer a certificate of reactivation for each shipment, confirming that the spent carbon has been recycled in a manner that meets or exceeds all applicable Resource Conservation and Recovery Act (RCRA) and Benzene National Emissions Standards for Hazardous Air Pollutants (NESHAP) regulations.

Prior to reactivation, spent carbon must be profiled and tested to ensure that it can be safely and efficiently reactivated within the permit limits of the reactivation facility. Typically, a profile form on the spent carbon is completed and a small sample of the spent carbon is provided for testing. Some contaminants, such as polychlorinated biphenyls (PCBs), may not be accepted at certain vendors' plants. Determination of the spent carbon's regulatory status (RCRA hazardous, state hazardous, nonhazardous or falling under the sludge exemption) is the responsibility of the generator of the spent carbon.

Green advantage. Besides recycling spent carbon and eliminating waste to the environment, reactivation can offer other environmental advantages. A refinery that reactivates its spent carbon



FIG. 2 Activated carbon remains a cost-effective treatment technology for air, water and process purification.

may be eligible for environmental credits from regulatory agencies for waste minimization. One example is the sludge exemption, which allows spent carbon to be handled as a nonhazardous waste, and is exempt from the regulations for hazardous waste as described in *40 CFR 262*. The sludge exemption only applies to spent carbon that is not exposed to any wastes specifically listed in *40 CFR 262*, and is only used when the generator of the spent carbon intends to send it to a facility where the material will be reactivated for reuse. As defined in *40 CFR 260.10*, “sludge means any solid, semi-solid or liquid waste generated from a municipal commercial or industrial wastewater treatment plant, water-supply treatment plant or air pollution control facility exclusive of the treated effluent from a wastewater treatment plant.”

The US Environmental Protection Agency (EPA) further provides that a spent carbon may be classified as a sludge when it contains *no listed hazardous waste* and is returned to a reactivation facility where the spent carbon is reclaimed. Since the spent carbon in these applications meets the definition of a sludge, it is not considered a solid waste and therefore, is not considered a hazardous waste.

The sludge exemption must be accepted by the governing state environmental regulations in both the generator’s home state and the state in which the reactivation facility resides. To claim the exemption, the refinery must contact its state environmental regulatory agency to obtain its approval.

Spent carbon profiled as RCRA sludge exempt can be transported either as a DOT-regulated hazardous material or as a

non-DOT-regulated material. The choice is determined by the quantity, in one container, of the hazardous substance on the spent carbon. If that quantity equals or exceeds the reportable quantity (RQ) for the hazardous substance, the spent carbon is a DOT-regulated Class 9 hazardous material. If that quantity is less than the hazardous substance’s RQ, the spent carbon is not DOT regulated.

Case Study: US West Coast refinery. A refinery in Washington state is using reactivated carbon to meet environmental compliance for VOC emissions. The refinery was using virgin carbon in many carbon adsorbers for VOC emissions at its sewer vents and effluent plant to meet the requirements of a consent decree associated with the Benzene NESHAP rule. This rule requires a 95% reduction of VOCs (or 98% benzene reduction) from vapor emissions at various points throughout the refinery. The refinery was also using significant manpower from its personnel and an onsite contractor to service these carbon filters. In addition, the refinery was shipping approximately 200,000 lbs annually of hazardous spent carbon to a disposal facility for landfill or incineration.

This refinery wanted to reduce costs, manpower requirements, hazardous waste and safety risk/liability while ensuring continued compliance with the consent decree requirements.

Solution. After contacting a water-treatment systems/services vendor, the refinery chose a turnkey solution that would standardize their activated carbon equipment, significantly reduce their cost, lower manpower requirements, reduce overall safety risks/liability and eliminate onsite hazardous waste. The solution consists of two types of standardized carbon adsorbers to replace the various adsorber types in use and a service contract that provides offsite carbon change-out for new adsorbers. The adsorbers are staged in a separate area and shipped to the vendor’s facility in another part of Washington, where the carbon is replaced; the fresh filters are then shipped back to the refinery. The vendor provides reactivation services for the spent carbon, and provides fresh reactivated carbon for refilling the vessels.

Results. The new system/service combination will allow more efficient exchange of adsorber vessels under the consent decree timeline constraints (8 hours or 24 hours) and will reduce manpower requirements at the refinery. Since the spent carbon is being reactivated, it is considered an exempt waste, not a hazardous waste. Accordingly, the refinery will completely eliminate the transport and disposal of hazardous waste from its processes, and will meet environmental compliance for handling of spent carbon, as the carbon will be reactivated in lieu of landfilling or incineration. The refinery will also reduce safety liability for its workers. Because of all these factors, the refinery has projected an annual cost savings of approximately \$300,000 to \$500,000.

Greener options. Achieving regulatory compliance while operating profitably and producing quality products via the refining process can be challenging. Fortunately, for the removal of organic contaminants, activated carbon remains a tested, reliable technology to help achieve regulatory compliance and product purification goals. Using reactivated carbon provides an even more cost-effective and environmentally beneficial solution for refineries to consider. **HP**

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NOMENCLATURE

API	American Petroleum Institute
BOD	Biological oxygen demand
EPA	Environmental Protection Agency
BTEX	Benzene, toluene, ethylbenzene and xylene
COD	Chemical oxygen demand
DAF	Dissolved air flotation
DOT	Department of Transportation
MTBE	Methyl tertiary butyl ether
NESHAP	National Emission Standards for Hazardous Air Pollutants
PCB	Polychlorinated biphenyls
RCRA	Resource Conservation and Recovery Act
RQ	Reportable quantity
TOC	Total organic compound
VOC	Volatile organic compound

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