

CONTROL OF THE SO_x EMISSIONS DURING THE PETROLEUM COKE COMBUSTION IN FLUIDIZED BED

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Abstract. The petroleum coke (petcoke) is a fuel of low volatile content and sulfur content of 1-8%. The production of petroleum coke is increasing due to the increasing demand for heavy oil processing. The low price and increased production of petroleum coke from high sulfur make its combustion for power generation attractive. Petcoke is the fuel of choice for many fluidized bed combustion (FBC) boiler operators, due to its low cost, high availability and high heating value. This system offers the means for efficiently burning a wide variety of fuels while maintaining low emissions. (FBC) has emerged as an environmentally attractive method for burning petroleum coke in lower operating temperature between (850-900⁰C) and it is divided into essentially in two subgroups - Bubbling (BFBC) or Circulating (CFBC) fluidized bed combustion. Generally, (FBC) systems are capable to remove over 90% of SO_x by adding of limestone also, offers the following advantages. Flexibility fuel, low combustion temperatures, low SO_x and NO_x emissions, and high combustion efficiency. This paper describes fluidized bed combustion process, and environmental performance in the control of the pollutants emissions during the petroleum coke combustion.

Keywords: Sulfur, petroleum coke, fluidized bed combustion, sorbent, pollutants.

1. INTRODUCTION

Petroleum coke (or petcoke) is a by-product of oil refining and is produced through the thermal decomposition of heavy petroleum. Composed mainly of carbon, it is generally cheaper than coal, and the price varies depending on the volumes produced, and on worldwide demand. Petcoke has a higher calorific value than coal, and contains less volatile matter and ash. Many industries, has been interest in the use of petcoke as an alternative fuel for coal, because of the low cost. The main uses of petcoke are as an energy source for power generation, cement production and iron and steel production (Fernando, 2001). The worldwide production of petroleum coke increased in the last years because of a great need to process heavier crude oils, while the demand for transport fuels greatly exceeded the need for heavy products (Coal Trans International, 2000 a).

The USA is the world's largest producer of petroleum coke, producing about three-quarters of world supplies. The higher sulphur levels in petroleum coke result in higher SO₂ emissions and for this reason petroleum coke is generally fired in fluidized bed combustion (FBC). The FBC concept was used around 1940 in the chemical industry to promote catalytic reactions. In the 1950s, the pioneering work on coal-fired fluidized-bed combustion was begun in Great Britain, particularly by the National Coal Board (Elliot and other, 1981). FBC process is represented a potentially lower cost, more effective and considered to be clean technology able to reduce NO_x and SO_x emissions through the addition of limestone during the low operating temperature between 850-900⁰C (DOE, 2003). Fluidized bed combustion is an emerging technology for the combustion of fossil and other fuels and is attractive because of several inherent advantages it has over conventional combustion systems. These advantages include fuel flexibility, low NO_x emissions, and in situ control of SO₂ emissions and represent an increasing potential market for petroleum coke.

2. CHARACTERISTIC OF THE PETROLEUM COKE (PETCOKE)

The petroleum coke is a solid material resulting from high temperature treatment of petroleum fractions. It consists of carbonaceous material and contains some hydrocarbons having a high carbon hydrogen ratio. Petcoke derives from three processes: Delayed coking, fluid coking or flexicoking.

- ❖ Delayed coking is the most widely used process, accounting for some 93% of world production,

- ❖ Fluid coke, which accounts for about 6% of petcoke production,
- ❖ Flexicoke, which accounts for about 1% of petcoke is produced by a variant of the fluidized bed process.

They have different physical and chemical properties, higher calorific values than coal and contain less volatile matter also all three are effective in converting heavy crude fractions and concentrating the contaminants in the coke (Bryers, 1994; Dymond, 1998). Delayed coke has a lower ash content and a higher volatile content than fluid coke or flexicoke and hence has the most potential as a boiler fuel.

Calcined coke is produced from delayed process at temperatures up to 1200°C. Petroleum coke and calcined coke are composed of elemental carbon. The difference between them is the concentration of residual hydrocarbon. Petroleum coke content high residual hydrocarbon and calcined coke content less hydrocarbon, higher elemental carbon and generally less sulphur. The quality of petcoke is most often judged by their sulphur and metal content. Generally the lower-sulphur and metal petcoke are used as a carbon source and the high- sulphur petcoke are used as a fuel (Dymond, 1998). The figure 1 shown the petroleum coke.



Figure 1: Petroleum coke (<http://www.coqueverde.com.br>)

3. COMBUSTION OF PETROLEUM COKE AND COAL

(FBC) combustor can burn coal with high efficiency and within acceptable level of emission pollutants. The carbon monoxide, carbon dioxide, sulphur dioxide, nitrogen oxide and char content in stack gases are the major emission pollutants in FBC combustors with respect to atmospheric environmental conditions. The combustion of the petroleum coke in large-scale facilities has been limited due to its high sulfur and little volatiles and ashes content. Commonly, petroleum coke is blended with coal in proportion suitable to meet sulphur emissions compliance. In the fluidized bed combustion the stability of calcium sulfate, (CaSO_4) during in situ sulfur dioxide capture with limestone (calcium carbonate, CaCO_3) at temperature (850-950°C) and atmospheric pressure. Under pressurized conditions (PFBC), an additional aspect is direct conversion of calcium carbonate CaCO_3 , without the intermediate calcium oxide (CaO) due to the partial pressure of carbon dioxide CO_2 . There is no interaction between coal and petroleum coke particles. In a mixture the coal burn independently of the petroleum coke and the petroleum coke reaction when its own ignition temperature achieved. This observation has practical implications for fluidized bed combustion (FBC) boilers burning coal and petroleum coke mixture in that it's important to preheat the bed to a temperature that is above the petroleum coke ignition point before petroleum coke feeding commences (R. W. Voyles). Table 1 shown the comparison between petroleum coke and coal. Also, the Table 2 shown contains the fuel data for the two fuels and for the blend.

Table 1: Petroleum coke and coal comparison (Stephan and others, 1996)

	Petroleum coke	Typical coal
Sulphur, %	2-6	1-3
Ash, %	<1-5	10-15
Volatile matter, %	6-11	25-30
HGI	35-80	60-70
HHV, GJ	30-35	19-30
Vanadium, ppm	<50-2000	2-100

Table 2: Fuel data (Stephan and other, 1996)

	Coal	Petroleum coke	Blended fuel data
Sulphur, %	2.5	4.7	2.95
Ash, %	9.3	2.6	7.97
HHV, GJ/t	26	31	27.2
Cost, \$/t	32.1	27.1	31.17

3. FLUIDIZED BED COMBUSTION (FBC)

Fluidized-bed combustion (FBC) is one of the major advanced technological, which has been developed to create combustion systems to minimize NOx production, remove SOx, and burn a wide range of fuels. This system is attractive because of several inherent advantages it has over conventional combustion systems. These advantages include fuel flexibility, low NOx emissions, and in situ control of SO2 emissions. The combustion temperature in a fluidized bed boiler is low of (850-900°C), which directly induces lower NOx emissions. This system also allows a cheap SOx reduction method by allowing injection of lime directly into the furnace. The figure 2 shown the diagram of the fluidized bed combustion (FBC).

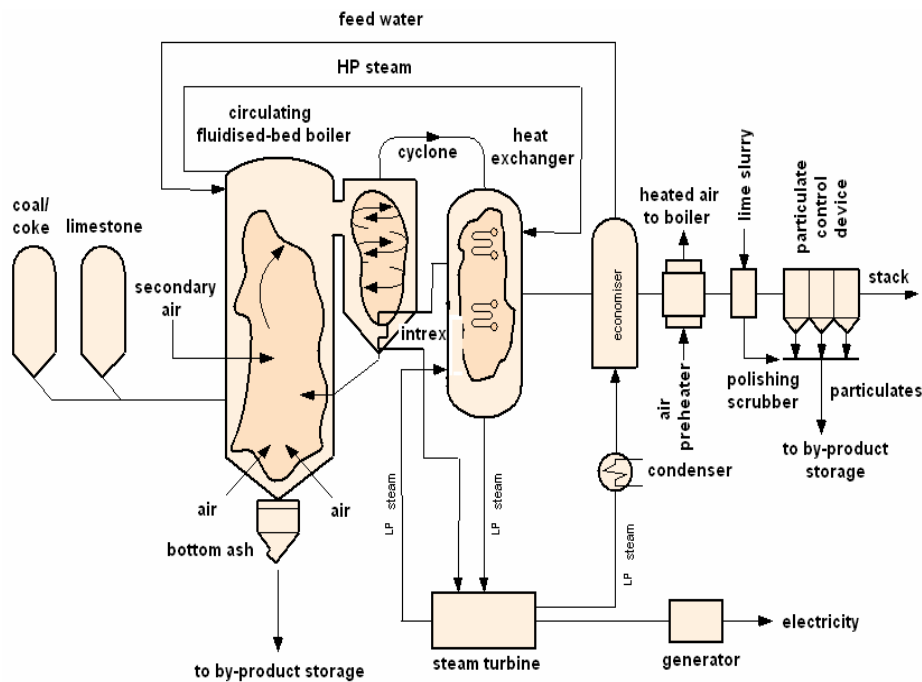


Figure 2: JEA CFB demonstration plant (US Department of Energy. 2000)

The FBC systems are divided into two major groups, atmospheric systems (AFBC) and pressurized systems (PFBC), and two minor subgroups, bubbling (BFBC) or circulating (CFBC) fluidized bed.

- ❖ (AFBC) are operated at atmospheric pressure and use a sorbent such as limestone to capture sulfur released by the combustion of coal.
- ❖ (PFBC) are operated at elevated pressures and also use a sorbent.
- ❖ (BFBC) unit normally operates in reducing atmosphere and use a dense fluid and low fluidization velocity to effect good heat transfer. Bubbling fluidized bed doesn't have as great an ability to absorb sulphur dioxide (SO_2) and is used to burn lower quality fuels with high volatile matter and small plants. The figure 3 shows the diagram of the bubbling fluidized bed combustion (BFBC).

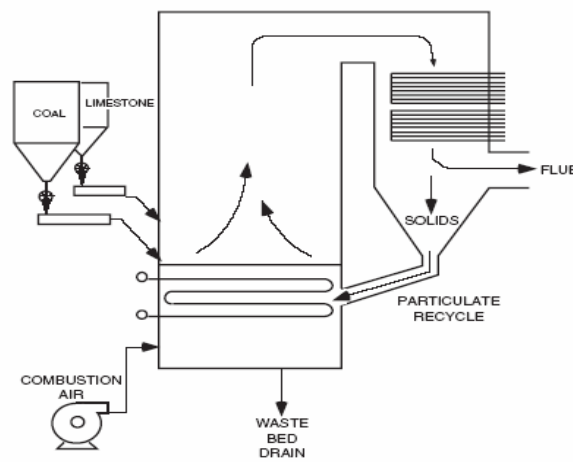


Figure 3: Bubbling fluidized-bed combustion (Gaglia and others, 1987)

- ❖ (CFBC) was developed to create combustion systems to minimize NO_x production, remove SO_x , and burn a wide range of fuels. The use of this technology has been proven by the success of the number of large CFB units operating worldwide over last one decade. This system can burn with high efficiency including low-grade fuels even fuels that cannot be burn in conventional (PC) boilers. CFBC uses high fluidization velocity and fire fuels with high fixed carbon and absorb sulphur dioxide and reduce overall emissions. Circulating fluidized bed combustion is viable for power generation and used for much larger plant. The figure 4 shows the diagram of the circulating fluidized bed combustion (CFBC).

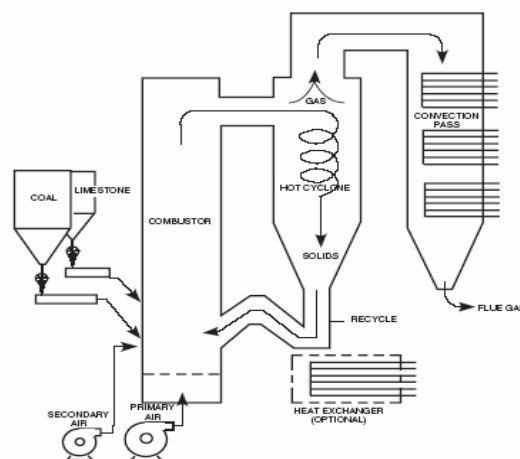


Figure 4: Circulating fluidized-bed combustion (Gaglia, and others, 1987)

4. CONTROL OF THE POLLUTANTS EMISSIONS

Fluidized bed combustion (CFB) system controls the total plant emissions and (CFBC) systems are designed to burn solid fuels while controlling many of these emissions. Pollutants emissions depend of the fuel burned and the combustion. A selective non-catalytic reduction (SNCR) system control the NO_x emissions by injects ammonia into the furnace where it reacts with NO_x to form nitrogen (N₂) and water vapor. Flue gas desulphurization (FGD) also is a process typically used for reducing SO₂ emissions from the exhaust gas system of a coal-fired boiler.

4.1 Control of SO₂ emissions

Coal and oil contain sulphur and when these fuels are burnt the sulphur is released as sulphur dioxide and sulphur trioxide. Both of these are air pollutants. The quantity of sulphur retained by the ash is usually only a small proportion of the total, and there are very few high-sulphur coals that contain sufficient free lime in the ash to reduce the sulphur oxides emission to acceptable levels. One of the principal advantages of fluidised combustion is the possibility to feed additives such as limestone to the combustor where they act as sorbents and augment the fixing of sulphur. The combustion of fuels containing sulfur results in pollutants occurring in the forms of SO₂ (sulfur dioxide) and SO₃ (sulfur trioxide), together referred to as SO_x (sulfur oxides). The level of SO_x emitted depends directly on the sulfur content of the fuel. Methods of SO_x reduction include to low sulfur fuel, desulphurization the fuel, and a flue gas desulphurization (FGD) systems.

- ❖ Fuel desulphurization, which applies to coal, involves removing sulfur from the fuel prior to burning.
- ❖ Flue gas desulphurization involves the utilization of scrubbers to remove SO_x emissions from the flue gases.

Generally the desulphurization by limestone involves two high-temperature gas-solid reactions: calcination and sulfation. One way of capture emissions of these oxides of sulphur is to absorb them on solid calcium oxide, produced by calcining limestone (E. J, Anthony).

During the (FBC) the retention of sulfur dioxide released during the combustion process by particles of sorbent material i.e. limestone. At operating conditions, the calcium in limestone is converted into calcium oxide and then reacts with the sulfur dioxide generated by the combustion process as indicated below:



The CaO, react with SO₂, in the presence of oxygen to give calcium sulfate



The equation (9) and (10)



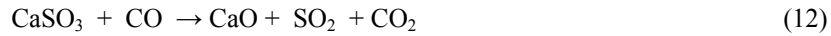


Table 3: Sulfation reaction Moss (1970, 1975)

Lower temperature T <850°C	High temperature T >850°C
CaSO ₃ Stable	CaSO ₃ Unstable
$\text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_3$ $\text{CaSO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4$	$\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$ $\text{CaO} + \text{SO}_3 \rightarrow \text{CaSO}_4$

4.2 Determination of the sulphur retention

Table 4: Petroleum coke composite (Salvador et al 2005)

Petroleum coke fuel	C %	H %	O %	N %	S %	A %	HHV (KJ/kg)
	87.05	3.89	2.43	2.03	4.05	1.25	34450

$mC = 4.8 \text{ (kg/s)}$ $\text{HHV} = 34450 \text{ (KJ/kg)}$ $R = 8.314 \text{ (KJ/kmol.K)}$
 $T_f = 1123 \text{ (K)}$ $T_0 = 298.15$ $\text{Ca/S} = 2$ $\% \text{CaO} = 0.45$

Calculus of the conversion to CaCO₃ for CaSO₄



Resolution

$$\Phi = mC.PCI \quad \Phi = 165360 \text{ (KJ/s)} \quad (14)$$

Calculus of Gibbs free energy

$$\Delta h_{\text{CaCO}_3} := 4.1868 \int_{T_0}^{T_f} \left(19.68 + 0.01189T - \frac{307600}{T^2} \right) dT \quad (15)$$

$$\Delta s_{\text{CaCO}_3} := 4.1868 \int_{T_0}^{T_f} \frac{\left(19.68 + 0.01189T - \frac{307600}{T^2} \right)}{T} dT \quad (16)$$

Table 5: Solution of Gibbs free energy variation for the calcination reaction

	CaCO ₃	CaO	CO ₂	O ₂
$h_f \text{ (kJ/kmol)}$	-1207682.46	-635514.37	-393772.73	0
$s_f \text{ (kJ/kmol.K)}$	88.760	39.775	213.778	29.375

$$\Delta G = (h_f \text{CaO} + h_f \text{CO}_2 - h_f \text{CaCO}_3) + (\Delta h \text{CaO} + \Delta h \text{CO}_2 - \Delta h \text{CaCO}_3) \dots \dots \dots - T_b \cdot [(s_f \text{CaO} + \Delta s \text{CaO}) + (s_f \text{CO}_2 + \Delta s \text{CO}_2) - (s_f \text{CaCO}_3 + \Delta s \text{CaCO}_3)]$$

$$\Delta G = -2422,3 \text{ (KJ/kmol)} \quad (17)$$

Calculus of the conversion to CaCO₃ for CaSO₄

$$K := e^{\left(\frac{-\Delta G}{R \cdot T_f}\right)} \quad K = 1,296207 \quad (18)$$

$$K := \frac{\left[\left(\frac{0.56\lambda}{mf}\right)^{0.56} \cdot \left(\frac{0.44\lambda}{mf}\right)^{0.44}\right]}{\left(\frac{mf - \lambda}{mf}\right)} \quad \lambda = 0.0061 \quad (19)$$

$$X_{\text{Sulphation}} := \frac{\left[\frac{\lambda - (0.56\lambda)}{80}\right]}{\left(\frac{\%CaO \cdot mf}{56}\right)} \cdot 100 \quad X_{\text{Sulphation}} = 77.5 \text{ (\%)} \quad (20)$$

Calculus of sulphation retention efficiency

$$T_f = 1123 - 273 = 850^\circ\text{C}$$

$$\text{Ca/S} = 1 \quad \text{RS} = -1455.225 + 3.7055 \cdot T_f - 0.00225 \cdot (T_f)^2 \quad \text{RS} = 68.83 \text{ \%} \quad (21)$$

$$\text{Ca/S} = 2 \quad \text{RS} = -1680.8 + 4.294 \cdot T_f - 0.0026 \cdot (T_f)^2 \quad \text{RS} = 90.6 \text{ \%} \quad (22)$$

$$\text{Ca/S} = 2 \quad \text{RS} = -1257.9 + 3.292 \cdot T_f - 0.002 \cdot (T_f)^2 \quad \text{RS} = 95.3 \text{ \%} \quad (23)$$

Table 6: Equilibrium constant K_c

Temperature	298,15	448,15	598,15	748,15	898,15	1048,15	1198,15	1348,15	1498,15	1648,15
lnK _c	-53	-29	-17	-10	-5	-2	1	2	4	5

The figure 5 shown the temperature of CaCO₃ versus o equilibrium constant K_c of the reaction (13)

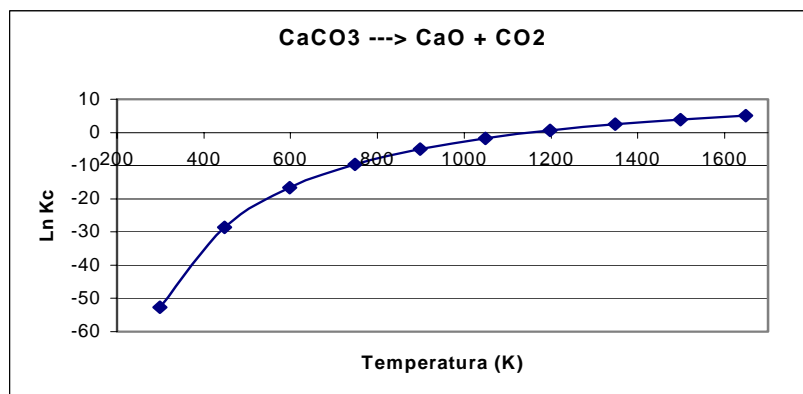


Figure 5 Shown the temperature of CaCO₃ versus equilibrium constant K_c

42. Control of NO_x emissions

Combustion of fossil fuel generates oxides of nitrogen. The most important forms of air pollutants are NO, NO₂, collectively known as NO_x and nitrous oxide (N₂O). There are two sources of Nitrogen oxides formed during combustion of fossil fuels: either molecular nitrogen in the combustion air or the nitrogen bound in various forms in the fuel. According to (Fiveland and Wessel (1991)), there are three mechanisms for the formation of nitrogen oxides.

- ❖ Thermal NO_x – the reaction between oxygen and nitrogen in the combustion air at temperatures up to 1300°C in oxidizing atmosphere,
- ❖ Fuel NO_x – the oxidation of coal-bound nitrogen compounds at temperatures up to 750°C,
- ❖ Prompt NO_x – the fixation of atmospheric nitrogen by hydrocarbon fragments in reducing atmospheres.

The contribution of fuel and thermal NO_x to the total NO_x emission can be in the order of 80% fuel and 20% thermal for a bituminous coal with high nitrogen content (Hesselmann, 1997b). NO formation can be described as a shuttle reaction (Zeldovich, 1946):



In fluidized bed combustion (CFB), the NO_x levels are usually controlled by using a relatively low combustion temperature. The main flue gas NO_x reduction technologies include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR), which both usually utilize ammonia to destroy NO_x (Fan Zhen and others, June 2006). These technologies are designed to control specific pollutants, such as NO_x emissions have two categories:

- ❖ Minimizing the NO_x formation in the combustion process,
- ❖ Reducing the NO_x level in the produced flue gas.

5. ENVIRONMENTAL BENEFITS

(FBC) technology has demonstrated the capability of producing very low emissions of nitrogen oxides, considerably much lower than conventional combustion technologies and low enough to meet current standards in most countries. In some countries, to meet very stringent emission norms additional measures may be necessary to reduce NO_x to acceptable norms. Fluidized bed combustion technology due to lower combustion temperatures, NO_x production is reduced substantially and controlling addition of limestone can control production of SO_x. The major environmental benefit of selecting this system is the removal of SO_x and NO_x emissions. This system offers the following advantages:

- ❖ Fuel Flexibility
- ❖ Low SO₂ Emissions
- ❖ Low NO_x Emission
- ❖ High combustion efficiency

6. CONCLUSION

Fluidized bed combustion (CFB) boiler technology is an advanced method for utilizing coal and other solid fuels in an environmentally acceptable manner. The low combustion temperature allows SO₂ capture via limestone injection, while minimizing NO_x emissions. The technology provides the capability to burn a wide range of fuels including coal, petroleum coke, and blends of the two. Also, fluidized bed systems are generally capable of removing over 98% of SO₂. (CFB) is an excellent choice due to its fuel flexibility and lower operating and maintenance cost. The use of petroleum coke is of both economic and environmental importance. The low price and abundant availability in the market world

make it a very attractive fuel. Petroleum coke has a high carbon and sulfur contents and it's a difficult fuel with respect to pollution concerns.

Fluidized Bed combustion technology has demonstrated the capability of producing very low emissions of nitrogen oxides, considerably much lower than conventional combustion technologies. This system, reduce NO_x emissions productions and control SO_x emissions by addition of limestone, due to lower combustion temperatures between (850-900°C).

7. REFERENCES

- Bryers R W (1994) **“Utilisation of petroleum coke and petroleum coke/coal blends as a means of steam raising”**. In: Coal blending and switching of low-sulfur western coals, Snowbird, UT, USA, 26 Sept-1 Oct 1993. New York, NY, USA, American Society of Mechanical Engineers, pp 185-206 (1994)
- CoalTrans International (2000a) **“Petcoke: a threat to coal”**. CoalTrans International; 24-25 (Mar/Apr 2000).
- DOE, Fluidized-Bed Combustion: An R&D Success Story (U.S. Department of Energy, Washington, D.C.), www.fossil.energy.gov/programs/powersystems/combustion/fluidizedbed_success.shtml (accessed September 17, 2003).
- Dymond R (1998) **“The emerging petcoke market. World Coal”**; 7 (12); 18-23 (Dec 1998).
- Elliot, M. A. (editor), **“Chemistry of Coal Utilization, Secondary”** Suppl. Vol. (John Wiley & Sons, New York, 1981).
- E.J.Anthony, R.E.Talbot, L.Jia, and D.L.Granatstein **“Agglomeration and Fouling in three Industrial Petroleum Coke - Fired CFBC Boilers Due to Carbonation and Sulfation”**
- Fan, Zhen , Song Wu, Andrew H. Setzer **“Ammonia – free NO_x control system”** Foster Wheeler North America Corp. June 2006
- Fernando R (2001) **“The use of petroleum coke in coal-fired plant”** CCC/55, London, UK, IEA Coal Research, 42 pp (Nov 2001).
- Fiveland W A, Wessel R A (1991) **“A model for predicting formation and reduction of NO_x in three-dimensional furnaces burning pulverised fuel”**. Jnl Institute Energy; 64; 41-54 (Mar 1991).
- Gaglia, B. N. and A. Hall, **“Comparison of Bubbling and Circulating Fluidized-Bed Industrial Steam Generation”**, in Proc. of the International Conference on Fluidized-Bed Combustion, p. 18 (May 3–7, 1987).
- Hesselmann G (1997b) **“Coal-over-coal reburn testing, modelling and plant feasibility”**. COAL R 1 41, Harwell, UK, Energy Technology Support Unit, 55 pp (1997).
- <http://www.coqueverde.com.br>.
- Moss **“Fixed sulfur petroleum coke fuel and method for its production”** Dec 1972, Aug, 1980.
- R. W. Voyles & Don Zierold, **“Petroleum Coke firing in a Circulating fluidized bed Boiler”**, 12th International Conference on Fluidized bed combustion, San Diego, CA USA, May 9 – 13, 1993.
- Salvador, 2005, and Swain, 2003 **“Progress of petroleum coke combusting in circulating fluidized bed boilers—A review and future”** .
- Stephan B, Yee B H, Rosenquist W A (1996) **“Petroleum coke as a viable alternative fuel”**. In: Power- Gen International 96, Orlando, FL, USA, 4-6 Dec 1996. pp 259-267 (1996).

U.S. Department of Energy, “**Notice of Intent to Prepare An Environmental Impact Statement and Notice of Floodplain and Wetlands Involvement for the Proposed Jacksonville Electric Authority (JEA) Circulating Fluidized Bed (CFB) Combustor Project**”, October 14, 1997.

US Department of Energy (2000) “**Clean Coal Technology Demonstration program -program update as of September 1999**”. DOE/FE-0415, Springfield, VA, USA, NTIS (Apr 2000).

Zeldovich Y B (1946) “**The oxidation of nitrogen in combustion and explosions**”. Acta Physicochem, USSR; 21; 577-628 (1946).