

# **Petroleum Coke**

#### **Understanding Petroleum Coke in the Refining Process**

• Petroleum coke (petcoke) is one of the many products manufactured during the oil refining process. During the refining process, a number of valued consumer nondurable goods including gasoline, diesel fuel, jet fuel, lubricating oils and waxes are separated leaving reduced or heavy crude that cannot be recovered without further processing. The residue crude may be refined using a delayed coker to breakdown, or crack, large carbon molecules to produce petroleum coke, or petcoke, which has a variety of uses including as a cost-effective fuel.

Composition Of Coke From A Delayed Coker		
Component	Raw/Green coke as produced	Coke calcined at 2375 °F
Fixed carbon, wt %	80 - 95	98.0 - 99.5
Hydrogen, wt %	3.0 - 4.5	0.1
Nitrogen, wt %	0.1 - 0.5	
Sulfur, wt %	0.2 - 6.0	
Volatile matter, wt %	5 - 15	0.2 - 0.8
Moisture, wt %	0.5 - 10	0.1
Ash, wt %	0.1 - 1.0	0.02 - 0.7
Density, g/cm <sup>3</sup>	1.2 - 1.6	1.9 - 2.1
Metals, ppm weight:		
Aluminum	15 - 100	15 - 100
Boron	0.1 - 15	0.1 - 15
Calcium	25 - 500	25 - 500
Chromium	5 - 50	5 - 50
Cobalt	10 - 60	10 - 60
Iron	50 - 5000	50 - 5000
Manganese	2 - 100	2 - 100
Magnesium	10 - 250	10-250
Molybdenum	10-20	10-20
Nickel	10 - 500	10 - 500
Potassium	20-50	20 - 50
Silicon	50-600	50 - 600
Sodium	40-70	40 - 70
Titanium	2-60	2 - 60
Vanadium	5 - 500	5 - 500

• Petcoke's chemical composition is primarily elementary carbon.

• Coking is not new technology, the first modern coker was installed at Standard Oil of Indiana Whiting refinery in the 1930s. Currently, petcoke is processed at more than 140 refineries around the world.

#### Petroleum Coke is a Valued Commodity

- Petcoke is a growing internationally traded commodity and is fueling the growth of developing economies. Market growth is due to advancements in technology that have increased the production of shale oil and natural gas both in the U.S. and globally.
- Cokers have been an integral unit of many refineries since first installed in the 1930s, and well before the introduction of Canadian oil sands. Since that time a complex system of international petcoke trade has evolved that connects producers with ultimate end users, with a history of safely storing, handling and transporting petcoke by ocean freight, barges, rail and truck.
- Today, delayed cokers are being built and operated on a variety of crude oils in locations such as China, India, the Middle East and South America to maximize the yield of transportation fuels from a barrel of crude.

#### **Petroleum Coke Production**

- According to the Energy Information Administration, the petroleum refining industry converts crude oil into more than 2,500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feedstocks for the petrochemical industry.
- Petroleum cokers are installed in refineries to convert the residue crude separated during the distillation of crude oil that produces transportation fuels including gasoline, diesel fuel and jet fuel, as well as lubricating oils and waxes.
- Coking is a thermal cracking process used to convert low value residual fuel oil to higher value gas oil, petcoke and lighter petroleum stocks. Delayed coking is the most widely used process today.

### **Uses of Petroleum Coke**

- Petroleum coke is typically used as a source of energy, or as a source of carbon for industrial application.
- Fuel grade petcoke represents nearly 80 percent of worldwide petcoke production and is a source of fuel for cement kilns and electric power plants.
- Calcined petcoke (CPC) has the highest carbon purity and is used to manufacture energy, as well as in aluminum, graphite electrode, steel, titanium dioxide and other carbon consuming industries.
  - Aluminum: Worldwide, more than 85 percent of all CPC is used to produce anodes for smelting alumina into aluminum via the Hall-Héroult process, and there is no other commercially viable method to produce primary aluminum (bauxite ore is refined into alumina via the Bayer Process at alumina refineries). While originally anthracite coal was used as the carbon source, CPC supplanted anthracite as soon as CPC became commercially available due to its superior combination of electrical conductivity, resistance to chemical and physical degradation in the smelting pot, higher carbon content, and low contaminants (i.e. ash).

- Titanium Dioxide: Calcined petcoke is used in the production of Titanium Dioxide (TiO2), a naturally occurring mineral used as a pigment for plastic, paint, sunscreen and food coloring. Two significant uses of Titanium Dioxide are as a substitute for lead in paint and as a whitener for paper.
- Steel: Petcoke is a partial replacement for metallurgical coal as a feedstock for coke oven batteries, and as a partial substitute for pulverized coal directly injected into blast furnaces. Petcoke that is specially produced to have a needle-like crystal structure is called needle coke. Needle coke is used to produce the electrodes used in electric arc furnace (EAF) steel production. No other material has needle coke's combination of electrical conductivity and physical properties required for EAF electrodes.
- Calcined petcoke is also used as a recarburizer in the steel industry. Recarburizers are used to make minor adjustments to carbon content to ensure that each batch of steel meet specifications for carbon content.
- Other uses: Calcined petcoke is used in lime production; lime is used in many industrial processes including steel production. Brick and glass manufacturers use CPC as a substitute for fuel oil because coal cannot be used due to its much higher ash (5-20 percent for coal vs. 0.5 percent for petcoke). CPC is gasified to produce ammonia and urea ammonium nitrate, which is then used in fertilizer production, and by pulp and paper mills.



## World Petroleum Coke Use

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• Internationally, the industries using petcoke exported from the United States are the same as the U.S. industries that use it, with the exception that a very small percentage of exported U.S. petcoke is used by the steel and calcining industries.

• If a refinery does not have a coker, then the residue crude is either used to produce asphalt, blended with some valuable lighter products to produce residual fuel oil, or goes through an alternative conversion process.

## Trends in Petroleum Coke Production

- Petcoke production in the United States is increasing at a significantly slower pace than overall worldwide production. From 2007 to 2012, U.S. production increased by two percent, while world (excluding U.S.) production increased by 35 percent.
- World petcoke production increased approximately 20 million MT from 2007 to 2012.

## **U.S. Exports of Petroleum Coke**

- The majority of U.S. petcoke has historically been exported and that trend is expected to continue.
- While domestic production has almost recovered to pre-recession levels (2012 production = 98 percent of 2008), demand for petcoke in the United States is declining.
- From 1992 to 2008, approximately 55 percent of U.S. petcoke was exported. That number jumped to 69 percent in 2012, driven by a global market for petcoke as a source of electricity generation in large part because of its high caloric value, low ash and lower price relative to coal.

### **Domestic Use vs. Exports**

- Domestically, U.S. petcoke demand continues to fall because of reduced use by the cement and power industries. This continued decline in U.S. petcoke demand is due to these industries using less of it as a solid fuel. In addition, since the recession, the United States has seen no recovery in demand for calcine petcoke which had been the largest demand segment.
- Residual fuel oil use (petcoke is used to make residual fuel oil) in the U.S. has been declining for decades because natural gas and coal are much more economical fuels to use in industrial applications and power generation. In 2012, petcoke accounted for just 0.2 percent of U.S. power generation.
- U.S. petcoke is exported because it is typically more economical, depending on location, to export than to sell domestically because U.S. coal prices are substantially lower than international coal prices.

### Petroleum Coke is Not Unique to Canadian Crude

- Cokers have been an integral unit of many refineries since the 1930s, well before the introduction of Canadian crude sourced from oil sands. The vast majority of crude oils in the world will produce petcoke if they are refined in a refinery equipped with a coker, although the amount will vary.
- Arab Medium will yield approximately 8 percent by weight as petcoke, while heavier crude oils from Venezuela, Mexico, or Alberta yields approximately twice as much petcoke.

### **Oil Sands Imports from Canada to Regions**

• Increasing volumes of heavy Alberta crude will make its way to the U.S. by either rail or pipeline.

- Pipelines meant to carry Alberta crude to U.S. refineries have already been built. The major new pipeline to be built is the Keystone XL pipeline that will link Hardisty, Alberta with Steele City, Nebraska.
- Rail or pipeline will carry more volumes of heavy Alberta crude oil to the U.S. Gulf Coast (USGC), which has the largest concentration of advanced, complex refining capacity in the world.
- The impact heavy Alberta crude oil will have on USGC petcoke production depends on which imported crude oils are displaced. There will be little to no impact on USGC petcoke production if heavy Venezuelan or Mexican crude oils are displaced.

### Health and Environmental Impacts of Petroleum Coke

- The Environmental Protection Agency (EPA) does not classify petcoke as a hazardous waste nor does it pose health issues in humans.
- As part of the EPA's High Production Volume (HPV) Challenge Program, petcoke has been tested extensively for potential health and environmental impacts as well as eco-toxicity and was found to be highly stable with a low potential to cause adverse effects on aquatic or terrestrial environments. It also has a "low hazard potential" in humans, with no observed carcinogenic, reproductive or developmental effects.
- Petroleum coke is used as a substitute for coal. Since petcoke has a higher heat content than coal, less petcoke than coal is required to generate the heat necessary to maintain an industrial process. For example, a 500 MW electric generating unit (EGU) operating at full output will consume 211 ton/hour of Illinois Basin high sulfur coal, but requires only 166 ton/hour of petroleum coke.
- In looking at global CO<sub>2</sub> emissions from burning petroleum coke, petcoke almost always replaces coal, thus the increase in CO<sub>2</sub> emissions attributable to burning petcoke is the difference between CO<sub>2</sub> emissions from burning petcoke instead of coal (i.e. 0.004 MT CO2/MMBtu). Assuming that 90 percent of fuel use of petcoke displaced coal and the remaining petcoke use displaced residual fuel oil (i.e. Δ CO<sub>2</sub> emissions of 0.018 MT CO<sub>2</sub>/MMBtu), additional anthropogenic (i.e. manmade) CO<sub>2</sub> emissions from burning petroleum is 13 million MT of CO<sub>2</sub> in 2012, which is only 0.04 percent of the 34,466 million MT of global anthropogenic fuel-related CO<sub>2</sub> emissions in 2012. It should be noted that there are also significant natural and biogenic sources of greenhouse gas emissions, so petcoke's contribution to total greenhouse gas emissions is even smaller than the 0.04 percent of anthropogenic CO<sub>2</sub> emissions.
- Substituting petroleum coke for coal does not necessarily increase nitrogen oxides (NOx) emissions, it is dependent on the specific application and stack technology employed.
- While petroleum coke generally has higher sulfur content than coal, it does not necessarily translate into substantially higher sulfur dioxide (SO<sub>2</sub>) emissions. The largest market for fuel grade petcoke is the cement industry. In a cement kiln, typically more than 90 percent of sulfur compounds are absorbed in the clinker (which is then ground and blended with gypsum to produce cement). Some cement kiln operators prefer higher sulfur petcoke as the chemistry of the raw feed (e.g. limestone, clay, etc.) to some kilns requires substantial sulfur to assure proper sulfation of the clinker. In the power industry, petcoke is most efficiently burned in circulating fluidized bed (CFB) boilers. Typically a CFB boiler will capture 95 percent of SO<sub>2</sub>, and CFB boilers equipped with supplemental dry scrubbers capture more than 98 percent of SO<sub>2</sub> emissions.

### **Regulation of Petroleum Coke Storage and Handling Facilities**

Air: Fugitive Dust Control Plans

- Under existing state and federal laws, <u>petroleum coke storage and handling facilities</u> are or can be required to obtain approval of Fugitive Dust Control Plans. These plans detail measures that will control petroleum dust from being blown from storage sites. Fugitive Dust Control Plans can be required through:
  - $\circ$  State Implementation Plans for areas not in attainment of the PM<sub>10</sub> National Ambient Air Quality Standard under the Clean Air Act
  - Clean Air Act Title V permits or Permits to Install for higher emissions facilities
  - State laws that either mandate filing of Plans or allow state environmental agency to require Plans based on air quality measurements or substantive complaints
  - Fugitive Dust Control Plans contain detailed information demonstrating measures that will adequately control fugitive dust, including:
    - ✓ Technologies and methods to reasonably control fugitive dust emissions
    - ✓ Review of quantity, moisture content, specific gravity, and the particle size distribution of petroleum coke so as to develop more effective dust controls
    - ✓ Detailed record keeping of activities implemented under the plan
    - ✓ Schedule for installing controls necessary to successfully implement the plan
- State laws require environmental agencies to review and approve Fugitive Dust Control Plans. If a facility's proposed plan is disapproved, and subsequent versions remain unsatisfactory, environmental agencies can impose specific dust control measures. State environmental agencies often monitor petroleum coke storage and handling facilities, particularly those that have submitted a Fugitive Dust Control Plan, to ensure that fugitive dust is not creating issues in the surrounding area.

Water: Storm Water Pollution Prevention Plans

- The Clean Water Act prohibits the discharge of any pollutants to waters of the United States unless that discharge is authorized by a National Pollutant Discharge Elimination System (NPDES) permit. EPA regulations under the NPDES program govern the discharge of storm water from certain industrial facilities into covered water.
- Both EPA NPDES and similar state regulations often require petroleum coke storage and handling facilities to obtain an industrial storm water permit. To do so, these facilities must submit a Storm Water Pollution Prevention Plan.
- A Storm Water Pollution Prevention Plan identifies controls that will be put in place to minimize negative impacts, caused by offsite storm water discharges, to the environment. These controls minimize erosion and run-off of pollutants and sediment from petroleum coke storage and handling facilities into covered waters.
- Storm Water Pollution Prevention Plans include descriptions of potential sources of storm water run-off as well as topographical maps of the facility, descriptions of materials on-site, and direction of storm water flow. Storm Water Pollution Prevention Plans also address certain components such as:
  - Employee training
  - Preventative maintenance
  - Risk identification
  - Spill prevention and response procedures

- Recordkeeping and internal reporting procedures
- Petroleum coke storage and handling facilities with a Storm Water Pollution Prevention Plan are generally subject to inspection by state environmental personnel. These personnel verify that the description of potential pollutant sources is accurate, that the drainage map has been updated or otherwise modified to reflect current conditions, and controls to reduce pollutants in storm water discharges associated with are being implemented and are adequate.

#### Fire: Combustible Dust Permits

- The International Fire Code, adopted by most states and many localities, requires facilities producing combustible dust to obtain operational permits. Petroleum coke can, in certain conditions, become a combustible dust. Therefore, petroleum coke storage and handling facilities are often required by state and local law to obtain a combustible dust operational permit. These permits generally require adherence to National Fire Protection Association (NFPA) standards, such as:
  - NFPA 654 (Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids): Standards to control dust and ignition sources in order to prevent combustible dust explosions and minimize the danger and damage from an explosion. Standards include providing access to all hidden areas to permit inspection, controlling static electricity, and fire suppression systems.
  - *NFPA 69 (Standard on Explosion Prevention Systems):* Standards to prevent explosions generally, including inspection, maintenance, and fire suppression.