ENERGY SOLUTIONS

FUEL FLEXIBILITY IN A VOLATILE MARKET

HANDLING AND COMBUSTION OF GROUND PETROLEUM COKE IN THE PULP AND PAPER INDUSTRY

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January 20, 2010
Abstract:

This is an in-depth view of the domestic ground petroleum market with an emphasis on usage in the Pulp and Paper Industry. PetCoke is discussed from its origin at the refinery all the way to its delivery to the lime recovery kiln burner. Also discussed is the historical and current market for fuel grade coke.

Matrix Engineering / Matrix Industrial Systems have pioneered most of the pulp and paper sector of the fuel grade PetCoke market within the United States. Our patented Densi-Feed® Pulverized Fuel Feed and Delivery System delivers very precise and predictable fuel flow of this very difficult powder.
1.1 By-Product of Oil Refineries

Petroleum Coke, hereafter referred to as PetCoke, is a by-product created in oil refineries that are equipped with cokers. Cokers give them the ability to refine lighter fuels such as gasoline from the heavy tar-like substance left over after the initial treatments of crude. See the Figure 1a for a simple diagram of the refinery process.

![Figure 1a – Simple Refinery Diagram with Coker](source: Matrix Engineering, PLLC)

 Initially crude is heated in an atmospheric distillation column to around 600 °F where various light petroleum products are boiled off and collected. Then the crude is moved to a vacuum tower where it is placed under a strong vacuum effectively boiling off more of the lighter products. The leftover is a very heavy tar-like substance. At this point the refineries with coking capability have three different options on what to do with this heavy tar-like substance. The substance can be moved into an asphalt plant to make asphalt. The substance can be blended with some of the lighter products to make residual fuel oil. Or the substance can be heated further and processed in a Coker to continue to produce the lighter fuel products. The Coker is a batch process that removes the last of these lighter hydrocarbon chains from the heavy tar-
like substance. Once these lighter products are removed in the batch, PetCoke is the leftover product that is left behind.

1.2 Delayed Coking Process

There are three types of Coking processes, Delayed, Fluid and Flexicoke. Delayed coking accounts for 95% of all Coke production and accounts for all of the fuel grade PetCoke products. Therefore the Delayed Coking process will be the only process addressed here. Delayed Coking can produce Sponge/Shot Coke as well as Needle Coke. Needle coke is a premium grade specific product used for producing high quality carbon graphite electrodes. The technology to produce Needle Coke is proprietary and currently performed in a very limited number of refineries. Sponge and Shot Coke are the predominant products produced in Delayed Cokers.

There are various amounts of sponge and shot coke produced in Delayed Cokers. Many varieties of crude have a large number of cross-linkages with less than 6 carbon atoms. These crudes tend to produce isotropic or amorphous cokes and when they are visibly very porous they are called sponge coke. Shot coke is an abnormal type of coke resembling small spherical pellets. It is believed that residuum or remainder high in asphaltenes and low API Gravity favor shot coke formation. Blending aromatic materials with the feedstock and/or increasing the recycle reduces asphaltenes and thus reduces shot coke. (01)

Delayed coking is a thermal cracking process on the petroleum derived heavy tar-like feedstock. Thermal cracking is a refining process in which heat and pressure are used to break down, rearrange, or combine hydrocarbon molecules. Coking is a “semi-continuous” batch operation carried out in pairs of coke drums. Coking takes place in one drum in 24 hours while decoking is carried out in the other drum. A complete cycle is 48 hours. Coke is cut from the drum using high pressure water. Large drums are around 27 ft in diameter and around 115 ft tall. See Figure 1b for a diagram of the coking process.
In delayed coking the heated tar-like charge is transferred to large coke drums which provide the long residence time needed to allow the cracking reactions to proceed to completion. Initially the heavy feedstock is fed to a furnace which heats the residuum to high temperatures (900°-950° F) at low pressures (25-30 psi) and is designed and controlled to prevent premature coking in the heater tubes (Figure 4). The mixture is passed from the heater to one or more coker drums where the hot material is held approximately 24 hours (delayed) at pressures of 25-75 psi, until it cracks into lighter products. Vapors from the drums are returned to a fractionator where gas, naphtha, and gas oils are separated out. The heavier hydrocarbons produced in the fractionator are recycled through the furnace. (02)

After the coke reaches a predetermined level in one drum, the flow is diverted to another drum to maintain continuous operation. The full drum is steamed to strip out uncracked hydrocarbons, cooled by water injection, and decoked by mechanical or hydraulic methods. The coke is mechanically removed by an auger rising from the bottom of the drum. Hydraulic decoking consists of fracturing the coke bed with high-pressure water ejected from a rotating cutter. (02)
As PetCoke is discharged from the drum it is typically stored on site for a limited period (1 – 2 weeks) and then shipped to its next destination. PetCoke is distributed to end users based on its properties. The properties of PetCoke are determined primarily by the type of crude being refined as well as the cracking process. Light crude generally produces a softer, easier to crush PetCoke. Heavy crude produces a harder variety with a lower HGI. In addition, sweeter crudes yield lower sulfur PetCoke and sour crudes yield higher sulfur. Depending upon the crude type and the resulting level of sulfur in the PetCoke, it will be classified as anode grade or fuel grade coke (also known as green coke).

1.3 PetCoke Production is a Choice

In summary, PetCoke may be a by-product of the delayed coking process of a petroleum refinery, but it is a by-product of choice that is produced with a specific market in mind. If market conditions are not favorable for producing PetCoke as a by-product, then the refinery can produce asphalt or blend the tar-like feedstock into residual fuel oil. The third party PetCoke Pulverizing Facility purchases fuel grade coke with the specific purpose of processing it into a suitable fuel to burn in suspension by the end user. The Facility does not modify the chemistry of the fuel apart from reducing its moisture. The Pulp and Paper Mill customer purchases this product from the Pulverizing Facility as a fuel ready to burn and it is delivered to the Mill on a daily basis in order to meet the demand.
1.4 Preparation of Raw Green of PetCoke for Combustion

Typically when coke is used to fire a Kiln it is ground to a fine powder to enhance combustibility since burning it in suspension is desirable. As the coke is pulverized more and more, its surface area increases which also increases it combustibility and decreases each particle’s combustion time. This principal for pre-pulverizing PetCoke is true whether it is fired in a Cement Kiln or a lime recovery kiln.

Typically Cement Kilns use a much larger volume of fuel. Based on their usage most of them are Direct Fired with the Pulverizer on Site. In cases where Coke is added alongside coal, the Pulverizer is also a delivery system, with the discharge of the Pulverizer directly connected to the Kiln Burner. Typically Lime Recover Kilns use pre-pulverized PetCoke in an Indirect Fired System. In an Indirect System, the pulverizing can occur off-site with deliveries made to the site where it is stored, fed and burned as required to maintain the kiln operation. In either case, whether Directly Fired or Indirectly Fired the PetCoke must be pulverized prior to combusting in the Kiln.

In the Indirect Firing Case found in the Pulp and Paper Industry, Green PetCoke is produced at a refinery and procured by a third party for pulverizing so it can be delivered to the Mill as a finished fuel for temporary storage and ready for feed for combustion in the Kiln.

Raw or unground PetCoke is received at a Pulverizing Facility in varying size ranges depending upon the friableness of the coke itself and means by which it is mechanically removed from the Coker. Typically the size ranges from 1/8" to 6". The raw PetCoke has relatively high moisture content due to the hydro-blast removal technique from the Coker and its likely open air barge journey to the Pulverizing Facility. Typically the raw green coke arrives at the facility at approximately 8-10% moisture by weight.

The raw coke is received, foreign objects and metals are removed just prior to crushing and pulverizing to a specified particle size. A common particle size specification for effective burning in suspension in a lime recovery kiln is 90% passing 200 Mesh (or less than 75 Micron). Hot air is used in conjunction with the pulverizing process and as a result, the coke is also dried to less than 1% by weight.

To summarize, PetCoke undergoes the physical change in size from being pulverized to enhance combustion. This physical change is typical across industries and is a fundamental principal in combustion efficiency.
Outside of the loss of moisture, there are no chemical additions or alterations of its chemical make-up from the third party Pulverizer.

### 1.5 PetCoke Pulverizing Facility

Much of the domestic green PetCoke goes to cement kilns and power generation. In these market sectors, the PetCoke is generally left in its raw uncrushed state, mixed with coal and burned via a pulverizer and direct fired system on site. A small, but growing, market sector is on the rise in Pulp and Paper Lime Recovery Kilns. In this particular industry, the vast majority of these mills burn this fuel utilizing an indirect fired system. This allows the fuel to be pre-pulverized by a third party petcoke pulverizing facility and delivered to the mill as a finished fuel and ready to burn. PetCoke, unlike coal, does not have spontaneous combustion properties and can be pulverized and handled, and stored in a powdered state essentially without posing fire risk hazards. Therefore a central pulverizing facility can provide a fuel supply service to multiple PetCoke users within its regional distribution grasp.

Depending upon the proximity of the PetCoke Pulverizing Facility to the Refinery, the raw PetCoke is either received via truck, railcar or barge. However, due to the large quantities of material, barge is the likely optimum choice for a Pulverizing Facility. Here the raw coke is received and stored prior to pulverizing. Generally the raw coke is 3 inch in size down to 1/8” and contains about 8 – 10% moisture from its hydro-blasted removal from the Coker and its exposed journey to the pulverizing facility.

Once at the Pulverizing Facility, foreign metals are removed and the raw coke is pre-crushed as it is fed into a pulverizer. Hot air is used to dry and convey the pulverized coke to a separator and/or dust collector. At this point the PetCoke has been pulverized to 90% passing 200 mesh and dried to less than 1% moisture. From the separator and/or dust collector, the ground PetCoke is conveyed to a storage product silo, where it is off-loaded to pneumatic trucks or rail cars for delivery to the Mill. See Figure 1d for a typical off-site PetCoke Pulverizing Facility.
The purpose of pulverizing the coke to this degree is to ensure that it will burn in suspension in a kiln. Pulverizing and drying account for the entire process at the pulverizing facility. No additional ingredients are added or no special enhancements are made to the fuel to improve its performance.

1.6 Pulverized PetCoke Fuel Delivery System

Once the PetCoke has been dried and pulverized, pneumatic trucks or railcars in turn deliver the PetCoke as a finished fuel to a Pulp and Paper Mill customer for consumption on a daily or even shift basis depending upon the Mill’s demand. PetCoke is burned as a primary fuel in the Lime Recovery Kiln for those mills that are currently using it. PetCoke’s inability to spontaneously combust also gives it a relatively high ignition temperature. Due to its high ignition temperature, PetCoke must be burned alongside either Natural Gas or Fuel Oil. However, once the kiln is brought up to temperature (around 1000-1200F), PetCoke substitution can be increased incrementally to displace around 80% of the Natural Gas or Fuel Oil. Depending on emission limits, kiln dimensions, combustion aerodynamics and burning methods, a substitution value approaching 90% can be realized.

PetCoke is unloaded into a fuel delivery silo for storage just prior to burning. Depending upon burn rates and storage capacity, the pulverized PetCoke will remain in this silo 1 – 5 days prior to feeding out of the silo bottom to the kiln burner. The PetCoke is fed via a sophisticated feed scale system into a dilute phase pneumatic convey system to the Lime Kiln Burner. In these cases the kiln burner is designed to handle a pulverized fuel in addition to Natural Gas and/or Fuel Oil. Depending upon the configuration, the burner is either a Dual...
or Tri-Fuel style. See Figure 1e for a typical Pulverized PetCoke Delivery System schematic.

![Figure 1e - PetCoke Fuel Delivery System](image)

**Figure 1e - PetCoke Fuel Delivery System**

This is a simple diagram of a permanent installation for a PetCoke Fuel Feed and Delivery System. Fuel delivery consistency from this system is crucial for an efficient combustion and a steady kiln operation.

### 1.7 Mobile PetCoke Delivery System for the Trial Burn

Trial Burns in the United States can utilize a fully equipped, a mobile PetCoke Delivery System that is designed specifically for this purpose. See Photo 1f for a Mobile Test Unit from Matrix Engineering.

![Photo 1f - Trial Burn Delivery System](image)

**Photo 1f - Trial Burn Delivery System**

Great care was taken in the design of the trial burn feed system in order to maintain feed consistency and predictability allowing good combustion and kiln operation. In addition, proper instrumentation and trending controls are provided to document the fuel feed throughout the test. As a result there is a
high confidence level in the resulting data for emissions as well as a clear picture of any differences in the operation of the kiln.

The mobile system essentially contains two separate storage and feed systems. Each is a batch type system on load cells with a special proprietary feeder for smooth and consistent feed of the pulverized coke. Two weigh systems are required in order to prevent flushing during refills as well as to provide continuous uninterrupted measurement of fuel flow to the kiln. As System #1 is refilling, System #2 is feeding PetCoke to the Kiln Burner. As System #2 empties it begins to slow down as System #1 begins to start-up allowing a seamless feed transition between them with uninterrupted and continuously monitored flow to the Kiln Burner. See Figure 1g for a simple diagram of the unit.

![Figure 1g – Mobile Delivery System for TrialBurns](image)

Feed Consistency from this system is crucial for efficient combustion to obtain reliable data during a trial burn. A trial burn with a reliable system can help a mill determine the maximum allowable substitution level of PetCoke Burning as well as any downstream process impacts.

Each system storage hopper has its own self-contained filter for receiving pneumatic refills from an on-site storage pig. The mobile system also vents the storage pig as it receives loads of PetCoke from the Pulverizing Facility via pneumatic truck deliveries.
PETCOKE COMPOSITION AND INDUSTRY USES

2.1 General PetCoke Origin and Composition

PetCoke is a substance which remains in a process vessel called a Coker after treating heavy petroleum feedstock (i.e. the tar-like substance remaining after initial distillations of crude) with extreme heat and pressure. PetCoke is comprised mainly of elemental carbon, organized as a porous polycrystalline carbon matrix. In fuel grade or green coke, the pores of the matrix are filled with a hardened residuum remaining from the Coker feed. This residuum is volatile matter remaining from the feedstock that did not complete carbonization. Since the Coker is a batch process that comes to cycle completion upon being filled with carbonized feedstock. Whatever volatile matter left in the pores of the carbonized matrix structure when the Coker is filled to capacity, comes out with the PetCoke during the hydro blast and removal from the vessel. See Figure 2b for a schematic representation of a Delayed Coker Process. Fuel Grade Coke typically contains around 4% - 15% volatile matter. This is primarily affected by attained pressures, temperatures, and batch completion times within the Coker. (01)

2.2 Types of PetCoke

Green coke from a Delayed Coker can be physically classified in three different forms. These forms are sponge, shot and needle coke. Sponge coke is the most common form of green coke and has a porous crystalline appearance. Its pores vary in size and it has a dull black color. In reality sponge coke is a hybrid mixture of shot and needle coke. Sponge coke is typically derived from more virgin crude feedstocks. See Photo 2a for an image of sponge coke.
Shot coke appears as small hard spheres which are clumped together into friable amorphous groups. Shot coke has a lower API density and high asphaltene content which supports its spherical formation. See Figure 2b for an image of shot coke.

![Photo 2b - Shot Coke](image)

Needle coke is rare and typically used for anodes. It is derived from highly aromatic fractions during cracking in the coker and remains plastic longer during carbonization. This allows crystals to form needle-like ocicular structures which give needle coke a comparatively higher conductivity. Its color is more of a grey-silver as opposed to the dull black appearance of sponge and shot coke. See Figure 2c for an image of needle coke.

![Photo 2c - Needle Coke](image)

### 2.3 PetCoke as a Fuel for Combustion

Fuel grade sponge and/or shot coke is ground to a fine powder to enhance combustibility when burning it in suspension. As the coke is pulverized more and more, its surface area increases which also increases its combustibility and decreases each particle’s combustion time. A particle can only burn if there is sufficient oxygen present and the only place oxygen can come in contact with the particle is at its outer surface. A particle burns from the outside inward as it consumes the outside surface area of the particle. Therefore, the finer the particle, the more
efficient the combustion is at similar oxygen levels. A common particle size specification for effective burning in suspension in a lime recovery kiln is 90% passing 200 Mesh (or less than 75 Micron). See Photo 2d.

2.4 PetCoke as Compared to Coal as a Fuel

Coke is often compared to coal as a fuel. However, unlike coal, PetCoke does not have spontaneous combustion issues. Although their chemical make-up is somewhat similar, their physical appearance after pulverizing on a microscopic level is significantly different. A PetCoke particle has a fairly smooth spherical shape. A Coal particle is not spherical and has a much rougher surface. A spherical smooth shape minimizes surface area for oxygen to come in contact with. The random and rough surface of a coal particle gives it more room to harbor oxygen which makes it much more combustible at lower ignition temperatures. Coal typically has an ignition temperature of around 550 ºF where PetCoke (with 10% volatiles) is around 750 ºF. See Photo 4e.
Another difference between Coke and Coal is its heating value. Coke has a comparatively higher heating value at around 14,800 – 15,500 Btu/lb. Bituminous coal has a heating value that ranges from 11,000 – 14,000 Btu/lb. This difference in heating value is attributed to less hydrogen content in PetCoke when compared to coal. Hydrogen is released during combustion of coal and combines with oxygen to produce water vapor. PetCoke, having less hydrogen, produces a hotter, drier and more efficient flame. Although Coke has less hydrogen than coal, fuel grade green coke typically has more sulfur than coal.

Besides its high heat content, Coke is also very low in ash in comparison to Coal. Coke ash is generally 0.50% by weight.

### 2.5 Specific Trial Burn PetCoke Origin and Composition

Beyond the physical appearance, the precise chemical composition of the PetCoke is determined from the feedstock used in the coking process. The feedstock is derived from the virgin crude brought into the refinery.

An example of a typical PetCoke composition table is outlined below.

<table>
<thead>
<tr>
<th>Tests</th>
<th>Method</th>
<th>As Received</th>
<th>Dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture %</td>
<td>ASTM D4931</td>
<td>6.93</td>
<td>0.00</td>
</tr>
<tr>
<td>Ash %</td>
<td>ASTM D4422 (Mod)</td>
<td>0.35</td>
<td>0.38</td>
</tr>
<tr>
<td>Volatile Matter %</td>
<td>ASTM D4421</td>
<td>11.77</td>
<td>12.65</td>
</tr>
<tr>
<td>Fixed Carbon (by diff) %</td>
<td>ASTM D3172 (by diff)</td>
<td>80.95</td>
<td>86.97</td>
</tr>
<tr>
<td>Sulfur %</td>
<td>ASTM D4239 Method B</td>
<td>5.64</td>
<td>6.06</td>
</tr>
<tr>
<td>Gross Calorific Value Btu/lb</td>
<td>ASTM D5865</td>
<td>14209</td>
<td>15267</td>
</tr>
<tr>
<td>Carbon %</td>
<td>ASTM D5373</td>
<td>81.85</td>
<td>87.94</td>
</tr>
<tr>
<td>Hydrogen %</td>
<td>ASTM D5373</td>
<td>3.44</td>
<td>3.70</td>
</tr>
<tr>
<td>Nitrogen %</td>
<td>ASTM D5373</td>
<td>1.53</td>
<td>1.64</td>
</tr>
<tr>
<td>Oxygen (by diff) %</td>
<td>ASTM D5373 (by diff)</td>
<td>0.26</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 2f

**Trial Burn Petcoke Chemical Composition**
PETCOKE MARKET HISTORY, SIZE AND PRICING STRUCTURE

3.1 PetCoke History

The history of PetCoke can be traced back as far as the 1860’s. Early refineries in Pennsylvania boiled oil in primitive distillation stills to produce kerosene. A fire beneath the still heated and coked the oil at the bottom of the vessel. At the end of the batch kerosene process, workers would manually remove the heavy tar and coke from the still.

Later, Standard Oil developed and patented the first thermal cracking process at their Whiting, Indiana refinery in 1913. The first delayed coker was built in 1929 based on this patented cracking process. However, de-coking the vessel was quite a difficult task.

Approximately ten years later, Shell Oil developed a hydraulic means of de-coking a vessel at their Wood River, Illinois facility. Using high pressure water blasting they were able to make the de-coking process easy and predictable enough to convert the batch process to a more continuous approach. They could utilize multiple vessels and process in one while the other is being de-coked.

PetCoke production really began to increase steadily from the mid 1950’s to now based on the United States increasing use of petroleum based fuels and products. Coker expansions are the primary reason why the United States has been able to satisfy its growing need for lighter fuels by increase yields from existing refineries without building new ones.

Today, PetCoke is produced at refineries throughout the world and traded on an international basis as a fuel as well as for use in aluminum production.

3.2 PetCoke Current World Production

For fuel grade coke, the United States is, by far, the leading producer of PetCoke with over 50 Million Short Tons which accounts for 46% of the global market. Worldwide production of PetCoke in 2008 was 110 Million Short Tons. See Chart 3a for the global production distribution.
3.3 PetCoke Projected World Production

As lighter crudes are becoming harder and harder to find, worldwide coking capacity must increase to maintain yield from heavier crudes found in places such as the Alberta Oil Sands. Expected coke capacity increases through 2014 in the major global international markets are approximated in Chart 3b.
Currently PetCoke World Production is projected to rise from the 2008 level of 110 Million Tons to 128 Million Tons by 2014. This is an estimated 16% increase worldwide. The US portion is expect to reach 56 Million Tons in 2014, or an 11% increase over 2008 production levels.

The refinery infrastructure for additional coking in the United States also remains strong. Currently, there are 115 refineries in the United States and only 70 of those are equipped with cokers. (03)

3.4 Domestic PetCoke Market Distribution

Now examine the domestic uses for PetCoke produced by the United States. Chart 3c is a distribution of domestic coke usage from 2008.

![Chart 3c Domestic Fuel Petcoke Market 2008](image)

It is interesting to note that the majority of domestic coke is exported. As a result, the U.S. market price for coke is primarily dominated by the export market. In other words, large scale domestic purchases of petroleum coke are generally not driven by US market forces, but by International market forces. For example, the United States’ largest export market for its PetCoke production has typically been cement production in the Mediterranean Market. Other fuels that compete in this same industry are International Coal and Residual Fuel Oil. Therefore, these competing fuels on the other side of the world will have an effect on the US market.
3.5 Basis for Domestic PetCoke General Market Price

PetCoke is valued differently based on its sulfur content. The general principal here is the lower the sulfur content in PetCoke, the higher its value, and vice versa. Fuel grade coke sulfur levels tend to range from the 4% to 9% sulfur level. These sulfur levels are higher than most coals, even those that would be considered high sulfur coal. However, fuel grade coke also has a significantly higher energy value per pound as well (15,000 Btu/lb compared to 12,000 Btu/lb). Therefore it can certainly compete directly with high sulfur coals. One such coal is the South African Steam Coal. The South African Coal is a cheaper lower quality coal that theoretically can hold the price of PetCoke in check, if PetCoke prices rise dramatically, then South African Coal can potentially offset some of the US export market raising domestic inventories and lowering the domestic price. See the Mediterranean Market fuel price comparison in Chart 3d.

![Chart 3d](image)

**Chart 3d**

*Mediterranean Market Fuel Price* (03)

However, pricing coke is much more complex than trending the South African Coal market. Keep in mind, that PetCoke production is a choice based on the changing petroleum finished fuel market. If lighter fuels such as jet fuels and gasoline are in higher demand which is typically the case, then the economics for operating a coker are profitable. If heavier fuels such as residual fuel oils are in higher demand, then refineries have the option to reduce or bypass PetCoke production by blending more residual fuel oils. Since all of the PetCoke produced in the United States is either
exported or consumed domestically, the market price is determined by a combination of the PetCoke supply (which is dependent upon the price differential between light and heavy fuel production) as well as international PetCoke consumer needs.

Also, on a product quality level, raw PetCoke is graded based on the Sulfur it contains as well as its HGI or Hardgrove Grindability Index. These factors are determined by both the sourness and heaviness of the crude and vary from refinery to refinery.

With all of these factors in mind, the market price model is not a simple one. Currently there are no price indexes published for the general public on international petcoke pricing structures. PetCoke published prices as well as consulting is available through subscription services such as Argus or Jacobs Consultancy’s Pace Index and Quarterly Report. See Chart 3e for a spot pricing index over the past decade. The % Average is an indication of sulfur content.

![Chart 3e: Spot Prices for PetCoke 1996 – 2007](chart3e.png)

3.6 General PetCoke Market Simplified

A simple rule to keep in mind, when looking at the domestic PetCoke market, is the fact that PetCoke is a by-product of a finished fuel. The profitability of PetCoke is important to a refinery, but is not nearly as important as the profitability of the finished fuel. Also, the amount of PetCoke produced from a Coker is enormous, and is not practical for long term stockpiling. Therefore, generally speaking, at the end of the day, the PetCoke produced must move, no matter the price. Long term storage is
not desirable and land filling as a waste is simply not an economically viable option resulting in a significant negative price for the PetCoke.

As PetCoke prices fall, freight price barriers are also lowered allowing more PetCoke to be exported if it cannot be consumed domestically. On the other side of the spectrum, high PetCoke prices raise freight barriers and discourage exporting to compete against international coal, in particular South African high sulfur coal. This in turn will encourage rising domestic inventories and help to lower PetCoke pricing as a result. If PetCoke pricing lowers enough and becomes unprofitable or detrimental, then the refinery will choose to blend more residual fuel oil or produce more asphalt. They historically have not and will not waste or landfill the Petroleum Coke by-product. The quantities are massive, the cost is much more prohibitive to landfill than in giving it away, and there is a global demand for it as a fuel, as well as production of aluminum and titanium dioxide.

Some of the oil companies such as ConocoPhillips sell their own PetCoke all the way down to the energy consumer level. Others use brokers and strike long term deals for ridding themselves of their PetCoke production. As a result, depending on the refinery, PetCoke pulverizing facilities, cement producers, or other large users can often times receive long term agreements for either fixed or relatively stable pricing for PetCoke. This contributes to a less volatile more predictable market for large energy consumers of PetCoke.

### 3.7 Growing Market of PetCoke in Pulp and Paper

The PetCoke market for the Domestic Pulp and Paper Industry is a much smaller and more focused subset when compared to the international market in fuel grade petroleum coke. PetCoke has been burned primarily in the Lime Recovery Kilns to this point. However, there is also a potential market for burning PetCoke in Recovery Boilers to offset black liquor production or enhance its Btu value.

Currently there are approximately 23 kilns burning PetCoke in the United States. Collectively they burn an estimated 333,400 Tons annually. This is around 0.67% of the 50 Million Tons domestically produced. Excluding exports, it accounts for around 1.5% of the PetCoke domestically consumed.

The amount is small in comparison to the overall domestic market, but it is growing rapidly. From the mid 1980’s to 2004 there were only three lime recovery kilns burning coke in the US. By the end of 2006 there were 13 kilns and this has grown to 23 at the close of 2009. See Chart 5f below.
Rising energy costs along with improved PetCoke Burners and Pulverized Fuel Feed Systems has spurred the growth over the past 5 years. These innovations have spurred investment in regional pulverizing facilities which can provide a finished fuel, ready to burn to the industry. The Pulp and Paper industry is a highly competitive industry that is particularly sensitive to energy price volatility. Typically energy is the second largest expenditure behind payroll for a Mill. Therefore, increasing energy efficiency and/or obtaining cheaper fuel sources is a matter of survival in today’s Paper Mill.

### 3.8 PetCoke Sulfur Content and the Lime Recovery Kiln

The Lime Recovery Kiln in the Pulp and Paper industry is unique in its ability to handle sulfur in the fuel. Depending on the kiln size, geometry and combustion aerodynamics, much of the sulfur is absorbed into the available free lime in the air. What sulfur is not absorbed can often be handled with downstream emission controls such as a scrubber or electrostatic precipitator. In some cases, Mills need additional sulfur in their recycle process in order to maintain an acceptable sodium to sulfur ratio.
balance. However, in most other cases, where excess sulfur is not desirable, the PetCoke fuel prices are low enough to justify caustic addition to correct an imbalance.

3.9 Delivery Systems Require Low Capital Investment

The other advantage PetCoke offers, is that unlike coal, it is not subject to spontaneous combustion allowing it to be pre-pulverized and delivered to the mill as a finished fuel, ready to burn. The importance of this cannot be overemphasized. A pulverizing plant is expensive, difficult to maintain, and typically requires additional labor forces. In addition, the price differential between raw coke and pulverized coke is generally much smaller than the price differential between ground petcoke and a competing fuel such as natural gas or fuel oil.

It generally requires a minimum of 3-4 lime recovery kilns to support a reasonable return on investment for a pulverizing facility and fuel delivery system. Since most mills have only one or two such kilns, then they have been reluctant to make such a large investment. However, by receiving a pre-pulverized fuel, they are only required to invest in the fuel delivery system. This significantly lowers the capital spending barrier making PetCoke conversion projects highly affordable with quick returns in a highly competitive market.

With the recent addition of reliable and predictable trial burn mobile equipment, Mills can also fully test this new fuel at their site and quantitatively determine any process or emission impacts prior to capital investment. This practically eliminates risk in trying a new fuel and has also helped to incentivize the market growth.

3.10 Regional PetCoke Pulverizing Facilities

All of these factors have contributed to the current business model for regional PetCoke pulverizing facilities supplying the Pulp and Paper market. Each facility can provide fuel to surrounding paper mills based on comparative pricing as well as delivery freight costs. Currently there are six PetCoke Pulverizing Facilities for supply to the pulp and paper industry across the United States. They are listed in Table 5g in the order of establishment dates.
### Table 3g
#### Regional PetCoke Pulverizing Facilities
Serving the Pulp and Paper Industry

<table>
<thead>
<tr>
<th>Company</th>
<th>Location</th>
<th>Region</th>
<th>Year PetCoke Pulverizing Facility was Established</th>
</tr>
</thead>
<tbody>
<tr>
<td>PeTroCoke, Inc.</td>
<td>Campti, Louisiana</td>
<td>West South Central</td>
<td>1986</td>
</tr>
<tr>
<td>PeTroCoke, Inc.</td>
<td>Owensboro, Kentucky</td>
<td>East South Central</td>
<td>1988</td>
</tr>
<tr>
<td>DTE Pet coke, LLC</td>
<td>Vicksburg, Mississippi</td>
<td>West South Central</td>
<td>2004</td>
</tr>
<tr>
<td>Oxbow Carbon and Minerals</td>
<td>Tuscaloosa, Alabama</td>
<td>East South Central</td>
<td>2005</td>
</tr>
<tr>
<td>Sound Refining</td>
<td>Tacoma, Washington</td>
<td>Pacific North West</td>
<td>2006</td>
</tr>
<tr>
<td>Hiller Carbon, LLC</td>
<td>Marietta, Ohio</td>
<td>East North Central</td>
<td>2008</td>
</tr>
</tbody>
</table>

#### 3.11 PetCoke Pulp and Paper Market Size by Region

At the close of 2009, there are 23 Lime Recovery Kilns in the United States with the ability to receive and burn PetCoke. Twenty of these kilns were supplied by the regional pulverizing facilities earlier mentioned. The other three kilns utilize raw PetCoke and pulverize at the mill.

Assuming that these specific kilns operated at approximately 75% of their intended PetCoke substitution levels, the total estimated tonnage of PetCoke burned in the Pulp and Paper industry for 2009 was 333,400 Short Tons. Below is a distribution of the annual PetCoke tonnage in relation to the location in which it was burned. See Chart 3h.

![Chart 3h
Pulp and Paper PetCoke Market by Region](chart.png)
3.12 PetCoke for Pulp and Paper Historical Market Price

As a comparative to other competing fuels, PetCoke is generally priced in terms of its energy value, generally in dollars per million Btu ($/MMBtu). Historically, PetCoke has proven to be a less volatile and less expensive fuel when compared with Natural Gas and Fuel Oil. Below is historical data supporting this for Southern Mills burning PetCoke in Lime Recovery Kilns. The black line represents PetCoke and the range shown would account for freight in delivering to the Mill. Mills that are in closer proximity to the Pulverizing Facility see a lower price per MMBtu since shipping charges are lower. See Chart 3i.

![Chart 3i](image)

Data Source: Jacobs Consultancy

**Chart 3i**

*Historical Pulverized PetCoke Price for a Southern Mill (03)*

The general stability of PetCoke as well as its lower price is a great benefit to a Paper Mill. Stable and low energy prices allow a Mill to better predict and maintain profitability.
PETCOKE – A GREAT FUEL FOR THE LIME RECOVERY KILN

4.1 PetCoke Emissive Flame Efficiency Advantage

When compared to natural gas as a fuel for a lime recovery kiln, PetCoke has proven to be a more efficient fuel. Experience in recovery kilns thus far has shown a 4% -10% overall improvement in the amount of energy per ton of lime recovered. See Chart 4a for a heat flux comparison.

PetCoke has a much more radiant, emissive flame over natural gas. A PetCoke flame is shorter and bushier as compared to a long lazy natural gas flame. As a result, the PetCoke flame is brighter and hotter and more concentrated toward the very end of the kiln where the lime discharges. PetCoke fired kilns generally have a hotter front end temperature and a lower back end temperature as a result of the emissive flame.

"Radiation is the dominant mechanism of heat transfer in the burning zone of a rotary kiln, with more than 95% of the heat transferred in this way. The rate at which heat is transferred to or from a flame is controlled predominantly by the radiative exchange in the combustion chamber. The factors that affect this exchange are the temperatures, emissivity, and relative geometry of the flame and surroundings." (05)
"The emissive properties of a flame are a function of the concentrations of the spectrally emissive and absorptive gases (CO2, CO, H2O) from the combustion process and the particulates burden in the flame. Flames in rotary kilns fired with petcoke have a high particulates burden and hence a high emissivity, while natural gas flames have a low particulates burden and low emissivity. Natural gas flames are therefore at a disadvantage because the low emissivity results in a peak heat flux further down the kiln." (05)

See Chart 4b for a computational model for flame comparison.

Source: Richard Manning, Director –Kiln Flame Systems (KFS)
Pulp and Paper Magazine, December 2003

**Chart 4b – Flame Comparison Computational Model**

A natural gas flame is fairly long resulting in the hot zone occurring about 20 – 25 ft from the end of the kiln. Therefore the heat curve on a natural gas kiln peaks around 25 ft from the discharge. In this case less calcining will occur after it leaves the hot zone and before it is discharged. A PetCoke fired kiln, on the other hand, has a much more efficient heating curve by calcining more and more all the way up to its discharge. This effectively lengthens the kiln and improves the overall efficiency when compared to a natural gas fired kiln. Depending upon kiln geometry and original efficiency, Mills have seen a 3-10% overall efficiency improvement measured in MMBtu per ton CaO produced. See Photo 8c of a typical Petcoke flame.
4.2 PetCoke Sulfur can be a Benefit to some Mills

In general, a Paper Mill must maintain a stoichiometric balance between the sodium and sulfur in their liquor cycle in order to control the sulfidity of their white liquor. During normal operations, no matter how "tight" or "closed" a Mill may be, sodium and sulfur will be lost from the liquor cycle, and therefore a source of make-up must be provided for both chemicals. Sodium is usually supplied by adding 50% caustic soda. Sulfur is usually provided by a wide variety of sources, i.e., spent liquor from the chlorine dioxide generator if it is a bleached mill; sodium hydrosulfide; liquid sulfur; tall oil brine; or burning of NCG's in the lime kiln. Depending on the sulfur content of the petcoke burned, the sulfur contribution to some extent helps reduce the need for purchased sulfur, and therefore contributes positively to a Mill's bottom line. Some Mills have experienced a noticeable reduction in the amount of NaSH or Sodium Hydrosulfide that they have had to purchase since burning PetCoke.

Once a Mill starts burning petcoke in the lime kiln, it is important to keep track of any impact on the stoichiometric balance between the sodium and sulfur in the Mill's liquor cycle. First indication that a change has occurred usually will be an increase in sulfidity of the white liquor, or an increase in SO2 or TRS emissions from the Kiln's air cleaning equipment.
PETCOKE – NOT A FUEL ONLY

5.1 Other Uses for PetCoke

Although predominantly used as a fuel, PetCoke has several other uses as well. Below is a chart which divides the domestic usage.

![Domestic PetCoke Market - 2008](chart5a)

Data Source: Jacobs Consultancy

Below fuel usage, approximately 17% is used for anodes in the aluminum industry. This is generally the lower sulfur PetCoke. It can be calcined to remove volatiles prior to producing the anodes. In addition, some of the coking processes are proprietary and yield Needle Coke which is formed from needle-like ocicular structures. This structure gives needle coke a comparatively higher conductivity and is considered a premium for anode production. This needle coke is not considered to be fuel grade since it brings a much higher price on the market than other fuel grade cokes.

Among the 3% which constitutes all other industry, PetCoke is also calcined and used in the Titanium Dioxide industry as a reducing agent as well in the production of Dry Cell Batteries. PetCoke is also being utilized as a feedstock for various gasification processes.
5.2 PetCoke is not a Waste

PetCoke is a by-product of Oil Refineries but is an excellent fuel and a required staple for the aluminum industry. In addition it is exported from the United States and traded world-wide. This product is valuable enough and the market expansive enough that it has always proven to have a positive market value.

In addition, if the market value for PetCoke is positive, but yet not high enough to make the coking process profitable within the refinery, then they have other options available. These options are to produce asphalt or to blend more residual fuel oil. This in turn reduces PetCoke production and lowers the supply and as a result brings the price back into alignment. As a matter of fact, the price differential between lighter fuels such as gasoline and heavier fuels such as residual fuel oil blends is what the refineries track in order to decide whether or not to run the Cokers in the first place.

Even though profitability for the finished fuels takes precedent over this by-product called PetCoke, the expense of land filling these massive amounts of PetCoke would be so prohibitive that it is simply not a viable option when there are other alternatives present to produce the same finished fuels.

This being the case, historically PetCoke has never had negative value and has never been land filled as a result.

PetCoke is also traded internationally, with over 56% of our domestic coke being exported to foreign customers. The global market expands the demand and helps to stabilize PetCoke pricing structures so that if domestic supply increases and prices begin to slump, then overseas demand will increase since the lower prices will fund the exporting cost.

Therefore since coke is a byproduct of choice and is traded on a global scale, the supply and demand market will lower the price of PetCoke and consume it as fuel or as anodes in order to get rid of it. If the supply increases and the price of PetCoke drops to the point that blending residual fuel oil or producing asphalt is more profitable, then they will stop using their Cokers and produce less PetCoke.

In addition, PetCoke is an excellent fuel and in many ways superior to coal in Btu content and ash. These qualities certainly help to create its demand from large energy consumers in cement and power generation. In addition, PetCoke is absolutely required in significant proportions in making aluminum. It takes approximately one half ton of PetCoke to produce one ton of aluminum.
As a result of the ability to control supply by the refineries along with a domestic and international marketplace for fuel and metal production, PetCoke does not have a history of being land filled.
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