Rate-based Simulation of Coke Calcination in Rotary Kilns

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Abstract: This paper presents the simulation of the green petroleum coke calcining processes using the simulation program ASPEN HYSYS. The results are validated using actual industrial data. The present study provides a detailed description of the rate-based simulation. It considers the rate of physical and chemical phenomena of interest: the rate of moisture removal, the rate of volatile matter release and combustion, and the rate of coke dust and sulfur combustion. Data supplied by a local coke calcining kiln in operation are used to validate the simulation results. It is found that the rate-based simulation can be implemented as a useful tool to predict the operating conditions needed to control the content of undesirable impurities in the calcined petroleum coke, namely, sulfur, volatile matter and moisture contents. Except for the metal content, the simulation shows that it is possible for the kiln operator to process any type of green coke for varying sulfur, volatile matter and water contents by adjusting the amount of tertiary air and/or fuel.

1 INTRODUCTION

Aluminum industry anodes demand high quality standard of calcined petroleum coke (CPC). It requires a coke with no moisture, no volatile matter and low sulfur contents with an appropriate crystalline structure. This is achieved through calcination processes. It is accomplished by gradual heating of the green coke (GC) at ambient temperature to a temperature of around 1390°C in a rotary kiln (calciner). The kiln is operated as a counter-flow heat exchanger as described by Elkanzi (Elkanzi, 2007).

The determination of the calciner operation conditions are based on the following specifications of the GC: the moisture, the sulfur, the volatile matter (VM), and the metal contents. If any of these are not within the specified CPC requirements, then the operating conditions of the calciner should be adjusted in order to meet the allowable limit. However, if the problem in the GC is related to the metal content, then blending of different GCs is necessary to meet the desired conditions because metals cannot be removed by the calcination processes.

Elkanzi (Elkanzi, 2007) has reviewed different mathematical models which have been developed to describe petroleum coke calcination processes in rotary kilns. Some previous simulators were mainly written programs to solve the sets of simultaneous differential equations representing: the material balances, the energy balances, and the chemical reactions along the kiln (Li & Friday, 1974; Perron et al., 1990; Perron et al., 1992; Bui et al., 1993; Martins et al., 2001).

In a previous publication (Elkanzi, 2007), the rotary coke calcining kiln processes were simulated using a commercial simulator. The reactions were simulated as conversion reactions and the values of the conversions were obtained from a real kiln data.

The objective of this study is to simulate the rotary kiln processes based on the rate of these processes. The rate-based simulation would improve the prediction of the kiln operating conditions that control the contents of undesirable impurities in the calcined coke. The commercial software ASPEN HYSYS was used for this purpose and the processes were assumed to take place in mixed reactors in series along the rotary kiln.

2 RATE OF CALCINATION PROCESSES

The calcination processes are visualized to take place in three zones inside the kiln, as illustrated in Figure 1. In the moisture release zone, the water is removed from the coke at temperatures up to 400°C,

while the volatile matter (VOC) is driven off the coke between 400 and 600 °C. Then, the volatile matter is combusted between 600 and 1000 °C in the VOC release and combustion zone. Finally, the fuel is combusted, the coke de-sulfurized and the carbon oxidized in the temperature range from 1250 to 1400°C in the fuel combustion and calcined coke zone. All zones are simulated as continuous stirred tank reactors.

2.1 Moisture Release Rate

The water in the pores of the coke is heated by the counter flow of the flue gases in the kiln and evaporated. The evaporation reaction may be represented by:

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \tag{1}$$

However, the use of kinetic reaction in the HYSYS requires that either water liquid or water vapour to be represented by a hypothetical compound having the same properties as that of water.

The water release rate was described as a first order reaction (Lyons, et al, 1962) and given by:

$$R_w = k_w X_w \left(\frac{X_c G_c}{MW u_b A} \right) e^{(-E/RT)} \tag{2}$$

Where k_w is a constant equals to 2.549×10^7 s^{-1} and E is the release energy of about 4.1942×10^4 J/mol.

2.2 VOC Release Rates

The VOCs entrained in the pores of the coke are heated by the counter flow of the flue gases in the kiln and evolve into the gas phase. De-sorption and

evaporation "reactions" may be represented by:

$$CH_{4(ad)} \rightarrow CH_{4(g)} \tag{3}$$

$$H_{2(ad)} \rightarrow H_{2(g)} \tag{4}$$

$$C_{18}H_{12(l)} \rightarrow C_{18}H_{12(g)} \tag{5}$$
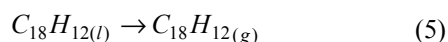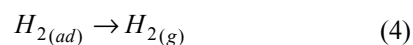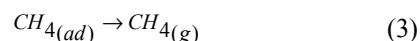
Hypothetical compounds were introduced with the same properties as that of the real VOCs. The rate of release of VOCs from the bed to the vapour phase was obtained from the experimental data of Dernedde et al (Dernedde, et al, 1986 and reported by Martins, et al, 2001) and is described by the following empirical correlation:

$$R_v = k_v \left(\frac{X_c G_c}{MW_v u_b A} \right) \frac{X_{v0}}{(X_c X_{v0})^n} (X_v)^n e^{\frac{-E}{RT}} \tag{6}$$

The values of the constants in Eq. (6) are given in Table 1.

Table1: Empirical constants for evaluating VOC release rates (Dernedde, et al., 1986).

VOC	k_v(s^{-1})	E(J mol^{-1})	n
H$_2$	9.17×10^1	4.37×10^4	1.5
CH$_4$	1.49×10^6	1.75×10^5	2.0
C$_{18}$H$_{12}$	1.09×10^{-1}	1.25×10^5	1.5

2.3 Combustion of VOC Rates

The combustion of VOCs was simulated by kinetic expressions in HYSYS. The VOCs released from the coke bed are oxidized by oxygen in the hot gases and would combust depending on the amount of
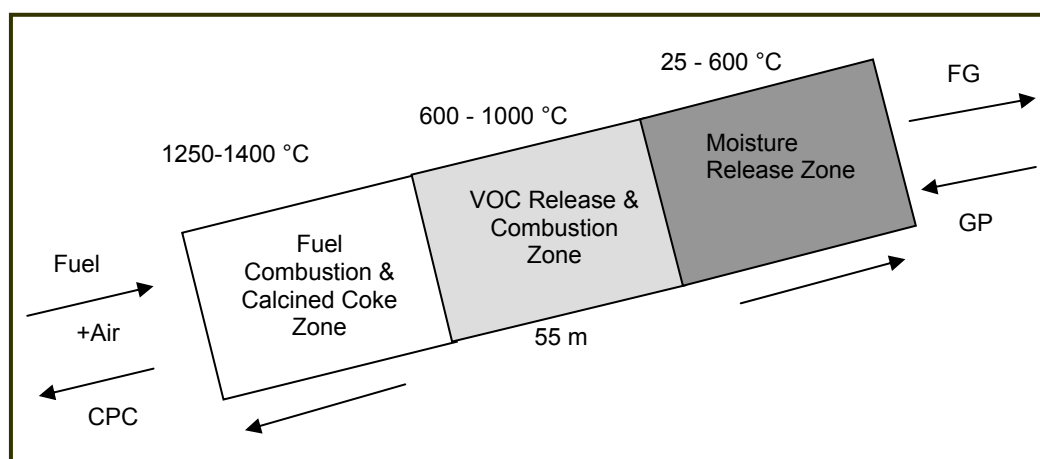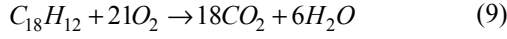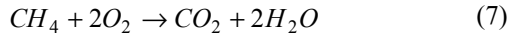

Figure 1: Calcining Processes Zones.

tertiary air entering this zone. The reactions may be represented by:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (7)$$

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (8)$$

$$C_{18}H_{12} + 21O_2 \rightarrow 18CO_2 + 6H_2O \qquad (9)$$

The rates of combustion of methane and hydrogen as released from the bed to the gas phase were obtained from the experimental data of Srinivasan (Srinivasan, et al., 1998) as:

$$R_{CH_4} = 7 \times 10^{11} \left(y_{CH_4}\right)^{-0.5} \left(y_{o_2}\right)^{1.5} e^{\frac{-30196}{T_g}} \qquad (10)$$

$$R_{H_2} = 2.45 \times 10^{11} [H_2]^{0.85} [O_2]^{1.42} e^{-\frac{20634}{T_g}} \qquad (11)$$

The rate of combustion of tar can be described by the empirical equation (Dernedde, et al, 1986; Howard, et al, 1973):

$$R_{ch} = k_{ch} [ch][O_2]^{0.5} [H_2O]^{0.5} e^{\frac{-E}{RT}} \qquad (12)$$

The values of the constants were as shown in Table 2.

Table 2: Constants of the combustion of Tar rate expression.

k_{ch} (cm^3 / mole-s)	E (J/ mole)	Reference
1.8×10^{13}	1.32×10^5	Dernedde, *et al.*, 1986.
1.3×10^{14}	1.25×10^5	Howard, et al., 1973.

2.4 Desulfurization and Carbon Oxidation Rates

The de-sulfurization and carbon dust oxidation reactions were simulated as two reactors. Oxygen from tertiary air reacts with the sulfur and the carbon dust to produce SO_2, CO_2 and CO according to the following reactions:

$$C + O_2 \rightarrow CO_2 \qquad (13)$$

$$C + CO_2 \rightarrow 2CO \qquad (14)$$

$$S + O_2 \rightarrow SO_2 \qquad (15)$$

The rates of entrained coke fines burn-up were reported in (Li, and Friday, 1974) and described by

the following equations:

$$R_{CO_2} = 6.84 \times 10^{13} [O_2] e^{\frac{-30800}{T_g}} \left(\frac{S_f \Delta L}{V}\right) \qquad (16)$$

$$R_{CO} = \frac{\left[1.08 \times 10^{12} e^{\frac{-62180}{T_g}} \left(P_{CO_2}\right)^{0.5} \left(\frac{S_f \Delta L}{V}\right)\right]}{\left[12.01 X \left(1 + \frac{P_{co}}{2887 e^{\left(-24624/T_g\right)}}\right)\right]} \qquad (17)$$

The rate of carbon monoxide can be simplified by neglecting the 1 in the dominator since the term $\{P_{CO} / (2887 \ e \ (-24624/Tg))\}$ is much greater than one, and hence equation (17) becomes:

$$R_{CO} = 2.62 \times 10^{14} \frac{\left(P_{CO_2}\right)^{0.5}}{\left(P_{CO}\right)^{1.0}} e^{\frac{-86804}{T_g}} \left(\frac{S_f \Delta L}{V}\right) \qquad (18)$$

The rate of oxidation of sulfur was reported (Lu, et al., 2004) and is described by:

$$R_s = 1.1 \times 10^{-11} e^{\frac{-4360}{T}} C_{SV} \qquad (19)$$

Since the units of Csv are in molecule/ cm^3, multiplying by Avogadro's number yields:

$$R_s = 6.6 \times 10^{12} e^{\frac{-4360}{T}} C_{SV} \qquad (20)$$

2.5 Fuel Combustion Rate

The fuel used in the kiln was natural gas and hence the rate of the fuel combustion is as given by equation (10). The results of the kinetic equation (10) were compared with normal conversion reaction and showed great deal of agreement.

3 HYSYS SIMULATION

The HYSYS simulation flow sheet of the coke calcinations processes is depicted in Figure 2 which shows the three calcination zones. The simulation was based on actual GC industrial data (ALBA 2010). Process simulation assumes good mixing inside the kiln; which is accomplished by rotating the kiln at an inclined position as well as by the presence of tumblers. Moreover, it was assumed that the reactions take place effectively in the gas phase.

As a result of these assumptions, the calcination

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processes were simulated to take place inside adiabatic continuous stirred-tank reactors. It is to be noted that there is no sharp demarcation between these reactors. In fact part of the VOCs is released in the moisture release "reactor" and a very little amount of VOCs is combusted in the VOC release "reactor" since the release zone is oxygen deficient.

The simulation procedure is similar to the one used before (Author, 207) featuring the concept of using "recycle" to simulate counter-current mass flow that is not allowed by HYSYS. The combustion of fuel (CH_4) is simulated by fuel combustion reactor, FCR, which is a conversion reactor. The flue gas from the burner is mixed with the outputs from the VOC combustion reactor (VOCCR) and enters the carbon combustion reactor (CCR). The CCR is simulated using equations (16) and (18), for which the carbon dust was simulated by hypothetical "carbons" so as not to confuse them with the rest of the coke carbon that was assumed not to react in the solid phase. The output from CCR enters the desulfurization reactor (DSR) that was simulated using equation (20). The solid output from DSR is the calcined coke product. The gas output is the "recycle stream" which is split into three streams: the first is mixed with the fresh GPC and enters the moisture release reactor (MRR, simulated using equation (2), for which the product water was simulated by a hypothetical water component), the second is sent to the VOC release reactor (VOCRR), and the third is mixed with the gas output from the MRR to form the flue gas that is sent to the incinerator. It may be noted here that the split ratio of the recycle stream is determined by trial and error in order for the temperature in MRR, VOCRR and VOCCR to fall within the operating range shown in Figure 1. Since it is assumed that the VOCs and

sulfur are not released in the MRR, they were mixed and sent to the VOC release reactor (VOCRR) that is simulated using equation (6) and the data of Table1. The components in the release equations (3), (4) and (5) were simulated by hypothetical components. The output from VOCRR is mixed with tertiary air and sent to the VOCCR that was simulated using equations (10), (11), (12), and the data in Table 2.

4 RESULTS AND DISCUSSION

Coke kiln industrial data (ALBA 2010) are compared with the simulation results using the same input feed and conditions. At this initial stage of work, the comparison is made between the compositions, flow rates, the temperature of the CPC, and the flue gas streams. The simulation results are depicted in Table 3 with the industrial values. There is a good agreement between the simulation results and the industrial results deviation of 11%.

The comparison reveals that the prediction of sulfur in the CPC is exact (zero error). However, the zero sulfur is an over prediction since oxidation of sulfur as predicted by equation (20) is considered only in the vapor phase.

It was found that the predicted CPC temperature is less than the industrial value by 0.9 %. However, the CPC real density is a function of temperature (Ibrahim and Ali, 2004), and hence the underestimate of the CPC temperature will have very little effect on the results.

The simulated flue gas temperature was higher than the actual data by about 11%. This can be explained by looking into the composition of the
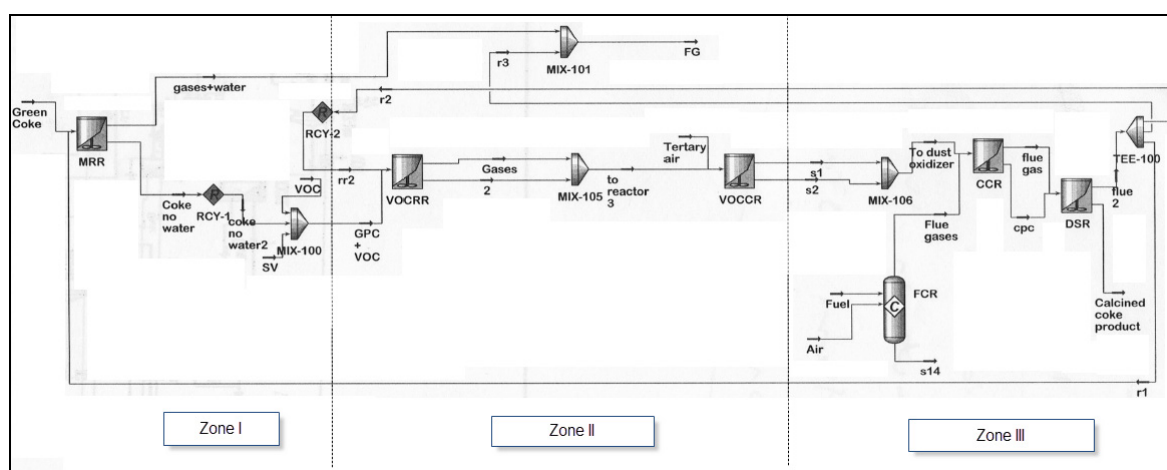

Figure 2: HYSYS Simulation of Kiln Processes.

Table 3: Simulation Results.

Stream	GPC		CPC		FG		Tertiary		Fuel		Fuel Air	
Condition	1	2	1	2	1	2	1	2	1	2	1	2
Temperature (K)	293	293	1663	1650	1373	1499	293	293	293	293	293	293
Pressure (kPa)	120	120	120	120	120	120	120	120	120	120	120	120
Flow Rate (kg/s)	9.7	9.762	7.44	7.27	20.60	20.62	14.0	14.0	0.276	0.276	4.77	4.77
Components Flow Rates (kg/s) C	7.925	7.925	-	-	0.24	-	-	-	-	-	-	-
C^*	0.0	0.062	-	-	-	-	-	-	-	-	-	-
CH_4	0.394	0.394	-	-	0.242	-	-	-	0.276	0.276	-	-
H_2	0.528	0.528	-	-	0.314	0.4	-	-	-	-	-	-
$C_{18}H_{12}$	0.134	0.134	-	-	0.072	-	-	-	-	-	-	-
H_2O	0.51	0.51	-	-	3.03	3.41	-	-	-	-	-	-
N_2	-	-	-	-	14.34	14.34	10.68	10.68	-	-	3.66	3.66
CO_2	-	-	-	-	1.84	2.24	-	-	-	-	-	-
CO	-	-	-	-	0.43	0.077	-	-	-	-	-	-
SO_2	-	-	-	-	0.060	0.069	-	-	-	-	-	-
S	0.211	0.211	0.169	-	0.0055	-	-	-	-	-	-	-
O_2	-	-	-	-	-	0.057	3.24	3.24	-	-	11.53	11.53
1 Industrial data , 2 this study , C* carbon dust												

flue gas where almost all volatile components and carbon dust were oxidized adding more heat than that of the industrial case. Moreover, the assumption of adiabatic operation would add to the overall rise in temperature.

5 CONCLUSIONS

This paper addressed the determination and adjustment of the green petroleum coke calcination in order to meet the allowable limits of the calcined coke specifications. The methodology is to simulate the processes that describe green petroleum coke calcination. The simulation was based on using physical and chemical reaction rate equations. The results of the simulation were compared with actual industrial rotary kiln data and there was a good agreement. The methodology of rate-based simulation described in this study may be used to predict coke calcining kilns performance regardless of the green coke composition. The sensitivity of the kiln performance to changes in green coke composition, fuel and tertiary air flow rates is left for future work. Further validations using industrial data are also necessary.

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APPENDIX

Nomenclature

A area per unit axial length, m.
C species molar concentration, $kgmol/m^3$
E activation energy, kj/kmol
G mass flow rate, kg/s
k rate constant, s^{-1}.
L axial distance along the kiln, m.
MW molecular mass, kg/kmol
P_i partial pressure of species i, kPa
R_i rate of reaction of species i, $kmol/m^3$. S
Sf total surface area of the coke fines/unit length of
the kiln, m.
T temperature, K.
u velocity, m/s.
V   volume of gas in the kiln, m^3.
X mass fraction, kg/kg.
y mole fraction, kmol/kmol.

Subscripts

b coke bed.
c coke or carbon
ch tar
g gas phase
l liquid phase
o   initial
voc volatile organic compound
v volatile
w water