9

Mass and Energy Balance

Heat balance calculations are usually carried out when developing new rotary kiln chemical processes or when improving old ones. No thermal process would work if too much heat is released or if there is a lack of sufficient thermal energy to drive the process, in other words, to maintain the reaction temperature. Heat balance can only be calculated with given mass balances as the boundary conditions, hence a quantitative description of the chemical processes on the basis of *physical or chemical thermodynamics* is required. While chemical thermodynamics establishes the feasibility of a particular reaction under certain reactor conditions, chemical kinetics determines the rate at which the reaction will proceed. Before we establish the global rotary kiln mass and energy balance, it is important to examine some fundamental concepts of thermodynamics that provide the pertinent definitions essential for the design of new rotary kiln bed processes.

9.1 Chemical Thermodynamics

Chemical processes are normally carried out at constant pressure (*isobaric*). Under isobaric conditions, the total enthalpy, or the total heat content of a chemical species consists of three thermodynamic properties (i) the heat of formation, (ii) sensible heat, and (iii) heat of transformation. When chemical elements react to form a compound,

a certain amount of heat is released to the environment in accordance with the First Law of Thermodynamics, which states that the internal energy, U, of a system changes as a result of the exchange of energy with the surroundings, in the form of heat, Q, or through some form of work, that is, $\Delta U = Q + \dot{W}$. Hence, consistent with energy conservation, the *heat of formation* of the reaction or for short *heat of reaction*, ΔH, is equal to the sum of the total enthalpies of the products minus the total enthalpies of the reactants as we saw in stoichiometric balances. The *sensible heat* is literally the heat that can be sensed because it is associated with temperature change, that is,

$$Q_s = \int_0^T C_p \mathrm{d}T \tag{9.1}$$

where C_p is the molar heat capacity of the species in $\mathrm{J \cdot mol^{-1} K^{-1}}$, that is, its specific heat times its molecular weight ($C_p M$). The heat of transformation is usually associated with phase change such as crystal transformation, melting, or evaporation and is expressed in $\mathrm{J \cdot mol^{-1}}$. For convenience, the total enthalpies of all chemical species are tabulated with respect to a reference temperature, T_0, at a standard pressure, p_0 which are usually taken to be 25°C (298.15 K) and 1 bar (0.9869 atm). Therefore, the enthalpy of a chemical species, i, might be expressed as (Themelis, 1995)

$$\Delta H_i = \Delta H_i^o + \int_{T_0}^T C_p \mathrm{d}T + \sum (\Delta H_{\mathrm{trans}}) \tag{9.2}$$

where ΔH_i^o is the total enthalpy of species at T_0. The last term in Equation 9.2 represents the heat that is absorbed or released in the phase transformations if any. For chemical compounds, the term ΔH_i^o is equal to the heat of formation of the compound at T_0, that is, $\Delta H_i^o = \Delta H_f^o$.

9.2 Gibbs Free Energy and Entropy

The Second Law of Thermodynamics, as was introduced by Clausius and Kelvin, is formulated on the basis of theoretical analyses of reversible cycles established by Carnot (Knacke et al., 1991). From the reversible Carnot cycle, it follows mathematically that the reversible exchange of heat, $\mathrm{d}Q_{\mathrm{rev}}$ between systems and surroundings, divided

by the absolute temperature T is a total differential dS, where S is the property of the state called entropy, that is,

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T} \tag{9.3}$$

The Second Law can therefore be stated as: The total entropy change in a system resulting from any real processes in the system is positive and approaches a limiting value of zero for any process that approaches reversibility (Themelis, 1995). The entropy of a reversible process is equal to the heat absorbed during the process, divided by the temperature at which the heat is absorbed (Equation 9.3). Reversibility denotes a process which is carried out under near-equilibrium conditions and therefore means that it is carried out most efficiently. Combining the First Law and the Second Law gives the expression

$$\mathrm{d}S = \frac{\mathrm{d}U + P\mathrm{d}V}{T} = \frac{\mathrm{d}H}{T} \tag{9.4a}$$

from which can be deduced that

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \tag{9.4b}$$

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T} \tag{9.4c}$$

$$S = S(U, V) \tag{9.4d}$$

With these expressions, the derivation from cyclic processes and reversible heat exchange could be abandoned in exchange for the state functions T, P, V, U, and S of the individual systems.

Similarly to the First Law, the total entropy of a chemical species, i, at its equilibrium state, temperature, T, and standard pressure, p_0, can be expressed as

$$\Delta S_i = \Delta S_i^{\mathrm{o}} + \int_{T_0}^{T} \frac{C_p dT}{T} + \sum\left(\frac{\Delta H_{\mathrm{trans}}}{T_{\mathrm{trans}}}\right) \tag{9.5}$$

where ΔS_i^{o} is the total entropy of the species at its equilibrium state and at T_0 (298.15 K) and standard pressure p_0 (1 bar or 1 atm). Equation (9.5) applies at absolute zero temperatures by setting $\Delta S_i^{\mathrm{o}} = 0$ and $T_0 = 0$. At 0 K, the entropy of all crystalline elements and compounds is

zero and for all other species, may be zero, that is, $\Delta S_{f,0} = 0$; a statement that defines the Third Law of Thermodynamics.

According to Gibbs, a phase is understood to be a chemically and physically homogeneous substance, irrespective of the amount and shape. Every phase has a limited region of existence with respect to composition, temperature, and pressure. Phases in equilibrium with each other are called coexisting phases. Single-phase systems are homogeneous phases while multi-phase systems are heterogeneous. Closed, homogeneous or heterogeneous equilibrium systems have maximum entropy that is a function of U and V (Equation 9.4). The Gibbs free energy of a species is a function of its enthalpy and entropy and is defined as:

$$G(T,P) = H - TS \tag{9.6}$$

G is a thermodynamic characteristic function that can be expressed in terms of its derivatives with respect to the corresponding independent variables. From the equilibrium requirement of maximum entropy follows the minimum Gibbs energy for chemical equilibrium, that is,

$$G = \min \text{ at constant } T,\ P \tag{9.7}$$

From the general definition of the Gibbs free energy, one can express the Gibbs free energy of a chemical species i at equilibrium in terms of its total enthalpy and total entropy at T, and standard pressure, p_0, that is,

$$\Delta G_i^o = \Delta H_i^o - T\Delta S_i^o \tag{9.8}$$

The heat capacities, enthalpies, entropies, and Gibbs free energies of chemical species at their equilibrium state and at standard temperature and pressure can be found in the public domain (e.g., Knacke et al., 1991). Some of these are presented in the Appendix. Usually, included in such tables are the dimensionless Planck's function B that allows a simple calculation of the equilibrium constant as

$$B_i^o = -G_i^o/RT \log 10 \tag{9.9}$$

$$\log K_r = \sum n_i^r B_i^o \tag{9.10}$$

where n_i are the stoichiometric mole fractions of the reaction (Knacke et al., 1991). A reaction will proceed at a given temperature when $\log K_r > 0$, similar to the situation that water boils when the temperature reaches 100°C. A useful tool for estimating chemical thermodynamic conditions of several processes is the HSC Chemical Reaction

and Equilibrium software (Outokumpu, 2002). Several example chemical equilibrium calculations using the HSC software can be found in Themelis (1995).

9.3 Global Heat and Material Balance

Thus far we have covered all the transport phenomena and transport processes that determine the conditions within the rotary kiln. These include bed material flow, fluid flow in the freeboard, combustion, and associated heat transfer that result in temperature distribution at any section of the kiln. With these, the extent of temperature-dependent chemical reactions involved in the pyroprocessing of minerals and materials can be established and from that, product quality can be estimated. While all the models covered thus far can provide details of the intrinsic behavior within the kiln, including whether the reactions will or will not proceed at the reactor temperatures, it is important to step outside and look at the kiln as a thermodynamic system that interacts with the atmosphere and, like all thermodynamic systems, determine the thermal efficiency. The basic approach to doing this is to consider the kiln as a furnace system composed of a control volume with well-defined spatial boundaries into which mass and energy enter at a certain rate and leave at another rate. It is important to keep track of material and energy crossing the boundaries by doing some accounting. The bookkeeping relation for keeping track is the mass and energy balance that is based on the steady-flow form of the First Law of Thermodynamics. If one mass flow rate exceeds the other, then mass is either accumulated or depleted. Also, if $\dot{Q}$ is the rate of heat flow into the furnace and $\dot{W}$ is the rate at which work is delivered to the surroundings, then the first law for conservation of energy requires that

$$\dot{Q} = \sum_{o} m_o h_o - \sum_{i} m_i h_i + \dot{W} = m_2 h_2 - m_1 h_1 + \dot{W} \tag{9.11}$$

where m and h are rates of mass and enthalpy crossing the system boundary. We know by now that rotary kilns are the equipment of choice when material processing requires high temperatures and long residence times. Because of these two important attributes, rotary kilns have also become the equipment of choice for waste destruction including hazardous waste fuels under the EPA's Resource Conservation Recovery Act (RCRA). Every kiln must therefore be permitted to

operate within certain operational limits so as to ensure that harmful pollutants, whether they be dust, metals, or any other chemical compounds, are not discharged into the atmosphere. A mass and energy balance must, therefore, be carried out for the operation to show, at a minimum, mass flow rates, temperatures, and pressures of all process input and output streams at each discrete unit operation within the overall process such as the rotary kiln and all auxiliary devices including coal mills, air pollution control devices, and so on. A mass and energy balance is also required to ensure that process variables do not exceed the design or permitted limits. Additionally, it is necessary to establish the thermal efficiency of the process so that necessary action can be taken to optimize fuel use and conserve energy.

9.4 Thermal Module for Chemically Reactive System

The problem of the mass and energy balance is addressed by considering the kiln as a combustion system in which fuel and oxidizer flow into a control volume and combustion products flow out. Without the details of all the transport models that have been discussed in the previous chapters, one should be able to relate the combustion products to the input mass flow rates and energies and to account for any mass or energy accumulation or destruction that might take place and how they do. The steady flow First Law Equation, Equation (9.11), may be written for the balance as

$$Q = H_p - H_r + \dot{W} \tag{9.12}$$

It is easy to envision that no shaft work is involved and that the work done on the surroundings is what transforms the raw material into usable material and which can be accounted for as energy of formation of the intended product. Therefore H includes chemical as well as thermal energy. The enthalpy H_p is the sum of the enthalpies of all product streams leaving the system and H_r is that for the entering reactant streams. The individual enthalpies may each be written as the product of the number of moles of the component in the reaction equation and the respective enthalpy per mole of the component. For example, for k number of products

$$H_p = n_1 h_1 + n_2 h_2 + \cdots + n_k h_k \text{ [kJ]} \tag{9.13}$$

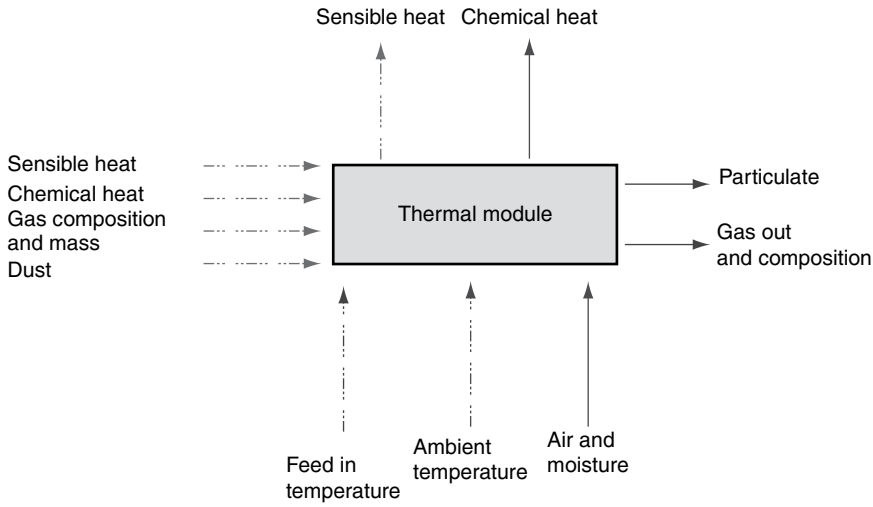


Figure 9.1 Thermal module for mass and energy balance calculations.

where n is the stoichiometric coefficient of the chemical equation and the enthalpies are on a per-mole basis. The enthalpy of any component of the reactants or products may be written as the sum of (i) its enthalpy of formation at the standard or reference temperature, T_0, and standard pressure, and (ii) its enthalpy difference between the actual state and the standard state of the components. Assuming pressure independence for now, the enthalpy for each component becomes

$$h(T) = h_f(T_0) + [h(T) - h(T_0)] \text{ [kJ/mol]} \tag{9.14}$$

where the term in the square brackets is the sensible enthalpy relative to the standard reference state. Hence the thermal module for the kiln component (Figure 9.1) can be balanced by balancing the streams and assigning enthalpies at the temperature state.

9.5 Mass Balance Inputs

As Figure 9.1 shows, a mass and energy balance requires knowledge of the conditions of the state; hence measurements of temperatures and pressures are required. For existing operation a complete audit is required to take measurements in addition to the data gathered by supervisory or monitoring instrumentation if any. The input to the

mass balance module may consist of mass quantities, chemical composition, and any other pertinent qualitative information. These include feed rate or product rate, fuel input, and measured or calculated product rates, and so on.

9.6 Chemical Compositions

The chemical compositions must include air composition in weight-%, fuel composition in weight-%, feed composition and moisture in weight-% dry feed basis, effective volatile content in weight-% on dry feed basis; for solid fuel combustion, volatile composition in weight-% dry feed basis, and product composition by specification on product weight basis.

9.7 Energy Balance Inputs

Energy inputs include (i) thermodynamic data such as specific heats, heats of combustion, enthalpies of phase change, densities, and so on, (ii) kinetic rate data, and (iii) their state, that is, input and output temperatures.

The mass and energy balance for a 15 by 300 ft (4.57 by 92 m) kiln for the dolomitic limestone calcination process is presented here. The procedure starts with information on the kiln dimensions and layout (Figure 9.2) followed by process audit, which provides the necessary

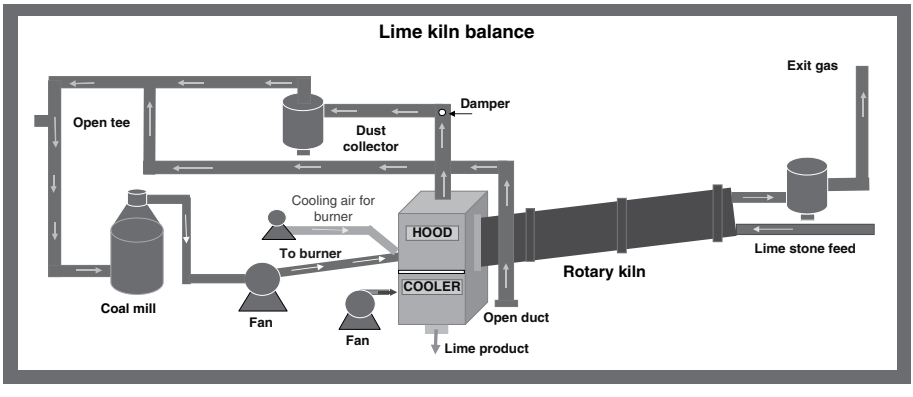


Figure 9.2 Process flow and component layout for dolomitic limestone calcination used for mass and energy balance calculation.

process data. The reference temperature used for enthalpy calculations is set at 25°C (298 K). Mass and energy balance is achieved from which the thermal efficiency and any other process efficiency indicators can be estimated.

9.8 Site Survey—Measured Variables

The tables that follow go through a site survey. Table 9.1 covers the ambient air to the cooler. Table 9.2 covers the cooling air to the burner. Table 9.3 covers the coal conveying air, and Tables 9.4 and 9.5 cover the limestone and the dust. Table 9.6 covers the properties of the natural gas input and the kiln exit gas. Table 9.7 covers the kiln dimensions and shell temperatures.

Table 9.1 Ambient Air to the Cooler*

	Measurement Number** (#)	Value (m/s)	Measurement Number (#)	Value (m/s)	Average Velocity (m/s)	Area (m^2)	Volume (m^3/s)
	1	8.45	14	9.00	8.73	0.237	2.069
	2	10.8	13	9.00	9.90	0.201	1.987
	3	14	12	12.00	13.00	0.164	2.134
	4	14.5	11	12.60	13.55	0.13	1.730
	5	15.5	10	14.60	15.05	0.091	1.373
	6	15.5	9	14.80	15.15	0.055	0.829
	7	14	8	14.00	14.00	0.018	0.255
Total	—	—	—	—	—	0.894	10.4

* Cooler fan outside diameter is 42 in. (1.07 m). Temperature is 78°F (25.6°C). Total area is 0.894 m^2. Note that the velocity of air into the fan (given in units of m/s) is usually measured at variable points on a radius. The numbered pair points (1 & 14, 2 & 13, etc.) are opposite sides of same radius. Density = 1.18 kg/m^3. Mass flow = 12.27 kg/s.
** Note that the distance between two measurement radial points is 0.08 m.

Table 9.2 Cooling Air to the Burner*

Fan	Side	Center	Volume (m^3/s)
Velocity (m/s)	11	9	–
Area (m^2)	0.02	0.01	–
Volume	0.2	0.1	0.3

* Internal diameter (ID) of fan is 0.1905 m (7.5 in.). Density = 1.19 kg/m^3. Flow rate = 0.36 kg/s.

Table 9.3 Coal Conveying Air*

Measurement Number	Value (m/s)	Area (m^2)	Volume (m^3/s)
1	6	0.456	2.736
2	6	0.355	2.128
3	5	0.253	1.267
4	3.5	0.152	0.532
5	2	0.051	0.101
Total		1.267	6.76

* Temperature = 149°C. Pipe outside diameter (OD) = 50 in. (1.270 m), total area 1.267 m^2. Distance between two measured points is 0.127 m. Density = 0.84 kg/m^3. Mass flow = 5.66 kg/s. Flows are split before entering the coal mill. The mixing air going to the coal mill $m_0 = 5.66$, with a temperature $T_0 = 278$°F. The air from the hood to the coal mill $m_1 = 0.28\%$, with a temperature $T_1 = 800$°F. The tempering air to the duct $m_2 = 0.72\%$, at a temperature $T_2 = 78$°F. The coal mill off-take $m_1 = 1.57$ kg/s through the hood duct. The tempering air $m_2 = 4.09$ kg/s ambient air.

Table 9.4 Limestone*

	HI-CAL					
	MW	Weight %	%C	Ca/Mg		
$CaCO_3$	100	95.61	11.47	42.96		
$MgCO_3$	84.3	1.7	0.24	–		
S	–	0.06568	–	–	**N_2**	1.52
H_2O	18	1.96	–	–	**O_2**	6.51
Inert	100	0.66	–	–	**C**	79.28
Total	–	100.00	–	–	**H**	5.02
	DOLOMITE				**H_2O**	3.00
	MW	Weight %	%C	Ca/Mg	**S**	0.080
$MgCO_3$	84.3	43.94	6.25	–	**Ash**	4.58
S	–	0.016	–	–		
H_2O	18	1.94	–	–		
Inert	100	1.46	–	–		
Total	–	99.99	–	–		

* The temperature of both the HI-CAL and the dolomite inputs was 78°C. For the HI-CAL, the %C in product was 0.08, and the flow rate was 47 short tons per hour (STPH) (11.48 kg/s). For the dolomite, the %C in product was 0.16 kg/s, and the flow rate was 52 STPH (13.1 kg/s).

Table 9.5 Dust and Coal Composition (Weight-%)

% dust	15								
Dust/product Temperature (°F)	1148								
		Composition (lab)	$CaCO_3$%	CaO%	$MgCO_3$%	MgO%	S%	Ash%	
		Weight-%	0.7	56.4	0.6	40	–	2.6	
Coal	170.5	Composition	N%	O%	C%	H%	H_2O%	S%	Ash%
Temperature (°F)		Weight-%	1.52	6.51	79.28	5.02	3.0	0.08	4.58

* The flow rate for coal is 6.7 STPH (6.08 metric ton/hr, or 1.69 kg/s).

Table 9.6 Natural Gas and Exit Gas Components*

Natural gas Composition	N_2%	O_2%	CO_2%	CH_4%	C_2H_6%	C_3H_8%	C_4H_{10}%	C_5H_{12}%	C_6H_{14}%
	1.35	0	1.25	94.5	2.5	0.011	0.03	0.04	0.02
Molecular weight (MW)	28	16	44	16	30	44	58	72	86
							MW of Natural Gas	=	16.9
Kiln exit gas Composition	N_2%	NO%	NO_2%	O_2%	CO%	CO_2%	H_2O%	SO_2%	
	–	–	–	0.5	–	–	–	–	

* Temperature = 1326°F, flow rate = 15,000 standard cubic feet per hour (424.75 m^3/hr, or 0.089 kg/s).

Table 9.7 Kiln Dimensions and Shell Temperatures*

Measured temperature on the surface of the kiln (°F)								
655	605	617	595	593	605	638	608	424
550	570	581	581	588	550	547	517	506
535	530	533	528	508	535	508	535	540
518	308	669	635	885	886	890	774	810
668	495	428	435	524	700	640	786	675
763	766	766	739	742	735	712	660	708
635								
Measured temperature on the surface of the kiln (°C)								
346	318	325	313	312	318	337	320	218
288	299	305	305	309	288	286	269	263
279	277	278	276	264	279	264	279	282
270	353	354	335	474	474	477	412	432
353	257	220	224	273	371	338	419	357
406	408	408	393	394	391	378	349	376
335								

* Kiln diameter, 15 ft (4.57 m); kiln length = 300 ft (92 m).
Note: Measurements run left to right and top to bottom.

9.9 Shell Heat Loss Calculations

Table 9.8 covers the calculated heat loss from the shell.

9.10 Calcination Module Calculation

Table 9.9 covers the calcinations module calculation, including heat of formation, heat of calcinations, and heat of water evaporation.

9.11 Combustion

Table 9.10 covers the heat of combustion reactions. Tables 9.11 and 9.12 cover the calculation of energy, of fuel for Table 9.11, and of natural gas for Table 9.12. Table 9.13 covers the calculation of the percent of water in air. Table 9.14 covers the heat capacity of the different components of fuel.

Table 9.8 Shell Heat Loss Calculated*

Shell Zone Temperature (°C)	Shell Zone Temperature (K)	Q1	Q2	Q3	Q5 (kcal/ m^2/hr)	Length (m)	Area (m^2)	Heat Loss kcal/h	Heat Loss kJ/h
346	619	0.51	4,177.75	5,628	7,763	1.75	18.434	143, 107	598,189
318	591	0.45	4,235.58	4,701	6,595	1.75	18.434	121, 580	508,203
325	598	0.46	4,221.55	4,923	6,877	1.75	18.434	126, 769	529,896
313	586	0.44	4,245.42	4,547	6,398	1.75	18.434	117, 950	493,031
312	585	0.43	4,247.37	4,516	6,360	1.75	18.434	117, 232	490,029
318	591	0.45	4,235.58	4,701	6,595	1.75	18.434	121, 580	508,203
337	610	0.49	4,196.83	5,319	7,376	1.75	18.434	135, 963	568,325
320	593	0.45	4,231.60	4,764	6,675	1.75	18.434	123, 050	514,347
218	491	0.25	4,397.47	2,189	3,283	1.75	18.434	60, 516	252,959
288	561	0.38	4,292.27	3,822	5,465	1.75	18.434	100, 748	421,129
299	572	0.41	4,272.16	4,131	5,865	1.75	18.434	108, 125	451,961
305	578	0.42	4,260.85	4,306	6,091	1.75	18.434	112, 275	469,309
305	578	0.42	4,260.85	4,306	6,091	1.75	18.434	112, 275	469,309
309	582	0.43	4,253.19	4,426	6,243	1.75	18.434	115, 092	481,085
288	561	0.38	4,292.27	3,822	5,465	1.75	18.434	100, 748	421,129
286	559	0.38	4,295.84	3,768	5,394	1.75	18.434	99, 439	415,657
269	542	0.34	4,324.99	3,323	4,812	1.75	18.434	88, 703	370,778
263	536	0.33	4,334.76	3,175	4,615	1.75	18.434	85, 078	355,627
279	552	0.36	4,308.10	3,581	5,150	1.75	18.434	94, 934	396,825
277	550	0.36	4,311.54	3,528	5,081	1.75	18.434	93, 669	391,536

278	550	0.36	4,311.54	3,528	5,081	1.75	18.434	93,669	391,536
276	549	0.36	4,313.25	3,502	5,047	1.75	18.434	93,040	388,906
264	537	0.33	4,333.15	3,199	4,648	1.75	18.434	85,677	358,128
279	552	0.36	4,308.10	3,581	5,150	1.75	18.434	94,934	396,825
264	537	0.33	4,333.15	3,199	4,648	1.75	18.434	85,677	358,128
279	552	0.36	4,308.10	3,581	5,150	1.75	18.434	94,934	396,825
282	555	0.37	4,302.89	3,660	5,254	1.75	18.434	96,850	404,835
270	543	0.35	4,323.34	3,349	4,845	1.75	18.434	89,315	373,338
353	626	0.53	4,162.60	5,877	8,073	1.75	18.434	148,814	622,042
354	627	0.53	4,160.41	5,913	8,118	1.75	18.434	149,640	625,494
335	608	0.49	4,201.00	5,251	7,291	1.75	18.434	134,404	561,810
474	747	0.85	3,859.52	11,325	14,604	1.75	18.434	269,218	1,125,330
474	747	0.85	3,859.52	11,325	14,604	1.75	18.434	269,218	1,125,330
477	750	0.86	3,850.99	11,490	14,796	1.75	18.434	272,745	1,140,075
412	685	0.68	4,024.52	8,252	10,973	1.75	18.434	202,274	845,503
432	705	0.73	3,973.56	9,176	12,077	1.75	18.434	222,637	930,624
353	626	0.53	4,162.60	5,877	8073	1.75	18.434	148,814	622,042
257	530	0.32	4,344.23	3,030	4423	1.75	18.434	81,538	340,829
220	493	0.25	4,395.14	2,228	3,337	1.75	18.434	61,513	257,124
224	497	0.26	4,390.33	2,308	3,446	1.75	18.434	63,532	265,563
273	546	0.35	4,318.33	3,425	4,946	1.75	18.434	91,167	381,077
371	644	0.57	4,122.42	6,547	8,902	1.75	18.434	164,098	685,928
338	611	0.49	4,194.73	5,352	7,418	1.75	18.434	136,746	571,599

(Continued)

Table 9.8—Cont'd

Shell Zone Temperature (°C)	Shell Zone Temperature (K)	Q1	Q2	Q3	Q5 (kcal/ m^2/hr)	Length (m)	Area (m^2)	Heat Loss kcal/h	Heat Loss kJ/h
419	692	0.69	4,006.92	8,568	11,352	1.75	18.434	209, 269	874,745
357	630	0.54	4,153.82	6,022	8,253	1.75	18.434	152, 134	635,920
406	679	0.66	4,039.40	7,987	10,654	1.75	18.434	196, 389	820,908
408	681	0.67	4,034.46	8,074	10,759	1.75	18.434	198, 339	829,059
393	666	0.63	4,070.99	7,431	9,981	1.75	18.434	183, 993	769,090
394	667	0.63	4,068.59	7,472	10,032	1.75	18.434	184, 929	773,005
391	664	0.62	4,075.77	7,347	9,880	1.75	18.434	182, 128	761,296
378	651	0.59	4,106.33	6,821	9,237	1.75	18.434	170, 281	711,777
349	622	0.52	4,171.29	5,734	7,895	1.75	18.434	145, 537	608,344
376	649	0.58	4,110.96	6,742	9,141	1.75	18.434	168, 501	704,333
335	608	0.49	4,201.00	5,251	7,291	1.75	18.434	134, 404	561,810
Total	–	–	–	–	–	–	–	7,255,192 kcal/hr (8,424 kJ/s)	30,326,702 kJ/hr (28,507,100 Btu/hr)

* Kiln shell diameter = 3.353 m, ambient air temperature = 301 K.

Table 9.9 Heat of Formation (For Calcination Calculation)*

Heat of Formation*

Heat of Formation at 25°C	**kcal/kmol**	**kJ/kmol**	**kJ/kg**	**MJ/kg**	**Btu/lb**
$H_f - CaCO_3$	289,500	1,211,246	12,100	12.10	5.22
$H_f - CaO$	151,700	634,701	11,314	11.31	4.88
$H_f - MgCO_3$	261,700	1,094,933	12,985	12.99	5.60
$H_f - MgO$	143,840	601,816	14,926	14.93	6.44
$H_f - CO2$	−94,052	−393,507	−8,943	−8.94	−3.86

Heat of calcination**

Heat of Reaction at 25°C	**kJ/kmol**	**kcal/kmol**	**kJ/kg**	**MJ/kg**	**Btu/lb**
$CaCO_3 \rightarrow CaO + CO_2$	183,038	43,748	1,829	1.829	0.79
$MgCO_3 \rightarrow MgO + CO_2$	99,611	23,808	1,181	1.181	0.51

Heat of Water Evaporation***

Heat of Evaporation	**kJ/kmol**	**kcal/kmol**	**kJ/kg**	**MJ/kg**	**Btu/lb**
$H_2O(l) \rightarrow H_2O(g)$ 25°C	–	–	2,452	2.45	1.06
$H_2O(l) \rightarrow H_2O(g)$ 57°C	–	–	2,365	2.37	1.02

* Boynton, 1980; Perry, 1984.
** Note: $CaCO_3 = CaO + CO_2$; 770 kcal/kgCaO ⇔ 180,734 kJ/kmol $CaCO_3$ or CaO.
*** Note: $H_2O \rightarrow H_2 + 0.5O_2 \rightarrow$ 970 Btu/lb of water at 212°F.

Table 9.10 Heat of Combustion Reactions

Heat of Reaction	**kcal/kmol**	**kJ/kmol**	**kJ/kg**	**MJ/kg**	**Btu/lb**
$N + O_2 = NO$	21,600	90,373	6,455	6.46	2,783
$C + O_2 = CO_2$	−94,052	−393,507	−32,792	−32.79	−14,139
$C + O_2 = CO$	−26,416	−110,523	−9,210	−9.21	−3,971
$H + O_2 = H_2O$	−57,798	−241,822	−120,911	−120.91	−52,135
$S + O_2 = SO_2$	−70,940	−296,808	−9,275	−9.28	−3,999

Table 9.11 Calculation of Energy of Fuel

	Fuel Composition		Heat of Combustion		
Elements	**Weight %**	**Coefficient**	**kJ/kg Fuel**	**MJ/kg Fuel**	**Btu/lb**
C	70	36.2	25,340	25.3	10,926
H	4.4	90	3,960	4.0	1,707
S	1.6	10.6	170	0.2	73
N_2	0.9	8	72	0.1	31
O_2	1.8	−10.6	−191	−0.2	−82
H_2O	0	0	0	0.0	0
Ash	15.3	0	0	0.0	0
Total	94	–	29,351	29.4	12,656

Table 9.12 Calculation of Energy of Natural Gas

	Stoichiometric Combustion				
	O_2 Required	**CO_2 Produced**	**H_2O Produced**	**Gross (kcal/mol)**	**Net (kcal/mol)**
CH_4	2	1	2	212.798	191.759
C_2H_6	3.5	2	3	372.820	341.261
C_3H_8	5	3	4	530.605	488.527
iso-C_4H_{10}	6.5	4	5	686.342	633.744
n-C_4H_{10}	6.5	4	5	687.982	635.384
iso-C_5H_{12}	8	5	6	843.240	780.120
n-C_5H_{12}	8	5	6	845.160	782.040
C_6H_{14}	9.5	6	7	1,002.570	928.930
O_2	−1	0	0	0	0

Table 9.13 Calculation of Percent of Water in Air

Ambient Air Conditions					**Calculation Factors**
Temperature		20	°C		0.00856
Relative humidity		60	%		0.99977
Humidity		0.00856	kg H_2O/kg dry air		
Humidity		0.01378	mol H_2O/mol dry air		
× H_2O		0.01359	mol H_2O/mol H_2O + mol dry air		
Humidity		1.38	%		
	N_2%	O_2%	CO_2%	H_2O%	Total %
	77.43	20.71	0.49	1.38	100.02

Table 9.14 Heat Capacity of Constituents

Component	T (K)	Heat Capacity (C_p) Formula	Kcal/kmol·K	kJ/kmol·K	kJ/kg	Btu/lb
$CaCO_3$	400	$19.68+0.01189T-307600/T^2$	22.51	94.2	0.94	0.41
CaO	700	$10.0+0.00484T-108000/T^2$	13.17	55.1	0.98	0.42
$MgCO_3$	692	16.90	16.90	70.7	0.84	0.36
MgO	692	$10.86+0.001197T-208700/T^2$	11.25	47.1	1.17	0.50
C	662	$2.673+0.002617T-116900/T^2$	4.14	17.3	1.44	0.62
CO	662	$6.6+0.0012T$	7.39	30.9	1.10	0.48
CO_2	962	$10.34+0.00274T-195500/T^2$	12.76	53.4	1.21	0.52
N_2	962	$6.5+0.001T$	7.46	31.2	1.12	0.48
NO	962	$8.05+0.000233T-156300/T^2$	8.11	33.9	1.13	0.49
NO_2	963	$36.07+0.0397\times T-0.0000288T^2$ $+7.87\times(10^{-9})\times T^3$		47.59	1.03	0.45
O_2	962	$8.27+0.000258T-187700/T^2$	8.07	33.8	1.05	0.45
S	389	$3.63+0.0064T$	6.12	25.6	0.80	0.34
SO_2	962	$7.7+0.0053T-0.00000083T^2$	12.03	50.3	0.79	0.34
Cl_2	962	$8.28+0.00056T$	8.82	36.9	0.53	0.23
H	962	4.97	4.97	20.8	20.79	8.97
H_2	962	$6.62+0.00081T$	7.40	31.0	15.48	6.67
$H_2O(l)$	283	4.18	4.18	17.5	0.97	0.42
$H_2O(g)$	283	$8.22+0.00015T+0.00000134T^2$	8.37	35.0	1.95	0.84
Coal	283	$0.205+(0.205\times10^{-3})\times\%VM+$ $(3.104\times10^{-4})\times T+(2.77\times10^{-6})\times\%VM$				

9.12 Energy Balance Module

Table 9.15 covers the formulas for use to determine the sensible energy for input streams, as well as the sensible heat for the coal conveying air, the inlet air, and the limestone.

Table 9.15 Sensible Energy for Input Streams

Coal		**kJ/s**
H_2O	$M_{H_2O} \times 0.97 \text{kJ/kg} \cdot \text{K} \times (T - 298)$	2.6
Dry coal	$M_{coal} \times (0.205 + 0.205 \times 10^{-3} \times (\%VM) + 3.104 \times 10^{-4} \times (T°C) + 2.77 \times 10^{6} \times (\%VM) \times (T°C) \times (25 - T°C)$	85
	Total	87
Natural gas		
N_2	$M_{O_2} \times (8.27 + 0.000258T - 187700/T^2) \times (11/0.23901) \times (T - 298)$	0
O_2	$M_{O_2} \times (8.27 + 0.000258T - 187700/T^2) \times (1/0.23901) \times (T - 298)$	0
CO_2	$M_{CO_2} \times (10.34 + 0.00274T - 195500/T^2) \times (1/0.23901) \times (T - 298)$	0
CH_4	$((MCH_4/16) \times ((33300 + 79930 \times ((2086.9/T)/\sinh(2068.9/T))^2 + 41600 \times ((991.96/T)/\cosh(991.96/T))^2) \times (T - 298)))/1000$	0.2
C_2H_6	$(MC_2H_6/16) \times ((40330 + 134220 \times ((1655.5/T)/\sinh(1655.5/T))^2 + 73220 \times ((752.87/T)/\cosh(752.87/T))^2)) \times (T - 298))/1000$	0
C_3H_8	$((MC_3H_8/13) \times ((51920 + 192450 \times ((1626.5/T)/\sinh(1626.5/T))^2 + 116800 \times ((723.6/T)/\cosh(723.6/T))^2)) \times (T - 298))/1000$	0
C_4H_{10}	$((MC_4H_8/13) \times ((71340 + 243000 \times ((1630/T)/\sinh(1630/T))^2 + 150330 \times ((730.42/T)/\cosh(730.42/T))^2)) \times (T - 298))/1000$	0
C_5H_{12}	$((MC_5H_{12}/13) \times ((88050 + 301100 \times ((1650.2/T)/\sinh(1650.2/T))^2 + 189200 \times ((747.6/T)/\cosh(747.6/T))^2)) \times (T - 298))/1000$	0
C_6H_{14}	$((MC_6H_{14}/13) \times ((10440 + 3.523 \times ((1694.6/T)/\sinh(1694.6/T))^2 + 236900 \times ((761.6/T)/\cosh(761.6/T))^2)) \times (T - 298))/1000$	0

(Continued)

Table 9.15—Cont'd

Coal conveying air		
N_2	$M_{O_2} \times (8.27 + 0.000258T - 187700/T^2) \times (11/0.23901) \times (T - 298)$	114
O_2	$M_{O_2} \times (8.27 + 0.000258T - 187700/T^2) \times (1/0.23901) \times (T - 298)$	27
CO_2	$M_{CO_2} \times (10.34 + 0.00274T - 195500/T^2) \times (1/0.23901) \times (T - 298)$	1
H_2O	$M_{H_2O} \times (8.22 + 0.00015T + 0.00000134/T^2) \times (1/0.23901) \times (T - 298)$	6
Inlet air		
N_2	$M_{O_2} \times (8.27 + 0.000258T - 187700/T^2) \times (11/0.23901) \times (T - 298)$	4213.4
O_2	$M_{O_2} \times (8.27 + 0.000258T - 187700/T^2) \times (1/0.23901) \times (T - 298)$	1157.7
CO_2	$M_{CO_2} \times (10.34 + 0.00274T - 195500/T^2) \times (1/0.23901) \times (T - 298)$	29.2
H_2O	$M_{H_2O} \times (8.22 + 0.00015T + 0.00000134/T^2) \times (1/0.23901) \times (T - 298)$	227
Limestone		
$CaCO_3$	$M_{CaCO_3} \times (19.68 + 0.01189T - 307600/T^2) \times (1/0.23901) \times (T - 298)$	5.8
$MgCO_3$	$M_{MgCO_3} \times 16.9 \times (1/0.23901) \times (T - 298)$	4.8
H_2O	$M_{H_2O} \times (4.1812 \text{kJ/Kg} \cdot \text{K}) \times (T - 298)$	1.1
S	$M_S \times (3.63 + 0.0064T) \times (1/0.23901) \times (T - 298)$	0.0
Inerts	$M_{inert} \times (10.0 + 0.00484T - 108000/T^2) \times (1/0.23901) \times (T - 298)$	0.0

9.13 Sensible Energy for Output Streams

Table 9.16 covers the sensible heat of the components of the output gas. Table 9.17 covers the lime product output sensible heat. Table 9.18 covers the sensible heat from the dust. Table 9.19 covers the heat releases from the combustion reaction. Table 9.20 covers the heat consumed by calcinations. Table 9.21 covers the material and energy balance for the dolomitic lime process. Table 9.22 gives a summary and analysis, including the material balance and the heat balance.

Table 9.16 Sensible Heat for Flue Gas Constituents

Flue Gas T(K)	Formula	kJ/s
N_2	$M_{N_2} \times (6.5 + 0.001T) \times (1/0.23901) \times (T - 298)$	10,750
NO	$M_{NO} \times (8.05 + 0.000233T - 156300/T^2) \times (T - 298)$	0
O_2	$M_{O_2} \times (8.27 + 0.000258T - 187700/T^2) \times (0.23901) \times (T - 298)$	57
CO	$M_{CO} \times (6.6 + 0.0012T) \times (1/0.23901) \times (T - 298)$	0
CO_2	$M_{CO_2} \times (10.34 + 0.00274T - 195500/T^2) \times (1/0.23901) \times (T - 298)$	8,017
H_2O	$M_{H_2O} \times (8.22 + 0.00015T + 0.00000134T^2) \times (1/0.23901)$	2,028
SO_2	$M_{SO_2} \times (7.7 + 0.0053T - 0.00000083T^2) \times (1/0.23901) \times (T - 298)$	1

Table 9.17 Sensible Heat for Lime Products

Lime Product	Formula	kJ/s
$CaCO_3$	$M_{CaCO_3} \times (19.68 + 0.01189T - 307600/T^2) \times (1/0.23901) \times (T - 298)$	86
CaO	$M_{CaO} \times (10.0 + 0.00484T - 108000/T^2) \times (T - 298)$	5,659
$MgCO_3$	$M_{MgCO_3} \times 16.9 \times (1/0.23901) \times (T - 298)$	35.5
MgO	$M_{MgO} \times (10.86 + 0.001197T - 208700/T^3) \times (1/0.23901) \times (T - 298)$	4013.9
S	$M_S \times (3.63 + 0.0064T)(1/0.23901)(T - 298)$	4.4
Inert	$M_{inert} \times (10.0 + 0.00484T - 108000/T^2) \times (1/0.23901) \times (T - 298)$	146

Table 9.18 Sensible Heat for Constituents of Dust

Dust	Formula	kJ/s
$CaCO_3$	$M_{CaCO_3} \times (19.68 + 0.01189T - 307600/T^2) \times (1/0.23901) \times (T - 298)$	1.7
CaO	$M_{CaO} \times (10.0 + 0.00484T - 108000/T^2) \times (T - 298)$	121.9
$MgCO_3$	$M_{MgCO_3} \times 16.9 \times (1/0.23901) \times (T - 298)$	1.1
MgO	$M_{MgO} \times (10.86 + 0.001197T - 208700/T^3) \times (1/0.23901) \times (T - 298)$	104.7
S	$M_S \times (3.63 + 0.0064T) \times (1/0.23901) \times (T - 298)$	0.1
Inert	$M_{inert} \times (10.0 + 0.00484T - 108000/T^2) \times (1/0.23901) \times (T - 298)$	3.1

Table 9.19 Heat Releases from the Combustion Reaction

From C
$C + O_2 = CO_2 \rightarrow -94{,}052\,\text{kcal/kmol} \leftrightarrow$
$-393{,}507\,\text{kJ/kmol}$

$\rightarrow (-393{,}507\,\text{kJ/kmol°C}) \times \text{kmol°C}$

From H
$H + O_2 = H_2O \rightarrow 57{,}798\,\text{kcal/kmol} \leftrightarrow$
$-241{,}822\,\text{kJ/kmol}$

$\rightarrow (-241{,}822\,\text{kJ/kmol H}) \times \text{kmol H}$

From S
$S + O_2 = SO_2 \rightarrow -70{,}940\,\text{kcal/kmol} \leftrightarrow$
$-296{,}808\,\text{kJ/kmol}$

$\rightarrow (-296{,}808\,\text{kJ/kmol S}) \times \text{kmol S}$

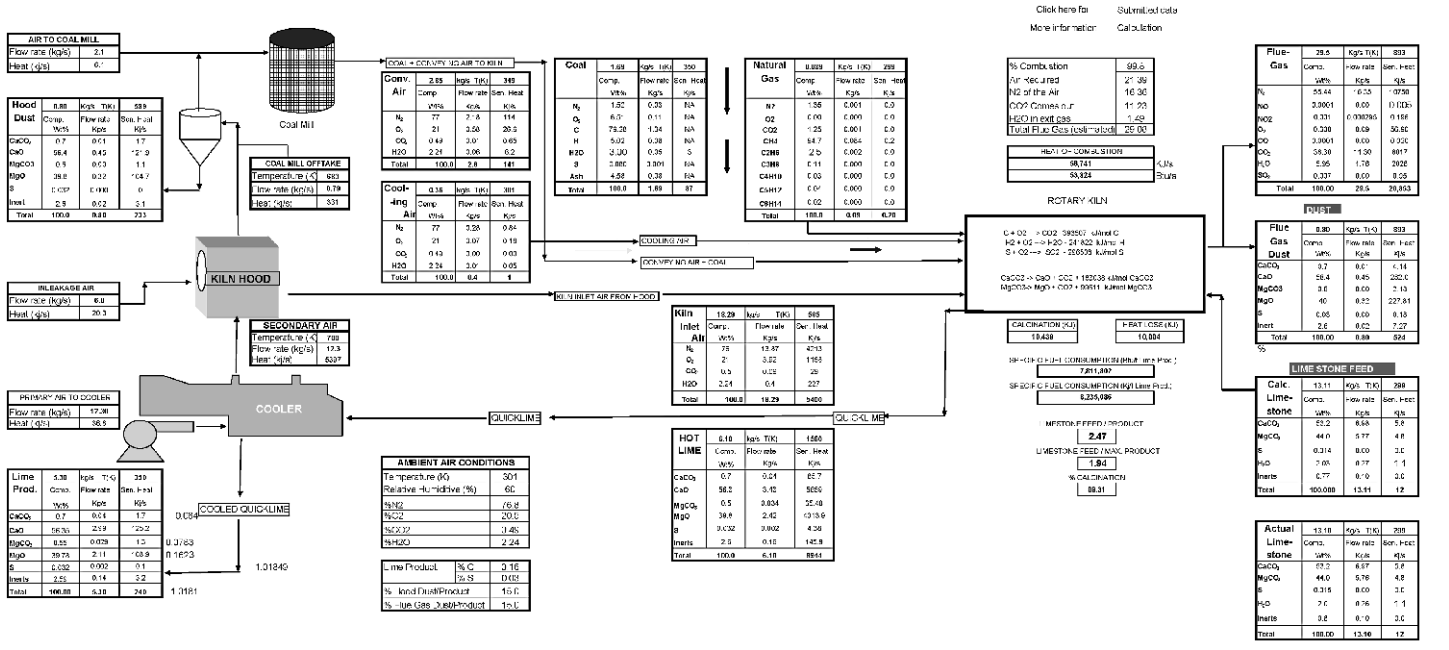
Heat of formation (J/mol)	CH_4	802,319	C_4H_{10}	2,658,446
	C_2H_6	1,427,836	C_5H_{12}	3,272,055
	C_3H_8	2,043,996	C_6H_{14}	3,886,643

Table 9.20 Heat Consumed by Calcination (H_r)

From $CaCO_3 = CaO + CO_2$ $H_r = H_f(CO_2) + H_f(CaO) - H_f(CaCO_3)$ $H_r = -94{,}052\,\text{kcal/kmol} - 151{,}700\,\text{kcal/kmol}$ $+ 298{,}500\,\text{kcal/kmol} = -43{,}798\,\text{kcal/kmol}$	
Heat consumed by $CaCO_3 = (183{,}038\,\text{kJ/kmol CaCO}_3) \times (\text{kmol CaCO}_3 \text{ reacted})$	12,668
From $MgCO_3 = MgO + CO_2$ $H_r = H_f(CO_2) + H_f(MgO) - H_f(MgCO_3)$ $H_r = -94{,}052\,\text{kcal/kmol} - 143{,}840\,\text{kcal/kmol}$ $+ 261{,}700\,\text{kcal/kmol} = -23{,}808\,\text{kcal/kmol}$	
Heat consumed by $MgCO_3 = (99{,}611\,\text{kJ/kmol MgCO}_3) \times (\text{kmol MgCO}_3 \text{ reacted})$	0
Heat of water evaporation (kJ/kg), $2{,}365 \times 0.27$	629
Heat loss (First Law of Thermodynamics) Heat loss = Inlet sensible heat + Heat of combustion − Outlet sensible heat − Heat of calcination − Heat of water evaporation	10,994

Table 9.21 Material and Energy Balance for Dolomitic-Lime Process

MATERIAL AND ENERGY BALANCE FOR DOLOMITIC-LIME PROCESS



ASSIGNMENT: Set up a mathematical model for material and heat balance around a lime kiln to compute:

1- Inlet air flow rate (kg/s),

2- Inlet limestone flow rate (kg/s)

4- Heat values of all streams (kJ/s)

Submitted Data

1- Composition of all streams (Wt%) except inlet air and limestone feed (calculated)

2- Temperature of each stream (K)

3- Flue gas flow rate (Kg/s)

4- Limes product (kg/s)

5- Dust flow rate (kg/s)

6- Ambient air to the hood

7- Percent of water in the inlet air

8- Ambient air to the cooler

ASSUMPTIONS:

1. Inert in limestone has molecular weight of 100

*** **Note: In this model we don't have to made the assumptions:**

1. Complete combustion reaction in the kiln
2. All Nitrogen in coal becomes N2 flue gas stream
3. All sulfur in coal becomes SO_2 in the flue gas

Table 9.22 Summary and Analysis for Material Balance and Heat Balance

Material Balance (kg/s)					
Feed Stream	**Actual**	**Balanced**	**Exit Stream**	**Actual**	**Balanced**
Limestone feed	13.1	13.1	Flue gas	–	29.50
Coal	1.69	–	Dust	–	1.59
Conveying air	2.8	–	Lime product	–	5.30
Natural gas	0.09	–	–	–	–
Cooling air	0.36	–	–	–	–
Inlet air	–	18.3	–	–	–
Material feed total	–	36.4	Outlet material total	–	36.4
Heat Balance (kJ/kg)					
Feed Stream	**Actual**	**Calculated**	**Exit Stream**	**Actual**	**Calculated**
Sensible heat	kJ/s	kJ/s	Sensible heat	kJ/s	kJ/s
Limestone	–	12	Flue gas	–	20,853
Coal	–	87	Flue gas dust	–	524
Conveying air	–	141	Hot lime	–	9,944
Natural gas	–	0.2	Heat of calcination	–	19,439
Inlet air	–	5,400	Heat of water evaporation	–	629
Cooling air	–	1	Total heat loss	–	10,994
Heat of combustion	–	56,741	Kiln heat loss	8,424	–
Total	–	62,383	–	–	62,383

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