PETCOKE CO-FIRING

USE OF PETROLEUM COKE AS AN ADDITIONAL FUEL IN THE LIME KILN

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Abstract:

This is an in-depth view of the usage of ground petroleum coke as a fuel for the pulp and paper lime recovery kiln. PetCoke is an economical choice as an additional fuel capable of displacing up to 70% of Fuel Oil. PetCoke is relatively inexpensive with little or no price volatility since it is a waste stream of the oil refinery. Depending on the ever changing price of fuel, a Mill which burns 100% fuel oil can typically save between 25% and 50% of their total kiln fuel costs by co-firing with PetCoke.

PetCoke, prepared for the lime kiln, is a fine powder with both cohesive and flushing tendencies. Controlling the feed consistency of this problematic powder is the key to unlocking an excellent fuel for the kiln which is on par with fuel oil in terms of kiln heat profile and lime re-burning quality.

Matrix Engineering / Matrix Industrial Systems have pioneered most of the pulp and paper sector of the fuel grade PetCoke market within the United States. Matrix also recently provided the first PetCoke fuel delivery system for a lime kiln in India. Our patented DENSI-FEED® Pulverized Fuel Feed and Delivery System delivers precise and predictable fuel flow of this very difficult powder.
PetCoke, an Economical Fuel:

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. Since PetCoke is a by-product of cracking lighter fuels, the PetCoke supply will increase along with the ever-growing demand for gasoline. Since PetCoke is a residual of a finished fuel, it will always be cheaper than the actual finished fuel such as Fuel Oil. Massive quantities of PetCoke are generated in the refining of a gasoline and stockpiling is not desirable. The oil company is smart enough to obtain a fair price for this useful waste, but by the end of the day, they are in business to sell finished fuels and all of the coke must be moved out of the way. This yields a more stable and predictable pricing structure for this PetCoke fuel market as compared to the finished fuels.

As a comparative to other competing fuels, PetCoke is generally priced in terms of its energy value, generally in US dollars per million Btu ($/MMBtu). Historically, PetCoke has proven to be a less volatile and considerably less expensive fuel when compared to Natural Gas and Fuel Oil. Below is historical data supporting this for US 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 1.

The general stability of PetCoke as well as its lower price is a great benefit to a Paper Mill. Historically, PetCoke unit cost is stable has been in the range of 25% - 75% the unit cost of the ever-changing Fuel Oil price. Stable and low energy prices allow a Mill to better predict and maintain profitability.
Petcoke in the US Paper Mill – A Short History Lesson:

Initially three mills in the USA attempted PetCoke burning systems for their lime recovery kilns back in the mid-1980’s. Results were mixed, the mills could see that PetCoke appeared to be a good fuel for co-firing with their primary fuel, however they were not able to burn very much of the fuel due to fuel feeding inconsistencies and the lack of a properly designed burner. Therefore the mills continued to burn at very low rates. Three mills and low rates yielded a low demand for PetCoke in the industry and did not spur a supply chain of fuel seeking new customers. PetCoke remained in this dormant and stagnant stage for around 20 years.

As US Natural Gas pricing began edging upward around 2003, mills and fuel suppliers began to re-examine the potential of PetCoke. Our initial Matrix PetCoke feed systems were commissioned in 2004 alongside modern burning expertise from the United Kingdom company, Kiln Flame Systems (KFS). These initial systems, broke the barriers of low substitution that had plagued the initial three Mills. Over the next 5 years, we continued to improve our technology to the current 4th generation DENSI- FEED® Fuel Delivery System installed in our 16th USA kiln and 1st Kiln in India (J-K Paper Limited, Unit: JKPM Jaykaypur, Odisha India.) Optimizing and streamlining our PetCoke feed for responsive and instantaneous control has been our main focus since our initial systems deployed in 2004.

The stagnant era from the mid-80’s to 2004, highlighted the limitations and process impact issues with PetCoke generating fear and doubt about the fuel across the industry. Many of the issues of these early mills were caused from improper fuel feed and combustion which was a result of the inferior PetCoke systems that they had. Much of our time and effort at Matrix over the past decade has been spent in proving the reliability of this fuel through feed stability and disproving doubts caused by make- shift feed systems that do not perform and have little or no instrumentation to define what is actually happening. Our current objective is to make sure India does not have a similar “20 year wilderness experience” than that of the United States. Our DENSI- FEED® fuel delivery technology is optimized to ensure maximum substitution levels and success with this difficult fuel.

Green or Fuel Grade PetCoke:

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 residual product that is left behind. Most of the PetCoke obtained from this process is considered a fuel grade or “green” petcoke. The majority of green coke is shot coke which appears as small hard spheres which are clumped together into friable amorphous groups. Shot coke has a lower API density and a high asphaltene content which supports its spherical formation. See Photo 1 for an image of shot coke.
This fuel grade or green coke has an initial moisture content of around 8-10% due to its water jet removal from the coker and it’s outside storage.

**Direct Fire Systems vs Indirect Fire Systems:**

In cement and power boiler applications, this green coke is consumed as fuel in a direct fire application. Using this method, the green coke is fed into a pulverizing mill and blown directly to the burner in the kiln or furnace. In these applications, the levels of heat and energy require vast amounts of fuel with relatively forgiving processes and are suitable for the direct fire approach. However, in a lime recovery kiln, taking the direct fire approach is not a viable option. The discharge line from the pulverizer is large requiring an enormous stream of air to convey the fuel to the burner. This almost eliminates the use of primary air and the ability to flame shape and optimize combustion in a smaller and cooler lime recovery kiln.

Therefore an indirect fire method is the best possible choice for firing the lime kiln. This indirect method also provides a buffer storage silo between the pulverizer and the burner. At the base of the storage silo is a powder feeding system for metering fuel in the proper proportion to the burner. In this case, a dilute phase pneumatic convey system carries the fed powder to the burner with an optimal amount of airflow for mixing the fuel and flame.
The indirect firing method also allows for the green coke to be pulverized remotely or off-site and delivered as a finished fuel, ready to burn. Since PetCoke is a very stable fuel with a high ignition temperature and is not prone to spontaneous combustion, off-site grinding is a sound and economical approach, eliminating the need for capital expenditure on the pulverizing system.

**Petcoke Composition and Lime Kiln Fuel Specification:**

PetCoke is a high calorific powder fuel that produces a bright emissive flame similar to fuel oil. It has virtually no moisture content and very low hydrogen composition, so water is not a by-product of its combustion. It also has a very low ash content, similar to Fuel Oil so no residuals pose an issue. It is 86-88% fixed carbon, therefore, it has a high and consistent heating value.

<table>
<thead>
<tr>
<th>Tests</th>
<th>Method</th>
<th>As Received “Green”</th>
<th>Dry “Pulverized”</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>
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<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 (8224 – 8600 kcal/kg)</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>
Trace metals in PetCoke are fairly low:
Vanadium – 325-2300 ppm
Nickel – around 300 ppm
Mercury – less than 1 ppb

Mills in the USA were initially worried about introducing even a small source of vanadium into the recovery boiler process. However, as time has proven over the past thirty years of PetCoke usage, no issues with vanadium have ever materialized.

Although PetCoke is a high calorific fuel, it is difficult to burn in suspension unless it is properly sized. A PetCoke particle burns on its surface from the outside to its inner core. Therefore, smaller particles are better for flame shape and complete combustion. The commonly used size specification for PetCoke fuel in the lime kiln is a minimum 90% passing 200 mesh (or less than 75 micron). Moisture content should be less than 1% (typically it is less than 0.5%). Ash content should be less than 1% (typically it is less than 0.5% on a dry basis).

Typical heating values for PetCoke will be between 8300 – 8600 kcal/kg. However, once a PetCoke supply is obtained with a consistent source, the actual heating value will be consistent as well (it may vary +/- 25 kcal/kg).

In the USA, PetCoke is traded on an energy unit basis (per Btu). However, in India, trades appear to be conducted in mass (per kg). When pricing PetCoke, it is important to look at the actual heating value and include that in the economic evaluation.

Within the USA, PetCoke is primarily delivered to the mill in pneumatic truck trailers, with a few mills receiving coke by pneumatic rail car. Pneumatic truck trailers offer a clean and simple way to receive coke with a low capital investment for unloading equipment, requiring only a positive displacement blower and a pipeline to the silo. However, in India, pneumatic truck trailers are not in abundant supply as they are in the US. Also, if multi-day travel distances are required from the PetCoke supplier to the mill, freight can be significantly higher than standard trucks, since standard trucks can be scheduled for a return shipment of another product. At any rate, this method of PetCoke delivery is preferred if available and freight costs allow.

PetCoke can be shipped via standard truck in 1000 kg bulk bags. This requires a bulk bag unloading and convey system to the storage silo. Depending on proximity and reliability of the PetCoke supplier, warehouse space for staging bulk bags is also suggested. The PetCoke storage silo can be sized for the particular kiln size and number of days desired for elevated storage. This is typically between 100 tonnes and 240 tonnes capacity.
Petcoke Combustion 101

Since the lime kiln is simply not hot enough to achieve a 100% sustainable PetCoke flame, PetCoke must be co-fired with a high calorific liquid fuel (such as Fuel Oil) or a suitable high calorific gas (such as US Natural Gas). Substitution levels under each scenario are different due to the volatility differences of the primary fuel that PetCoke is co-fired alongside.

Generalizing, a flammable gas burns easier than a flammable liquid. A gas fuel is already volatile and ready for instantaneous combustion. A liquid fuel must be atomized, heated, and volatized to vapor prior to being fully consumed in combustion.

However burning a liquid is easier still than burning a solid fuel. In this case, the solid particle must burn on its surface area from the outside to its inner core in layers until it is consumed. Therefore the burn time for PetCoke is always longer than for the volatized Fuel Oil. This is evident in the photo below by the short black plume of PetCoke consumed just beyond the burner tip.
Along the PetCoke particle’s journey, sufficient oxygen must be found at all points for complete combustion. This stresses the critical nature of instantaneous mixing of fuel, flame and oxygen even more in the case of burning a solid fuel.

Some of the staple fuels used in India (since a quality US grade Natural Gas is not available) are Biogas and the more common Producer Gas. These fuels are relatively low calorific gases as compared to US Natural Gas. To my knowledge, there are no current applications where these gases are co-fired with PetCoke. We believe that firing PetCoke alongside these fuels is certainly possible, but will likely require some level of Fuel Oil to remain in the mix. Since Biogas has a higher heating value of the two, I am more optimistic about further minimizing or possibly removing Fuel Oil from the mix with Biogas, however this has yet to be determined.

In general, PetCoke is an excellent, high calorific fuel with the following limitations.

1. PetCoke must be co-fired with Fuel Oil or Natural Gas. PetCoke cannot achieve 100% substitution levels in the lime recovery kiln. The process is simply not hot enough to support its sole combustion.
2. PetCoke cannot be introduced to a cold kiln. Operating temperatures must be established prior to displacing the primary "warm-up" fuel with PetCoke.
3. On US Natural Gas fired kilns, Matrix is able to achieve 80-85% substitution levels.
4. On Fuel Oil fired kilns, Matrix is able to achieve 65-70% substitution levels.

Obviously the burner design is essential in combustion. However, these levels of substitution are only attainable if the fuel feed to the burner is precise, steady and smooth. The burner is essentially an 8-10M long tube acting as an instantaneous
mixer for a chemical reaction consisting of fuel, flame and oxygen. The fuel’s journey within the burner lasts less than a second. Since a burner cannot create or destroy fuel once it has entered the burner itself. It can only mix the fuel that was delivered as it is delivered, second by second. Therefore, instantaneous command and control must be maintained over the powder fuel feed outside of the burner boundaries. Even the best, most well designed burner will not perform if the fuel feed is inconsistent. This is also true for a gas or a liquid fuel, but it is even more pronounced in a solid fuel. Since a solid requires longer burn times compared to the liquid or gas, fuel feed inconsistencies will be amplified and more obvious on the burner tip, often revealing as large black sporadic plumes.

**Pet coke Fuel Delivery – Densi-Feed® Approach:**

PetCoke exhibits extreme feed issues once pulverized into a fine powder for combustion. As the solid fuel is more finely ground to enhance combustion properties, it also becomes more difficult to feed to the burner in a consistent and predictable manner. One moment the fuel is cohesive in nature and feed flow is limited, the next moment the fuel flow is unlimited and flushes excessively to the burner. We refer to this as a “bridge and flush” phenomenon.

![Figure 2 – Matrix Densi-Feed® Fuel Delivery System](image)

The Densi-Feed® approach seeks to feed the PetCoke on a consistent basis by controlling product density throughout the burner delivery process. Our Densi-Feed® is specifically designed for feeding powder in a smooth, non-pulsating...
manner for optimized flame stability. In addition, our PetCoke Flow Meter instrumentation provides for instantaneous measurement, feedback and speed control of the DENSI-FEEDER®. The DENSI-FILTER® is an integral part of the density control and produces an ideal internal environment for accurate and repeatable measurement of the fuel feed by the flow meter.

Once the PetCoke has been fed and measured, a rotary airlock valve specifically designed for this fuel application, simply transfers the fed PetCoke into a dilute phase line for conveying it to the burner. This pneumatic convey system is also variable with flow control and pressure instrumentation to assist in flame optimization as well as confirming the requirements of the burner for combustion performance guarantees are being fulfilled.
Process Impacts: Gas/Solids Temperature Along the Kiln

In a typical kraft mill, calcium carbonate (CaCO₃) mud is converted into lime in order to generate white liquor for pulping. Lime mud is fed into the upper end of the kiln and its rotation and slight decline causes the mud to travel down its length from the cold or feed end to the discharge or hot/firing end. The burner is located on the firing end and an induced draft (ID) fan draws the heated gas from air introduced for combustion in a counter-current flow toward the feed end of the kiln. As the mud flows down the kiln, it is dried through a chain section and then heated up to a level where calcining occurs over the last third of its travel. During the calcining stage, the calcium carbonate is converted to calcium oxide (CaO). Typical gas and solids temperatures along the length of the kiln are graphically represented below.

![Figure 3 – Gas/Solid Temperature Along the Kiln](image)

Different fuels and fuel combinations can have different gas temperature profiles in a given kiln. The obvious optimal profile for gas temperature is a relatively linear increasing curve (after its moisture is driven off) with its low point at the feed end and it’s high point at the firing end.

Fuels with a high level of hydrogen give off considerable moisture in the combustion reaction when the hydrogen combines with the O₂ to form H₂O. These moisture prone fuels have longer flames pushing their maximum temperature levels farther down the kiln. In the case of US Natural Gas, this hot zone peaks around 30-40ft (10-13m) from the firing end.

High carbon, low hydrogen fuels such as Fuel Oil, tend to have dry, bright emissive flames that are more bushy in nature where its maximum temperature is anchored more closely to the firing end. PetCoke has a kiln firing flux curve which is essentially identical to that of Fuel Oil. Both PetCoke and Fuel Oil yield a more efficient kiln in terms of overall energy usage when compared to Natural Gas or other moist or low calorific fuel options. These high calorific, low moisture fuels tend to lengthen the kiln, allowing the calcining to occur over the full remaining length of the kiln instead of beginning to cool slightly at 10 meters prior to discharge.
In Figure 4 above, PetCoke when co-fired with US Natural Gas nearly duplicates the heat profile of a 100% Fuel Oil flame. In the case where PetCoke is co-fired with Fuel Oil, there is essentially zero change in the kiln’s heat flux profile from its previous 100% Fuel Oil flame.

In US Natural Gas fired kilns after a PetCoke conversion project, the kiln operators typically notice a rise in firing end temperature and a lowering of back end temperature as the heat flux profile corrects to look more like a Fuel Oil scenario. This is also an indication of efficiency improvement of overall energy consumption. PetCoke simply makes Natural Gas better and a more efficient fuel for the lime kiln. In terms of overall efficiency improvement, we generally saw a 3-10% improvement depending on the size of the kiln and how efficient it was prior to conversion. On Natural Gas fired kilns with excellent chain sections and tight fuel controls, we saw improvement in the 3-5% range. On older less efficient kilns that were not as tightly controlled in terms of energy use, we saw efficiency improvements in the 5-10% range.

Keep in mind that establishing an optimal heat profile is more than simply choosing the right fuel. The fuel must also undergo complete and efficient combustion, which involves instantaneous mixing of fuel and flame and oxygen so that the fuel is entirely and immediately consumed. Therefore, accurate and continuous monitoring of O$_2$ is vitally important. Depending upon the specific kiln circumstances, O$_2$ should generally remain around 1.5% to 3.0% at the feed end and CO levels should be low and steady as an indication of proper combustion. If O$_2$ levels drop below this, not enough oxygen is available to the burner for proper combustion. This could be due to a lack of ID Fan draft or the fuel rate may simply be too high for the current load condition in the kiln.
Often times the feed end temperature may actually rise in this condition, since much of the fuel may be combusting farther down the kiln which can also shift up the feed end temperature. In cases where the O₂ level is higher than the acceptable range, the ID draft could be too high which can also cause a rise in feed end temperature and cooling of the firing end, or the fuel level could be too low for the load in which case; things would begin to cool on both ends of the kiln.

Having a good firm understanding of the kiln and these temperature profiles from a process management and operational standpoint are essential in avoiding temperature fluctuations in the kiln. These temperature fluctuations and process inconsistencies are at the root of many kiln process issues including ringing. However, if PetCoke is introduced with a quality fuel feed system and burner specifically designed for the application along with adequate kiln instrumentation, then temperature fluctuation will not change as a result.

**Process Impacts: Ring Formation in Lime Kilns**

There are three types of common kiln rings, each of which may be caused by many different process variations and combinations thereof. There is much depth to this topic, the highlights of which will be examined here and in particular how they relate to kilns co-firing with PetCoke.

Back End Mud Rings occur in the drying section near the feed end or in the first third of the kiln. These are relatively soft in nature and their origin is moisture content related. In an effort to maximize energy efficiency most try to operate the feed end temperature as low as possible. If a mud ring appears then this feed end temperature may be too low allowing the moisture content in the mud to shift slightly causing a new sticking point and ring formation. On US Natural Gas fired kilns, this phenomenon has happened after a PetCoke conversion. As discussed in the previous section, when Natural Gas is co-fired with PetCoke, then the heat profile shifts, lowering the feed end temperature. In the specific case in which I am familiar, the Mill simply shifted the feed end temperature up slightly (approximately 5 degrees) and eliminated the issue. In many cases this may not be related to the kiln temperature, but instead a function of the solids content of the mud as it enters the kiln.

Mid-Section Rings occurring near the onset of the calcining zone are generally more troublesome and are attributed to a phenomenon where mud particles become sticky and adhere to the wall. When the temperature fluctuates and drops below 800°C a recarbonation reaction occurs.

\[
\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3
\]

Preventing mid section rings primarily involve increasing mud solids, better mud washing (reducing Na) and minimizing temperature fluctuations. PetCoke is essentially not a factor here if the fuel feed and combustion system are functioning properly.

\[
\text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4
\]
Firing End Rings are more of a chemical phenomenon that occur due to "recarbonation" after sticky sodium compounds adhere to the wall and continue to grow driven by the reaction. In this case the stickiness is not due to moisture, but rather due to molten Na near the end of the kiln.

In very general terms, high sulfur fuels can encourage the ring growth in this region. In a narrow temperature range (around 1100°C) sulphation of CaO occurs which tends to harden the ring.

PetCoke is a higher sulfur fuel and can contribute to a firing end ring. However mills that burn Natural Gas in the USA have no sulfur. US Kilns burning Fuel Oil have less than 2% sulfur content. When a US mill performs a PetCoke conversion project with a new sulfur source at 5.5%, the additional influx of sulfur into the process is more dramatic than a mill in India, where Fuel Oil is already at the 3-4% level.

The majority of ringing issues are sourced from temperature fluctuation in the kiln. Dr. Honghi Tran, Director of Pulp and Paper Centre at the University of Toronto conducted an extensive study with PetCoke firing at centerstage titled “Impacts of Burning High Sulfur Fuels in Lime Kilns”. In this study, Dr. Tran examines the composition of various rings and found actual sulfur deposits to be minimal and insignificant. He plainly states:

“In kilns that burn PetCoke, if ringing is an issue, it is more likely caused by flame instability that leads to wide temperature variation and ring growth through recarbonation, than by high sulfur content.”[6]

Dr. Tran’s conclusion re-iterates and stresses the main objective of my experience and best advice on a PetCoke Conversion Project: If you are planning to burn this fuel, you better do it properly with expertise demonstrated by a proven track record for actual PetCoke fuel feeding and combustion, or the results will be mixed at best and will lead to undesirable process impacts.

**Process Impacts: Increased Sulfur in the Process**

From an environmental standpoint, the Lime Recovery Kiln is an excellent place to burn a higher sulfur fuel such as PetCoke. The combustion zone of the kiln with the presence of lime dust acts as a scrubber combining to form calcium sulfate preventing much of the potential SO₂ from the emission gas stream.

The combustion of Sulfur:  \( S + O_2 \rightarrow SO_2 \)
The formation of Calcium Sulfate:  \( CaO + SO_2 + \frac{1}{2} O_2 \rightarrow CaSO_4 \)

There is also a minute amount of sodium that enters the kiln in the residual amounts of white liquor in the mud. This sodium also combines with SO₂ forming Sodium Sulfate (NaSO₄).
Figure 5 - Fate of Sulfur in the Recovery Process [5]

However, the desired end product from the kiln is Calcium Oxide (CaO) which is combined with the Sulfur Dioxide in the scrubbing process. It is important to consider how much or the CaO is depleted up in this reaction and where the CaSO₄ purged from the recirculation process.

The amount of CaO depleted in the reaction is minimal. In an extreme (and impossible) case of a Mill switching from 100% Natural Gas (with 0% Sulfur) to 100% PetCoke at 6.5% Sulfur content, the maximum possible amount of CaO converted if 100% of the Sulfur was consumed here is 2.4%[6] When this extreme scenario is compared with a mill in India already burning 3.5% Sulfur Fuel Oil, the additional loss of CaO will likely be in the 1% range.

In addition, not all of the sulfur is converted to calcium and sodium sulfate, some will leave as SO₂ emissions. A sulfur absorption curve was developed by Dr. Tran in his study of "Impacts of Burning High Sulfur Fuels in Lime Kilns". This curve was developed from the study of a Brazilian Kraft Mill and should not be considered conclusive for all mills, however, it can be used as an approximation tool in helping to predict emission impacts prior to implementation of a PetCoke conversion project. The curve evaluates Sulfur input in terms of kg of S per tonne CaO. As Sulfur input rises, the ability to absorb it into the process decreases and the level of SO₂ emissions correspondingly rise.
Below is a specific example of a Mill previously burning 100% Fuel Oil at 4% sulfur content, who is considering a PetCoke Conversion project at 65% Petcoke (6% sulfur content) and 35% Fuel Oil. This mill typically uses 148 liters of Fuel Oil per tonne CaO.

<table>
<thead>
<tr>
<th>Initial Scenario 100% FO</th>
<th>New Scenario 65% PC / 35% FO</th>
</tr>
</thead>
<tbody>
<tr>
<td>FO Sulfur Content</td>
<td>PC Sulfur Content</td>
</tr>
<tr>
<td>4.00%</td>
<td>6.00%</td>
</tr>
<tr>
<td>Liters FO / Ton CaO</td>
<td>PC Heating Value</td>
</tr>
<tr>
<td>148</td>
<td>8600 kcal/kg</td>
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<tr>
<td>S kg per Ton CaO</td>
<td>S kg per Ton CaO (PC/FO)</td>
</tr>
<tr>
<td>5.7 100% FO</td>
<td>8.2 5 S/Ton CaO</td>
</tr>
<tr>
<td></td>
<td>Net Sulfur Increase = 2.5</td>
</tr>
</tbody>
</table>

A NET INCREASE OF 44% Sulfur has minimal effect. Absorption drops to 97% from 98.5% SO2 increases from 50 to 130 ppm.
Process Impacts: Environmental Emissions

**Sulfur Dioxide SO₂:** As estimated in the previous section there will be an increase in SO₂ emissions as a result of firing PetCoke if its sulfur content is higher than the Fuel Oil previously burnt. If a wet scrubber is present at the mill, this additional SO₂ can be completely mitigated with chemical cost proven very minimal. If a mill only has an Electrostatic Precipitator (ESP), then these emission changes will need to be evaluated against permitted levels. Several US mills implementing PetCoke Conversion Projects only had ESP’s and in most cases, they found SO₂ increases to be lower than anticipated. In all cases, the increased emissions were manageable and did not prevent the use of the system.

If no additional allowance in SO₂ emissions is possible, then a lower sulfur content PetCoke can be sought. However, PetCoke is generally priced based on sulfur content where lower sulfur cokes are sold at a comparative premium.

**TRS:** Kilns burning PetCoke are generally more susceptible to TRS spikes. However TRS is generally controlled by keeping O₂ at the feed end above trigger points for TRS issues. Flame stability and precise, controllable fuel feed are important in maintaining a good O₂ level at the feed end. Also it is imperative that Kiln Operators are trained on how to increase PetCoke substitution levels by backing off of the Fuel Oil prior to adding additional PetCoke and to do this in the proper proportion.

**NOₓ:** NOₓ will rise in a PetCoke substitution with either Natural Gas or Fuel Oil. These levels have typically risen from 150-200 ppm to 300-400 ppm (based on exit gas at 2% O₂ dry basis)[4].

**CO:** PetCoke is a solid fuel with a low percentage of volatiles and a very high carbon content. Therefore once the volatiles are gone the particle consists almost entirely of carbon and must burn on its outer surface inward until it is consumed. As a result of this initial combustion, CO is formed and later oxidized into CO₂ as it moves away from the particle. This is why selection of the burner that provides a kiln audit and a specific design considering combustion aerodynamics is important to assure combustion is as complete as possible. Maintaining an acceptable CO level will also ultimately determine the final acceptable substitution level for PetCoke on the specific kiln (if other emissions are within acceptable levels).
Summary:
Co-firing PetCoke in a lime recovery kiln offers significant fuel savings. These savings typically range from 25% to 50% of the overall fuel expense for kilns burning fuel oil. However these savings can be offset by limited substitution levels and process impacts due to variation if the PetCoke is not properly handled. PetCoke is a powder fuel and is more difficult to feed and burn over typical liquid or gaseous fuels. More finely ground PetCoke smaller particles are easier to combust; however, the smaller particles are more difficult to meter in a predictable and consistent manner. PetCoke, if handled without experience and proven technology, can be both cohesive with limited flow and extremely fluid with excessive flushing, both of these tendencies are unacceptable for a fuel firing a critical process.

PetCoke is higher than sulfur than other fuels typically used, however, Mills that burn PetCoke properly are able maintain low process variation and temperature fluctuations, as a result they have minimized or eliminated process impacts. Any process impacts encountered at these Mills thus far have been manageable.

References:
1. Ben Ziesmer, Jacob’s Consultancy “Petcoke Market Outlook” – 2009 Gulf Coast TAPPI Petcoke User’s Forum Vicksburg