

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 and content sulfur of 1-8%. The petcoke production increase in the last years, due to the increasing demand for heavy oil processing. Petcoke is considered a fuel interesting because generally cheaper than coal. The higher levels of sulphur in petroleum coke result in higher SO_x pollutant emissions, is one of the reasons the petcoke is burned generally, in fluidized bed combustion (FBC). Fluidized bed combustion has emerged as an environmentally attractive method for burning a wide variety of fuels inclusive of petroleum coke. The FBC is considered to be clean technology able to reduce NO_x and SO_x emissions in lower operating temperature between (850-900°C) and this system is divided into two major subgroups - Bubbling and Circulating fluidized bed combustion. The fluidized bed combustion systems offers many advantages, flexibility fuel, low temperatures and high combustion efficiency. These advantages include, low NO_x emissions, and the control of SO_x pollutant emissions represent an increasing of the potential market for the petroleum coke. This paper describes the fluidized bed process, 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 produced through the thermal decomposition of heavy petroleum process. Composed mainly of carbon and contains high levels of sulphur and heavy metals such as vanadium and nickel. The price varies depending on the volumes produced and worldwide demand. The world production of petcoke grew by 50% between 1987 and 1998 and reached 50 Mt in 1999 and is possible to reach 100 Mt by 2010. The USA is the world's largest producer of petroleum coke, producing three-quarters of the world supplies (Fernando, 2001). The main uses of petcoke are as an energy source for power generation, cement production, iron and steel production. Fluidized bed combustion, concept was used around 1940 in the chemical industry to promote catalytic reactions. In the 1950, the pioneering work on coal-fired fluidized-bed combustion was begun in Great Britain, particularly by the National Coal Board (Elliot et al, 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 850-900°C (DOE, 2003). Fluidized bed combustion is an emerging technology for the combustion of fossil and other fuels and is attractive because this system have several advantages than others conventional combustion systems: flexibility fuel, low NO_x and SO_x pollutants emissions, low combustion temperature. The Table 1 shown the world production of petroleum coke.

Table 1: World production of petroleum coke

Regions	% Petroleum coke
North America	69.5
South America	9.1
Europe	8.5
Asian	6.9
Ex-Urss	5.0
Africa	0.5
Oceania	0.5

Source: Dynamics, (2004)

2. CHARACTERISTIC OF THE PETROLEUM COKE (PETCOKE)

The petroleum coke is a solid produced material resulting from high temperature treatment of petroleum fractions, and is composite of carbonaceous material and contains some hydrocarbons. Depending on the process of production, there are three types of petroleum coke: delayed, fluid coke and flexi-coking; all three types of petcoke have higher calorific values than coal and contain less volatile matter and ash.

- Delayed coking is the most widely used process, accounting for some 93% of world production and has lower ash content and a higher volatile content than fluid coke or flexicoke,
- 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.

The petcoke can be categorized generally for green coke or coke calcined. Calcined coke is produced from delayed process at temperatures up to 1200°C. Petroleum coke and calcined coke are composed of elemental carbon but the difference between them is the concentration of residual hydrocarbon. Calcined coke content less hydrocarbon, higher elemental carbon and generally less sulphur and petroleum coke content high residual hydrocarbon (American Petroleum Institute, 2000). The Table 2 shown one type of the petroleum coke constituents.

Table 2: Constituents of petroleum coke

Items	Petroleum coke
C%	87.9
%H	3.51
O%	1.1
S%	7.08
N%	1.51
VM%	10.09
Ash%	0.38
HHV [kJ/kg]	34350

Source: Salvador et al. (2005)

They have different physical and chemical properties, higher calorific values than coal and contain less volatile matter also; all three are in converting heavy crude fractions and concentrating the contaminants in the coke (Bryers, 1994; Dymond, 1998).

3. COMBUSTION OF PETROLEUM COKE AND COAL

Fluidized bed combustion can burn coal with high efficiency and within acceptable level of emission pollutants. During petroleum coke combustion with a high sulphur-content, fluidized beds have the ability to capture SO₂ in situ if calcitic limestone is added. The reaction of these additives with fuel-S to form sulphates is known as the sulphation process (Anthony et al, 2001). Generally petroleum coke is blended with coal in proportion suitable to meet sulphur emissions compliance. Petcoke is a fuel, which has low volatile fuels and poor ignition. So it may be to burn with a substantial proportion of bituminous coal, it is possible to burn 100% petcoke, but it will be necessary to do so in furnaces that are designed for low volatile fuels. In many cases, the petroleum coke can be blended with coal and there is no there is no interaction between coal and petroleum coke particles. The coal burn independently of the petcoke and the petcoke react when the own ignition temperature is achieved (Voyles et al, 1993). In the FBC the stability of calcium sulfate (CaSO₄) during in situ sulfur dioxide capture with limestone calcium carbonate (CaCO₃) at temperature (850-950°C) and atmospheric pressure. Under pressurized conditions (PFBC), an additional aspect is direct conversion of calcium carbonate CaCO₃, without the intermediate calcium oxide (CaO) due to the partial pressure of carbon dioxide CO.

4. 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 NO_x production, and removal SO_x. The temperature in FBC is lower (850-900°C) than for pulverized-coal combustion, and efficient combustion is achieved by the relatively long residence time of the fuel in the bed. The size and density of the particles determine the minimum velocity required to fluidize the bed FBC systems are divided into two major groups, atmospheric (AFBC), operating near of the ambient pressures and pressurized (PFBC), operating at elevated pressures. The two principal types of atmospheric (FBCs) are bubbling bed

(BFBC) and circulating bed (CFBC). The feature that varies between these two types is the fluidization velocity but, both use high-temperature cyclones to capture the solid fuel and bed material for return to the primary combustion chamber. The Table 3 shown the comparison between petroleum coke and coal.

Table 3: Petroleum coke and coal comparison

	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

Source: Stephan et al, (1996)

- In (BFBC), the fluidization velocity is relatively low in order to minimize solids carryover. The bubbling fluidized bed doesn't have as great an ability to absorb sulphur dioxide (SO₂) and is used to burn lower quality fuels with high volatile matter and small plants. The Figure 1 shows the diagram of the bubbling fluidized bed combustion (BFBC). The Figure 1 shown bubbling fluidized combustion.

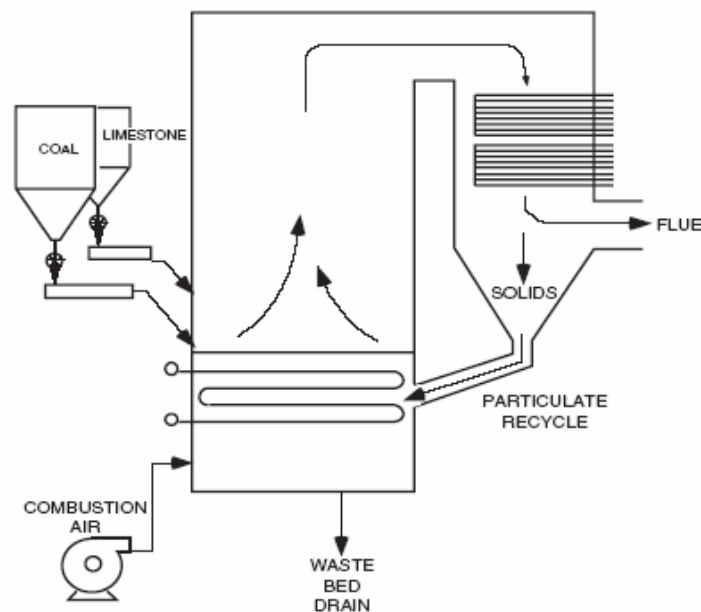


Figure 1: Bubbling fluidized-bed combustion (Gaglia et al, 1987)

- In (CFBC), employ high fluidization velocities for promote the carryover or circulation of the solids. The circulating fluidized bed maintains a continuous, high-volume recycle rate, which increases the residence time compared to the bubbling bed. Because of this feature, (CFBC) often achieve higher combustion efficiencies and better sorbent utilization than bubbling bed units. This system can burn with high efficiency including low-grade fuels even fuels that cannot be burn in conventional (PC) boilers. (CFBC) has as great an ability to absorb sulphur dioxide and reduce overall emissions, also, is viable for power generation and used for much larger plant.

Circulating fluidized bed plants are particularly suited for firing petroleum cokes as the long residence time promotes high burnout. Furthermore, the low volatile-matter content of the petcoke is compensated by the substantial amount of hot solids within the boiler, which provides a constant source of ignition and allows the system to operate efficiently over a wide load range. The Figure 2 shows the diagram of the circulating fluidized bed combustion.

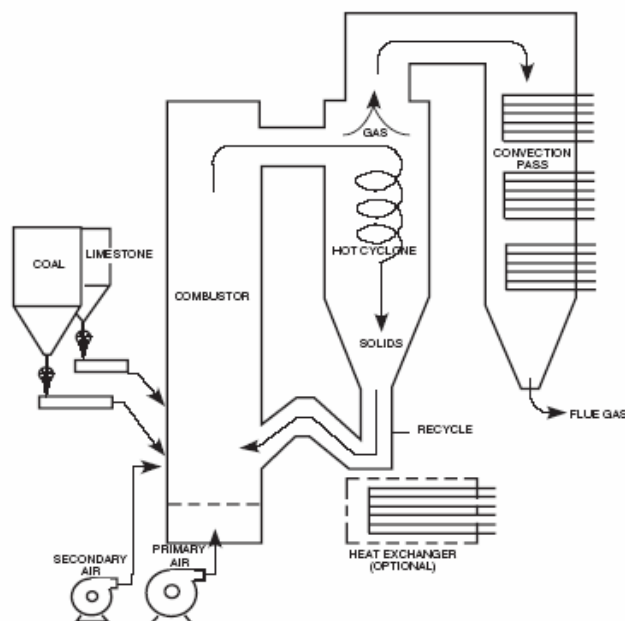


Figure 2: Circulating fluidized-bed combustion (Gaglia et al, 1987)

5. CONTROL OF THE POLLUTANTS EMISSIONS

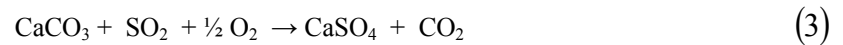
Control techniques for criteria pollutants emissions during the combustion may be classified into three categories: fuel treatment or substitution, combustion modification, and post-combustion control. Fuel treatment primarily reduces SO_2 and includes, fuel substitution involves burning a cleaner fuel. Combustion modification includes any physical or operational change in the furnace or boiler. Post-combustion control employs a device after the combustion of the fuel and is applied to control emissions of SO_2 , and NO_x combustion. Pollutants emissions depend on the rank and composition of the fuel, the type and size of the boiler, burning conditions, load, type of control technologies, and the level of equipment maintenance. The major pollutants of concern petroleum coke combustion are, sulfur oxides (SO_x), and nitrogen oxides (NO_x). Fluidized bed combustion (FBC) system is designed to burn solid fuels while controlling many of these emissions.

5.1 Sulphur oxides controls (SO_2)

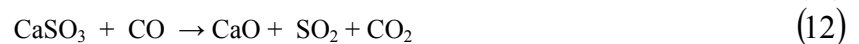
Gaseous SO_x from petroleum coke combustion are primarily sulfur dioxide SO_2 , with a much lower quantity of sulfur trioxide SO_3 and gaseous sulfates. These compounds form as the organic and pyretic sulfur in the petcoke are oxidized during the combustion process. Several techniques are used to reduce SO_x emissions from petroleum coke combustion. Flue gas desulphurization FGD techniques can remove SO_2 formed during combustion by using an alkaline reagent to absorb SO_2 in the flue gas. The lime and limestone wet scrubbing process uses the limestone to absorb SO_2 in a wet scrubber. Control efficiencies in excess of 91% for lime and 94% for limestone. When firing petroleum cokes, the high sulphur content necessitates the addition of large quantities of limestone, and this is adequate to maintain the bed. One of the principal advantages of FBC system is the possibility to feed additives such as limestone to the combustor where they act as sorbents and augment the fixing of sulphur. The SO_2 emissions resulting from the high sulphur levels in petroleum cokes are captured by limestone injected into the furnace capture rates of over 95%. The limestone-injection system is relatively simple, low-cost and easy to control compared to wet or dry FGD scrubbers. CFBs firing petcoke require Ca/S ratios between 3 and 3.5 for 98% sulphur removal, with the resulting ash containing a large proportion of calcium (Ericson et al, 2000). During the fluidized bed combustion process the retention of sulfur dioxide released by particles of sorbent material (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 sulphate



The Equation (9) and (10)



5.2 Nitrogen oxides controls (NO_x)

Combustion of fossil fuel generates oxides of nitrogen and the most important forms of air pollutants are NO, NO₂, 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 et al, 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):



Several techniques are used to reduce NO_x emissions during the combustion - combustion controls and post combustion controls. Combustion control methods are low NO_x burners (LNBs) reduce NO_x by suppressing NO_x formation during the combustion process and this technique is the most used method of controlling NO_x formation in all types of boilers.

LNBs limit NO_x formation by controlling the stoichiometric and temperature profiles of the combustion process in each burner zone.

The features of an LNB are:

- Reduction of the oxygen level in the combustion zone and to limit the fuel NO_x formation,
- Reduction of the flame temperature that limits thermal NO_x formation,
- Reduction of the residence time at peak temperature that also limits thermal NO_x formation.

Post combustion methods are: Selective non catalytic reduction (SNCR) and selective catalytic reduction (SCR)

- (SNCR) is a technique that involves injecting ammonia NH₃; the ammonia reacts with NO_x in the flue gas to produce nitrogen and water. The effectiveness of SNCR depends on the temperature where reagents are injected.

- (SCR) is a technique that involves injecting NH₃ into the flue gas in the presence of a catalyst to reduce NOx to nitrogen and then water.

Combustion and post-combustion controls can be used separately or combined to achieve the greater NOx reduction in the fluidized bed combustors (Ericson et al, 2000).

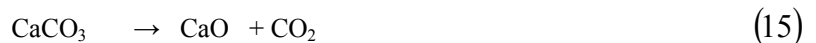
6. CALCULUS OF THE SULPHUR RETENTION (SO₂)

Given:

Operating conditions	
mC: mass flow rate	4.8 (kg/s)
Ca/S: mole ratio (sorbent only)	2
CaO: percent calcium	26 %
M _{CaCO₃} : molar mass	100 (kg/kmol)
M _{SO₃} : molar mass	80 (kg/kmol)
M _{CaO} : molar mass	56 (kg/kmol)
M _S : molar mass	32 (kg/kmol)
T _f : operating temperature in (FBC)	1123 (K)
T _g : variation of operating temperature (FBC)	825 (K)
T ₀ : inicial temperature	298 (K)
R: ideal gás constant	8.314 (KJ/kmol.K)
HHV: heating value	34350 (KJ/kg)

Resolution

The sulphation reaction is given for:



6.1 The heat in boiler can to be determinate by the following equation

$$\Phi = mC.HHV \Rightarrow \Phi = 164880 \text{ (kJ/s)} \quad (17)$$

Where:

Φ is the outflow of limestone.

6.2 Calculus of flow rate of calcium necessary

$$mf = \frac{\frac{\Phi}{HHV} \cdot \left[\frac{\%S}{100} \cdot \frac{M_{\text{CaCO}_3}}{M_S \cdot (\text{Ca/S})} \right]}{100} \Rightarrow mf = 0.00531 \text{ (kg/s)} \quad (18)$$

Where:

mf is the mass flow rate of limestone.

6.3 -Calculus of the Gibbs free energy with using the following expression (Perry et al, 1982).

$$\Delta h_{CaCO_3} = 4.186 \int_{T_0}^{T_f} \left(19.68 + 0.01189T - \frac{307600}{T^2} \right) dT \quad (19)$$

$$\Delta s_{CaCO_3} = 4.186 \int_{T_0}^{T_f} \left(\frac{19.68 + 0.01189T - \frac{307600}{T^2}}{T} \right) dT \quad (20)$$

Where, Δh is the enthalpy variation and Δs the entropy variation.

The following Table 4 shown the different values of the reactions.

Table 4: Different values of enthalpy and entropy reactions

	CaCO ₃	CaO	CO ₂	O ₂
h_f (kJ/kmol)	-1207682.46	-635514.37	-393772.73	0
s_f (kJ/kmol.K)	88.760	39.775	213.778	29.375
Δh (kJ/kmol)	93969.39	45298.02	40416.39	0
Δs (kJ/kmol.K)	143.6	69.87	62.59	0

$$\begin{aligned} \Delta G &= (h_f CaO + h_f CO_2 - h_f CaCO_3) + (\Delta h CaO + \Delta h CO_2 - \Delta h CaCO_3) \\ &\quad - T_f [(s_f CaO + \Delta s CaO) + (s_f CO_2 + \Delta s CO_2) - (s_f CaCO_3 + \Delta s CaCO_3)] \\ \Delta G &= -2422.3 \text{ (kJ/kmol)} \end{aligned} \quad (21)$$

$\Delta G < 0$, is a negative value, which says that if each component were present at 1 atm at 298K, the reaction would proceed spontaneously to the right to produce more products.

Where, ΔG is the variation of the Gibbs free energy (KJ/kmol)

6.4 - Calculus of the equilibrium constant is given for:

$$K_{eq} = e^{\left(\frac{-\Delta G}{R \cdot T_f}\right)} \Rightarrow K_{eq} \cong 1.296 \quad (22)$$

Where, K_{eq} is the equilibrium constant.

The following Table 5 shown the equilibrium constant K_{eq} and the temperature T(K)

Table 5: The variable of temperature versus the equilibrium constant K_{eq} and $\ln K_{eq}$

Temperature (T) in Kelvin (K)	Equilibrium Constant K_{eq}	$\ln K_{eq}$ equilibrium values
298	1.001	$9.777 \cdot 10^{-4}$
373	1.001	$7.811 \cdot 10^{-4}$
473	1.001	$6.610 \cdot 10^{-4}$
573	1.001	$5.085 \cdot 10^{-4}$
673	1	$4.329 \cdot 10^{-4}$
773	1	$3.769 \cdot 10^{-4}$
873	1	$3.337 \cdot 10^{-4}$
973	1	$2.994 \cdot 10^{-4}$
1073	1	$2.715 \cdot 10^{-4}$
1123	1	$2.594 \cdot 10^{-4}$
1173	1	$2.428 \cdot 10^{-4}$

The following Figure 3 shown the variation of temperature CaCO₃ versus the equilibrium constant lnK_{eq}

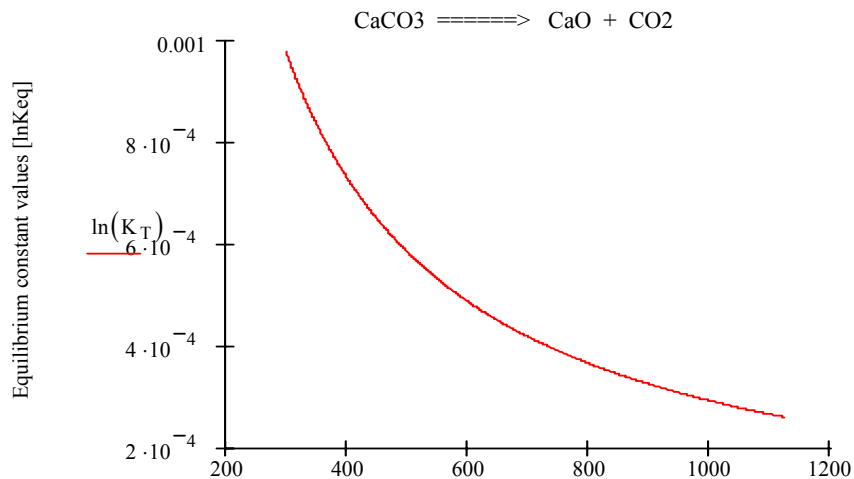


Figure 3: Variation of the temperature versus the equilibrium constant K_{eq}

6.5 - Calculus of the sulphation retention.

$$K_{eq} = 1.296 = \frac{\left[\left(\frac{0.56\lambda}{mf} \right)^{0.56} \times \left(\frac{0.44\lambda}{mf} \right)^{0.44} \right]}{\left(\frac{m_f - \lambda}{m_f} \right)} \Rightarrow \lambda = 0.00382 \quad (23)$$

where λ , is the value obtained using the MathCAD program. The sulphation expression is given for the following equation.

$$Y_{Sulphation} = \frac{\left[\lambda (M_{CaO} \times M_{CaCO_3} - M^2_{CaO}) \right]}{\left[\%CaO \times mf \times M_{SO_3} \times M_{CaCO_3} \right]} \times 100 \quad (24)$$

$$Y_{Sulphation} = \frac{\left[0.00382 \times (56 \times 100 - 3136) \right]}{\left[26 \times 0.00531 \times 80 \times 100 \right]} \times 100 \Rightarrow Y_{Sulphation} = 85,3\% \quad (25)$$

6.6 Calculus of the efficiency of sulphation retention

$$T_g = \Delta T = 1123 - 298 = 825 \text{ K} \quad (26)$$

$$Ca/S = 1 \quad RS = -1455.225 + 3.7055 \cdot T_g - 0.00225 \cdot (T_g)^2 \quad RS = 70.41\% \quad (27)$$

$$Ca/S = 2 \quad RS = -1680.8 + 4.294 \cdot T_g - 0.0026 \cdot (T_g)^2 \quad RS = 92.13\% \quad (28)$$

$$Ca/S = 3 \quad RS = -1257.9 + 3.292 \cdot T_g - 0.002 \cdot (T_g)^2 \quad RS = 96.75\% \quad (29)$$

Where, T_g is the operating temperature variation in the fluidized bed combustion, using for calculate the efficiency of sulphation retention.

According to the example (6.6), the average sulfur retention varies of 70.41% to 96.75% with a Ca/S ratio for petroleum coke and when the Ca/S ratios increase the sulfur retention increase also. The sulphur retention efficiency increase quickly with the increase in Ca/S.

7. ENVIRONMENTAL BENEFITS

Fluidized bed combustion 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, and high combustion efficiency.

8. CONCLUSION

Fluidized bed combustion (FBC) 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. The use of Ca/S ratio during the combustion process can be contributed of the sulphur retention in the fluidized bed. FBC is an excellent choice due to its fuel flexibility and lower operating and maintenance cost. 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).

9. REFERENCES

- American Petroleum Intitute, 2000, "Petroleum coke test plan", Petroleum HPV Testing Group, Consortium Registration #1100997, submitted to the USEPA (03/31/2000).
- Anthony, E. J. and Granatstein, D. L., 2001, "Sulfation Phenomena in Fluidized Bed Combustion Systems" progress in Energy and Combustion Sciences 27 (2): 215-236.
- 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).
- DOE, 2003, "Fluidized-Bed Combustion" An R&D Success Story (U.S. Department of Energy, Washington, D.C.), September 17, 2003).
- Dymond, R., 1998, "The emerging petcoke market. World Coal" 7 (12); pp 18-23 (Dec 1998).
- Dynamics, 2004 :Disponivel em <http://www.dynamicmecanica.com.br/industrias.html>. Acesso em (25 Nov, 2004)
- Elliot, M. A. (editor),1981 "Chemistry of Coal Utilization, Secondary" Suppl. Vol. (John Wiley & Sons, New York, (1981).
- Ericson A, and Mohn N, 2000 "The role of solid fuel in US power generation":meeting environmental and economic hurdles in a competitive power market. Paper presented at: Electric Power 2000, Cincinnati, OH, USA, 12 pp 4-6 Apr 2000.
- Fan, Z. , Song .W, 2006 "Ammonia -free Nox 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 and 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, 1987 "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).
- J.M.Commandre and S.Salvador 2005, "Lack of correlation between the properties of a petroleum coke and its behavior during combustion", Fuel Processing Technology, 86, pp.795-808.
- M. Hartman and R.W. Coughlin, 1976 "Reaction of sulfur dioxide with limestone and the grain model", AICHE J. 22 (3) 490-498 (1976).
- Perry, R.H. and Chilton.C.H, 1982, "Chemical Engineers Handbook" McGraw-Hill International Book Company, Fith Edition, International Student Edition.
- Stephan. B, and Rosenquist W. A ,1996 "Petroleum coke as a viable alternative fuel". In: Power-Gen International

- 96, Orlando, FL, USA, pp 259-267 (4-6 Dec 1996).
- 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).
- Voyles, R.W and Zierold. D, 1993 "Petroleum Coke firing in a Circulating fluidized bed boiler", 12th International Conference on Fluidized bed combustion, San Diego, CA USA, (May 9 -13, 1993)
- Zeldovich, Y. B ,1946 "The oxidation of nitrogen in combustion and explosions".Acta Physicochem, USSR; 21; 577-628 (1946).