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An Equilibrium Model of NO_x Emission in Gas Turbine Combustors

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Abstract

In this study, an equilibrium model for NOx emission in gas turbine combustors was developed. The model is based on the governing thermodynamic, materials, and energy balance equations. Results obtained from the model simulation were compared with operational data from a local gas turbine power plant. There was about a 3 to 6 percent deviation for the periods considered. Consequently, the model is reliable in the design of new combustors and in assessing the pollutant emission during operations. It was established that factors that affect NO_x formation include flame temperature and quantity of excess air used. Furthermore, the results revealed that the most important parameter that governs the formation of NO_x is flame temperature, as the formation of NO_x rises exponentially with an increase in the combustor flame temperature.

Keywords: Nitrogen oxide, Combustors, Emissions, Modelling, PEMS

1.0 INTRODUCTION

Oxides of nitrogen (NO_x), carbon monoxide, and other products of combustion have long been identified as harmful to humans and the environment [1]. There are three methods of monitoring NO_x emissions industrially. The first is by periodic measurements, via sampling; the second is by the installation of continuous emissions measuring systems (CEMS), and third by predicting the emissions through algorithm-based software utilizing parameters that affect the pollutant formation. This method is called parametric emissions monitoring system (PEMS). Purchase and maintenance costs of PEMS are cheaper than continuous emission monitoring systems, which require the installation of on-site emission monitoring equipment [1]. Combustion in a gas turbine is essentially clean due to a large amount of excess air and the steady nature of the process. As a result, there have not been many problems associated with gas turbine emissions apart from the need to eradicate smoke from the exhaust [2]. Nevertheless, control of emissions has recently become probably the most important factor in the design of industrial gas turbines, as there has been greater awareness about the causes and effects of pollution as the

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number of installed gas turbines increase. Gas turbine designers are continually faced with the challenge of improving the efficiency of the turbine while reducing emissions to meet regulations. This challenge is particularly difficult because the two performance indicators are conflicting: To improve cycle efficiency, a very high maximum temperature is needed. However, higher temperatures favour the formation of major pollutants, especially oxides of nitrogen (NO_x). Nonetheless, reducing available air to lower maximum cycle temperature and hence reduce NO_x formation will lead to incomplete combustion, and therefore increased amount of carbon monoxide (CO) and unburnt hydrocarbon (UHC) emissions produced. Virtually all gas turbine manufacturers use some form of lean-premixed gas turbine combustor; also called dry low NO_x (DLN) combustor, for their gas turbine engines [3]. Thus, DLN is currently the most widely used combustor design method for reducing NOx and CO emissions in gas turbines. In Lean-Premix combustion, the fuel and excess air are mixed upstream of the combustion zone. This helps to create a homogenous mixture, thereby leading to a reduction in NO_x and CO emissions.

Although it is expected that a stoichiometric mixture of fuel and air gives complete combustion, it is impossible in practice. This is because there is limited time for the combustion process. Consequently, more oxygen than the stoichiometric amount is needed to achieve a complete reaction between oxygen and the combustible components in the fuel [4]. Thus, gas turbines are operated with excess air. Using excess air means operating with a quantity of air that is more than the theoretical amount required for complete combustion. Other reasons why gas turbines operate lean mixtures are to reduce the flame temperature and not to exceed the metallurgical limits of the material of construction.

The amount of excess air used in industrial gas turbines typically ranges between 100% - 600% [5]. The maximum temperature achievable in the combustor is at the stoichiometric conditions, and as the amount of air deviates from the stoichiometric requirement, the temperature of the combustion system decreases. The NOx formation in a leanpremixed combustion system at gas turbine operating conditions mainly depends on the Zeldovich mechanism, which is often also regarded as thermal NO_x. This is the predominant medium of NO_x formation, especially in natural gas-fired gas turbines [6]. Other mechanisms for NO_x formation include the prompt NO_x and the fuel NO_x mechanisms. The fuel NO_x mechanism describes how organically bound nitrogen in the fuel oxidises to NO. Due to small amounts of nitrogen in natural gas, this mechanism is of little significance in natural gas-fired combustion [3]. However, the mechanism becomes important when burning fuels that contain nitrogen compounds such as coal. Nitrogen oxides are produced in the central hot region of the combustion chamber by oxidation of atmospheric nitrogen, and most of the NO_x formed is nitric oxide [6].

There has long been a need to establish methods of evaluating pollutant emissions. The high cost of CEMS has made it difficult to determine the emissions impact of gas turbines, especially in relatively small units. Thus, a parametric emissions monitoring system (PEMS) will more readily inform stakeholders of the emission impact of gas turbines [7]. Several researchers have published some form of parametric models for NO_x emissions in gas turbine combustors. A considerable number of works on parametric emissions modelling of gas turbines was done by Hung [3]. In 1975, a description of an analytical model used to determine NO_x emissions for a specific model of conventional gas turbine combustors; the solar turbine was studied. Furthermore, amendments made to the model to include the effects of water injection, operation at low air/fuel ratio, primary air leaning, fuel with low calorific value, and fuel/air premixing were also studied. Since the distinctive feature in this model is how the diffusion was accounted for, it was ultimately called the diffusion-limited mixing model. The model showed a good agreement with laboratory and industrial data but was only used as a design tool for reducing NO_x in combustors.

Hung's published work on a PEMS where the diffusion-limited mixing model was referenced, but not

directly used. Instead, the PEMS was based on a performance emissions program that was established for various gas turbine models that utilizes field data on NO_x emissions [8]. The program was developed by gathering NO_x data, correcting it to ISO conditions, and establishing the ISO corrected NO_x as functions of fuel/air ratio and water/fuel ratio, where applicable. In 2003, CMC solutions published a pure statistical-based PEMS. This PEMS was developed from past CEMS data. The PEMS was installed on two GE frame 7 gas turbines.

The algorithm was based on an initial 40 to 60 hours of data acquired from a CEMS. CMC solutions didn't however provide the details of the algorithm. They gathered an additional 720 hours of CEMS data which formed the basis of generating a final algorithm. They didn't utilize any fundamental engineering principle in their approach and therefore is strikingly different from the method adopted in this research work. Several semi-analytical expressions have also been developed to determine NO_x emissions from gas turbines [9-12]. The semi-analytical approach usually combines statistical data with parameters derived from governing engineering laws, such as combustor temperature.

Lewis (1991), [11], presented an equation to show the amount of NO_x formed in lean, homogenous combustion. Lewis correlation is given in Equation 1:

$$NOx = 3.32 * 10^{-6} * exp(0.008Tc) P^{0.5} [ppmv]$$
(1)

This equation assumes that NO_x formation is solely dependent on after-combustion temperature and pressure and is completely independent of the combustion gases' residence time. Lewis asserted that this is because the pertinent time is not the combustion product's residence time but the time required for the molecules involved to relax, that is primarily the Nitrogen molecules, and this remains the same for all combustion systems using air as the oxidant. Rokke et al. (1993) [13] developed a NO_x correlation given in Equation 2:

$$NOx = 18.1P^{1.42}m_a^{0.3}FA^{0.72} \ [ppmv] \tag{2}$$

Their correlation was applied to five natural gasfired turbines with power output ranging from 1.5 MW to 34 MW and was found to satisfactorily predict the NO_x emissions from them. Although the combustion temperature dependence of NO_x is not apparent in their developed model, its influence is acknowledged by the fuel-air ratio term. Bakken and Skogly (1995) [7] published a correlation that was specifically developed for GE-LM 2500 gas turbines for NO_x prediction given in Equation 3:

$$NOx = 62 * P_3^{0.5} * (FA)^{1.4} * exp\left(-\frac{653}{T}\right)$$
(3)

P₃ is the compressor discharge pressure, FA is the fuel to air ratio, and T is the combustor discharge temperature. Their correlation was developed from field measurement and simulated data at atmospheric conditions ($T_0 = 15^0$ C, $P_0 = 1$ bar, $\varphi_0 = 60\%$). Marshall et al. (1997) [13] published a PEMS model to develop CO and NO_x emission algorithms for small stationary gas turbines in natural gas pipeline compression stations. The general forms of the NO_x and CO predictive algorithms were based on fundamental engineering principles, but the forms of these algorithms were said to be proprietary they presented no details of how their algorithms were developed. In addition, these studies [14-20] have also predicted NOx emissions in a combustor using different models.

There is currently no universally accurate parametric model, and all available models have their strengths and limitations. Modern engineering is concerned about the environment. Thus, in the design of modern-day gas turbines, the environmental impact should be treated as of equal importance as efficiency and profitability. A reliable parametric model can help engineers to consider environmental impact in their design and simulations. In this study, an equilibrium model for NO_x emissions in natural gas turbines has been developed. The model is validated with actual plant data, and parametric studies are carried out to determine the effect of temperature, pressure, and concentration on NOx emissions.

The model in this work has relied on fundamental engineering principles, as against the purely statistical or semi-analytical models commonly developed.

2.0 MATERIALS AND METHOD

2.1 Model Development

An equilibrium expression for the fixation of nitrogen and oxygen is given in Equation 4:

$$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO \tag{4}$$

Based on Equation (4), an equivalent thermal equilibrium expression for the process is given in Equation 5:

$$K_{eq}^{\theta} = \frac{(p_{NO})}{(p_{O2})^{\frac{1}{2}} * (p_{N2})^{\wedge} (1/2)}$$
(5)

Where K_{eq}^{θ} is the thermal equilibrium constant or dissociation constant

 p_{NO} is the partial pressure of NO, p_{N2} is the partial pressure of N₂ and p_{O2} is the partial pressure of O₂.

It is noteworthy that nitric oxide (NO) is the primary oxide of nitrogen, and is the oxide formed by hightemperature fixation of nitrogen and oxygen [6]. After NO formation, however, some fraction may get converted to other oxides of nitrogen. Consequently, this work is accounting for oxides of nitrogen formation by considering the quantity of NO producible by thermodynamic equilibrium.

Equation 5 can be rewritten as shown in Equation 6:

$$p_{NO} = K_{eq}^{\theta} * (p_{O2})^{\frac{1}{2}} * (p_{N2})^{\frac{1}{2}}$$
(6)

From Dalton's law of partial pressure given in Equation 7:

$$p_i = \frac{n_i}{n_t} * P_t \tag{7}$$

Where: p_i is the partial pressure of a component, P_t is the system total pressure; n_i is the number of moles of a component, and n_t is the total number of moles of all components in the system.

Relating Equations 6 and 7, an equivalent expression becomes:

$$\frac{n_{NO}}{n_t} * P_t = K_{eq}^{\theta} * \left(\frac{n_{O2}}{n_t}\right)^{\frac{1}{2}} * P_t^{\frac{1}{2}} * \left(\frac{n_{N2}}{n_t}\right)^{\frac{1}{2}} * P_t^{\frac{1}{2}}$$
(8)

On simplification of Equation 8, a resulting equation is given by:

$$\frac{n_{NO}}{n_t} * P_t = K_{eq}^{\theta} * (n_{02})^{\frac{1}{2}} * (n_{N2})^{\frac{1}{2}} * \frac{P_t}{n_t}$$
(9)

By further simplifying Equation 9; Equation 10 is derived and is given by:

$$\frac{n_{NO}}{n_t} = K_{eq}^{\theta} * \frac{(n_{02} * n_{N2})^{\frac{1}{2}}}{n_t}$$
(10)

Since mole fraction of a component ' y_i ' is given in Equation 11:

$$y_i = \frac{n_i}{n_t},\tag{11}$$

Equation (10) can be rewritten as shown in Equation 12:

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$$y_{NO} = K_{eq}^{\theta} * \frac{(n_{02} * n_{N2})^{\frac{1}{2}}}{n_t}$$
(12)

To derive an expression for the equilibrium constant K_{eq}^{θ} , experimental data for the operating temperature range, extracted from thermodynamic and

transport properties of fluids tables, compiled by [21] is

 Table 1: Natural logarithm of equilibrium constant for NO

6	1	
Temperature (K)	$InK_{eq}^{ heta}$	
1000	-9.353	
1200	-7.541	
1400	-6.245	
1600	-5.273	

Analysis of the data on Table 1 with Microsoft Excel gives a good correlation for InK_{eq}^{θ} as depicted in Figure 1.

From the correlation Equation 13 in Figure 1,

$$In(K_{eq}^{\theta}) = 8.6957 In(T) - 69.32 \tag{13}$$

Consequently,

0

-1

-2

-3

-4

-6

-7

-8

-9

-10

hey)nl

200

400

600

presented in Table 1.

$$k_{eq}^{\theta} = exp^{(8.6957In(T) - 69.32)} \tag{14}$$

Combining Equations 12 and 14, the expression developed for NO_x in this research work is given in Equation 15:

800

1000

1200

1400

y = 8.6957ln(x) - 69.32

1600



Where y_{NOx} = mole fraction of NO_x in the exhaust, T = combustor temperature (K) n_{O2} = amount of oxygen in products stream (kmol/s), n_{N2} = amount of nitrogen in products stream (kmol/s), n_t = total amount of products (kmol/s).

The assumptions in the application of this model include: Firstly, the oxygen available for thermal fixation with nitrogen to form NO_x is the excess oxygen in the combustion chamber after the amount required by stoichiometry has reacted. Secondly, the NO_x production takes place after the main combustion has occurred and the adequate temperature has been achieved to enable nitrogen and oxygen fixation.

2.1 Plant Description

The gas turbine considered in this study is one unit of a 4*112.5 MW, simple cycle gas turbine power plant shown schematically in Figure 2. It was completed in 2013, and gas is supplied through the Excravos-Lagos Pipeline System. It is located in Edo State Nigeria. The plant operating condition is given in Table 2.



Figure 2: Schematic of the simple gas power plant

Figure 1: NO_x correlation of InK_{eq}^{θ} with temperature

Temperature (K)

S/N	Operating Parameters	Value	Unit
1	Air temperature into compressor	303	K
2	Air flowrate into compressor	376.75	Kg/s
3	Air pressure into compressor	101.33	Кра
4	Air temperature out of compressor	631.5	Κ
5	Outlet pressure of air from compressor	973.7	Kpa
6	Fuel gas (natural gas mass flow rate)	6.7	Kg/s
7	Air/fuel ratio at full load	56/1	
8	Inlet pressure of fuel gas	22800	kPa
9	Inlet temperature of fuel gas	328	Κ
10	Outlet temperature from combustion chamber	1263.5	Κ
12	Maximum exhaust temperature of turbine Outlet	832	Κ
13	Lower heating value of fuel	45390	kJ/kg
14	Compressor isentropic efficiency	87.8	%
15	Turbine isentropic efficiency	89.4	%
16	Combustion efficiency	99	%

.. .

2.2 Fuel

The plant under consideration in this study is fired by natural gas. The composition is given in Table 3.

	Tuble 5. 1 der Composition										
S/N	Components	Molar Composition (%)									
1	Nitrogen	0.73									
2	Methane	86.66									
3	Carbon dioxide	3.12									
4	Ethane	6.08									
5	Propane	2.13									
6	i-Butane	0.39									
7	n-Butane	0.4									
8	n-Pentane	0.26									
9	n-Hexane	0.23									
	TOTAL	100									

Table 3: Fuel Composition

2.3 Materials and energy balance

The equation for complete combustion of hydrocarbon given in Equation (16):

$$C_{x}H_{y} + \left(x + \frac{y}{4}\right)O_{2} + 3.76\left(x + \frac{y}{4}\right)N_{2}$$

$$\rightarrow xCO_{2} + \frac{y}{2}H_{2}O$$

$$+ 3.76\left(x + \frac{y}{4}\right)N_{2}$$
(16)

This is used to determine the material balance of the

combustibles, assuming complete combustion.

Also, a constant pressure combustor is assumed for the energy balance and a reference temperature of 25 $^{\circ}$ C was chosen. The constant pressure combustion equation is given in Equation (17):

$$H_{P(T2)} - H_{P(25)} + \Delta H^0_{RX(25)} + H_{R(25)} - H_{R(T1)}$$

= 0 (17)

Where

 $\Delta H^0_{RX(25)}$ is the enthalpy of reaction at 25 °C, $H_{P(T2)}$ =Enthalpy of products at combustor exit, $H_{R(T1)}$ = Enthalpy of reactants at combustor inlet, $H_{P(25)}$ =Enthalpy of products at 25 °C, $H_{R(25)}$ =Enthalpy of reactants at 25 °C. (18)

$$H = m * C_P * \Delta T \tag{19}$$

 C_p = specific heat capacity at constant pressure, and ΔT = change in temperature

3.0. RESULTS AND DISCUSSION

This section presents the materials and energy balance streams. Also, the model developed as given by Equation (15) was solved, and appropriate charts were plotted with the MATLAB software. Tables 4 to 9 presents the materials and energy balance results for all the streams

	Table 4: Materials Balance Stream: Fuel													
					Gravim etric Compos ition	Actual Mass=G V*mf	FUEL Actual Molar Flow (kmol/s)	REACT ION EQUAT ION	Moles of O ₂ Reqd (kmol /s)	Mass of O2 Reqd (kg/s)	Moles of H2O Produced (kmol/s)	Mass of H2O Produce d (kg/s)	Moles of CO ₂ formed (kmol/ s)	Mass of CO ₂ Produce d (kg/s)
1	Methan e	S/ N	Co mp.	13.90 286	0.72816 6681	4.878716 765	0.30410 2522	$CH_4 + 2O_2 = CO_2 + 2H_2O C_2H_6 + 25O_2 = CO_2 + 2F_2O C_2H_6 + 2F_2O_2 = C_2H_2O_2 + C_2H_2O_2 = $	0.6082 0504	19.4619 53	0.608205045	10.95681 388	0.3041 0252	13.38355 2
2	Ethane	6. 08	30.0 7	1.828 256	0.09575 5459	0.641561 575	0.02133 5603	$3.5O_2 = 2CO_2 + 3H_20$ $C_3H_8 + 5O_2 = 0$	0.0746 7461	2.38951 28	0.064006808	1.153082 651	0.0426 7121	1.877959 755
3	Propan e	2. 13	44.0 97	0.939 266	0.04919 4345	0.329602 112	0.00747 4479	$3O_2 = 3CO_2 + 4H_2O C_4H_{10} + 65O = 0$	0.0373 724	1.19587 93	0.029897917	0.538610 975	0.0224 2344	0.986855 496
4	i- Butane	0. 39	58.1 23	0.226 68	0.01187 2418	0.079545 198	0.00136 8567	$0.5O_2 = 4CO_2 + 5H_2O$ $C_4H_{10} + 65O_2 = -65O_2 - 500$	0.0088 9568	0.28465 3	0.006842833	0.123273 639	0.0054 7427	0.240922 469
5	n- Butane	0. 4	58.1 23	0.232 492	0.01217 6839	0.081584 818	0.00140 3658	$4CO_2 + 5H_2O$ $C_5H_{12} + 8O_2 =$	0.0091 2378	0.29195 18	0.00701829	0.126434 501	0.0056 1463	0.247099 968
6	Pentan e	0. 26	72.1 5	0.187 59	0.00982 5083	0.065828 055	0.00091 2378	$5CO_2 + 6H_2O$ $C_6H_{14} + 9.5O_2 = 0$	0.0072 9902	0.23356 14	0.005474266	0.098618 911	0.0045 6189	0.200768 724
7 8	n- Hexane CO2 Nitroge	0. 23 3. 12 0.	86.1 77 44.0 1 28.0	0.198 207 1.373 112 0.204	0.01038 1157 0.07191 7155 0.01071	0.069553 749 0.481844 937 0.071762 701	0.00080 7103 0.01094 8533 0.00256	6CO ₂ + 7H ₂ O	0.0076 6748	0.24535 18	0.005649724	0.101779 773	0.0048 4262 0.0109 4853	0.213123 722 0.481844 937
9	n TOTA L	73 10 0	14	502 19.09 297	0864 1	6.628237 209	0.35091 4519		0.7532 3802	24.1028 63	0.727094884	13.09861 433	0.4006 3911	17.63212 708
						AMW =	19.0929 689		Mass of Air Reqd.	103.445 77	Percen			
			F	uel Avera Ma	age Molecul ss/Total Mo	ar Weight = le = 19.093	Total	Stoichiom R	etric Air F atio =	Fuel 15.43 97	excess air =	262.7 %		

Table 5: Energy Balance Stream: Fuel

	ΔH_{f}					ΔH.			$C_p = \mathbf{R}(\mathbf{A} + \mathbf{B}')$	$T + CT^2 + DT^4$	-2)
Fuel Comp.	(298.15k) (kJ/kmol)	MM (kg/kmol)	Mass (kg/s)	Specific gas Const, R (kJ/kgK)	REACTION EQUATIO N	(298.15k) (kJ/kmol)	ΔH _r (298.15k) (kJ)	A	В	С	D
Methane	-74850	16.043	4.87871676 5	0.51826341 7	$\begin{array}{l} CH_4+2O_2=\\ CO_2+2H_2O \end{array}$	-802310	- 243984.5	1.70 2	0.00908 1	0.000002164	
Ethane	-84680	30.07	0.64156157 5	0.27650482 2	$\begin{array}{c} C_2H_6 + 3.5O_2 \\ = 2CO_2 + \\ 3H_20 \\ C_3H_8 + 5O_2 = \end{array}$	-1427820	-30463.4	1.13 1	0.01922 5	0.000005561	
Propane	-103850	44.097	0.32960211 2	0.18855024 2	3CO ₂ + 4H ₂ O	-2043990	- 15277.76	1.21 3	0.02878 5	0.000008824	

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i-Butane	-134600	58.123	0.07954519 8	0.14305008 3	$\begin{array}{l} C_{4}H_{10} + \\ 6.5O_{2} = \\ 4CO_{2} + \\ 5H_{2}O \end{array}$	-2648580	3624.758	1.93 5	0.03691 5	0.000011402	
n-Butane	-126150	58.123	0.08158481 8	0.14305008 3	$\begin{array}{l} C_{4}H_{10} + \\ 6.5O_{2} = \\ 4CO_{2} + \\ 5H_{2}O \end{array}$	-2657030	3729.562	1.67 7	0.03785 3	0.000011945	
n- Pentane	-146500	72.15	0.06582805 5	0.11523908 5	$\begin{array}{l} C_5H_{12}+8O_2\\ =5CO_2+\\ 6H_2O\\ C_6H_{14}+\\ 9.5O_2= \end{array}$	-3272020	2985.318	2.46 4	0.04535 1	- 0.000014111	
n-Hexane	-167300	86.177	0.06955374 9 0.48184493	0.09648166 0.18892297	$\begin{array}{c} 6\text{CO}_2 + \\ 7\text{H}_2\text{O} \end{array}$	-3886560	- 3136.856	3.02 5 5.45	0.05372 2 0.00104	- 0.000016791	-
CO_2	-393520	44.01	7 0.07176279	2				7	5 0.00059		115700
Nitrogen	0	28.014	1	0.29679803			_	3.28	3		4000
TOTAL							303202.1				

Table 6: Energy Balance Stream: Fuel (Cont:d)									
	m C ₂ at t = 328K								
Mathana	4 20244	0.022061	5 47150E 06	0	10 66285830	2 195596692	11 24507558		
wieulane	4.30344	0.022901	-5.4/1591-00	0	10.00283839	2.165560065	11.24397336		
Ethane	0.200634	0.00341	-9.86493E-07	0	1.129756507	1.760947899	1.213119314		
Propane	0.075384	0.001789	-5.48381E-07	0	0.559993446	1.698998357	0.603142211		
i-Butane	0.022018	0.00042	-1.29743E-07	0	0.135724036	1.706250533	0.145837676		
n-Butane	0.019572	0.000442	-1.39407E-07	0	0.138893647	1.702444768	0.149474937		
n-Pentane	0.018692	0.000344	-1.07046E-07	0	0.111749041	1.697589911	0.120017626		
n-Hexane	0.0203	0.000361	-1.12679E-07	0	0.117769452	1.693215005	0.126424649		
CO_2	0.496759	9.51E-05	0	-10532.4	0.406638798	0.843920453	0.430062419		
Nitrogen	0.069861	1.26E-05	0	85.19622	0.074585045	1.039327534	0.074795556		
TOTAL	5.226659	0.029834	-7.49534E-06	-10447.2	13.33796836		14.10884997		
					$H_{f(298.15)} =$	3976.715268			
					$H_{f(328k)} =$		4627.702789		

Notes:

 $\begin{array}{l} H_{f\,(298.15)} = enthalpy \ of \ fuel \ at \ 298.15K \\ H_{f\,(328)} = enthalpy \ of \ fuel \ at \ 328K \end{array}$

	Table 7: Energy Balance Stream: Air														
			C _p =R	A + B' DT^	Γ + C1 ^-2)	[^2 +	ΔH f (29 8)	R (kJ/km olK)		m.C _p Co	oefficier	nts	m.C _p at t = 298.15K	C _p at t = 298.1 5K	m.C _p at t = 631.5 K
Com p.	GV Comp	Act. Mass Flow (kg/s)	A	В	С	D			Const ant	Т	T ^2	T^-2			

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O2 N2	0.233 0.767	87.78 275 288.9 673	3.63 9 3.28	0.0005 06 0.0005 93	2270 0 4000	0 0	0.25983 6 0.29679 8	83.00 246 281.3 089	0.011 541 0.050 859	0 0	517767.4 808 343059.6 416	80.61895 300.3316	0.918 392 1.039 328	88.99 253 314.2 864
TOT AL		376.7 5						364.3 114	0.062 4	0	174707.8 392 H _a (298.15) =	380.9506 113580.4	H _{a(631.} 5) =	403.2 789 25467 0.6
											$H_{r(298,15)}$ = $H_{f}+H_{a}$ (298,15) = $H_{r(Tin)} = H_{a}$	117557.1 (631.5)+ H _f (328) =	25929	8.3188

Notes:

 $H_{a(298.15)} =$ enthalpy of air at 298.15K

 $H_{a (631.5)} =$ enthalpy of air at 631.5K

 $H_{r(Tin)}$ = enthalpy of reactants at inlet conditions = enthalpy of fuel at inlet + enthalpy of air at inlet

	Tuble 0. Energy but nee bit cunt. Houses													
			Cp=F	R(A + BT	$C + CT^2 +$		Specific							
	MOL	MAS		DT^-	-2)		gas		m.Cp Co	efficie	ents			
	AR	S					constan					m.Cp	C _p at	
	MASS	FLO				ΔHf	t					at t =	t =	ΔH_{f}
PRODU	(kg/k	W				(298).kJ/	(kJ/km	Const		Т		298.1	298.1	(298)
CTS	mol)	(kg/s)	Α	В	C D	kmole	ol.K)	ant	Т	^2	T^-2	5K	5K	.kJ
					-						-			-
		17.63	5.4	0.001	1157		0.18892	18.17	0.003		385409.	14.88	0.843	1576
CO_2	44.01	213	57	045	00	-393520	3	789	481	0	8725	011	92	60
							-				0.120			-
		13.09	34	0.001	1210		0 46153	20.97	0.008		731497	24 41	1 863	1758
H ₂ O	18 015	861	7	45	1210	-241820	2	764	766	0	0796	408	867	26
1120	10.015	289.0	32	0.000	0	241020	0 29679	281.3	0.050	0	3/31//	300.4	1 030	20
Na	28 014	207.0	J.2 8	503	4000	0	0.27077	788	0.050 871	Ο	943144. 9379	062	328	0
182	20.014	39	0	595	4000	0	0	/00	0/1	0	8578	002	526	0
		(2 (7	20	0.000	-		0.25092	(0.21	0.000		-	E0 10	0.010	
0	21 000	03.07	3.0	0.000	2270	0	0.25985	00.21	0.008	0	3/3001.	38.48	0.918	0
O_2	31.999	989	39	506	0	0	6	214	372	0	9/81	308	392	0
											-			-
		383.4						380.7	0.071		344717.	398.1		3334
TOTAL		496				-635340		464	491	0	3048	835		86
											Hp (298.15)	11871		
											=	8.4		

Table 8:	Energy	balance	Stream.	Products
I abic U.		ounditie	ou cum.	1 TOuucto

Note: $H_{p(298.15)}$ = enthalpy of products at 298.15K

Table 9: Products Flow Stream						
	Molar Flow	Molar Mass		Molar Flow	Mass flow	
Component	(kmol/s)	(kg/kmol)	Mass Flow(kg/s)	(kmol/h)	(kg/h)	
CO_2	0.400639106	44.01	17.632127	1442.300783	63475.65747	
H_2O	0.727094884	18.015	13.098614	2617.541581	47155.01158	
N ₂ (Fuel +Air	10.31766305	28.014	289.03901	37143.58699	1040540.446	
O ₂ (Excess)	1.99005865	31.999	63.679887	7164.211141	229247.5923	
TOTAL	13.43545569		383.44964	48367.6405	1380418.707	

		x		
Month	NO _x Conc. (ppm)	Developed model (ppm)	Deviation	Percentage Deviation
April 2018	135	127.779	-7.221	5.348
May 2018	132	127.779	-4.221	3.198
June 2018	136	127 779	-8 221	6 044

Table 10: Model comparison with Plant data

Energy balance Equation;

$$\begin{split} H_{P(T2)} - H_{P(25)} + H_{P(25)} - H_{r(25)} + H_{r(25)} - H_{r(Tin)} \\ &= Q + W = 0 \\ H_{P(T2)} - H_{P(25)} + \Delta H_{r(25)} = H_{r(Tin)} - H_{r(25)} \\ H_{P(T2)} = H_{r(Tin)} - H_{r(25)} - \Delta H_{r(25)} + H_{p(25)} \end{split}$$

$$\begin{array}{l} 390.746439 \times T + 0.071491T^2 - 344717.3048T^{-1} \\ = 259298.319 - 117557.1274 \\ - (-303202.1) + 118718 \\ + 380.7464397T + 0.071491T^2 \\ - 344717.3048T^{-1} = 563661.2916 \end{array}$$

On solving the non-linear equation, T = 1207.4 K

Assuming that there is a maximum 3% absolute temperature drop due to heat losses and dissociation, *Combustor temperature* = 0.97×1207.4 . Therefore, Combustor temperature = 1171.178 K

In this Microsoft Excel model, non-linear C_p equations taken from [22] have been utilized, and no approximation has been made in the enthalpies of reactions and other parameters.

3.1 Comparison with Plant Data

Table 10 presents the result of the solving Equation





(15) and the deviations from a measured emission from the

plant. Figure 3 shows the NOx concentration plot for three months. As observed, the concentration remains constant, for the model developed in this study, while for the plant data, NOx concentration decreases up to 135-132 ppm, and then increases back to 136 ppm.boilers as reported by [1].

Table 10 shows that there is a close agreement between the equilibrium model developed for NO_x emission and actual plant data. The calculated value of NO_x gives 5.35%, 3.20%, and 6.04% deviation from actual plant data in April, May, and June 2018 respectively. In addition, this result confirms that thermal NO_x is predominant in nitrogen oxides formation mechanism, especially in natural gas-fired

3.2 Effect of temperature on NO_X emission

A graphical representation of the effect of temperature on NO_x emission is given in Figure 4. The graph was plotted with MATLAB; from the solution of Equation (15) at different combustor temperatures.

Figure 4 depicts the importance of combustor temperature to NO_x concentration in the flue gas. An increase in combustion temperature causes an exponential rise in NO_x emissions. At 1000 K for instance, the concentration of NO_x is only 32.34 ppm. However, when the combustion temperature becomes 1600 K, the



Figure 4: Effect of Temperature on NO_x Emission

concentration of NO_x becomes 1926 ppm. Consequently, the combustion temperature is a very important parameter

in the NO_x emissions control strategy. The flame temperature must be carefully monitored to ensure that NO_x concentration in the exhaust gases is kept within the required level.

3.3 Effect of N_2 Concentration on NO_X Emission

Figure 5 depicts the effect of increased N_2 concentration in the combustion chamber on NO_x emission. The graph is a result of solving Equation (15) with MATLAB, at different nitrogen concentrations in the combustion chamber.

It was observed that NO_x emission increases with an increase in N₂ molar concentration. At a constant temperature of 1171.18 K, when the N₂ concentration in the combustor is 76.8%, NO_x emission is 127.8 ppm. As the concentration of N₂ increases to 83.5%, NO_x emission increases to 133.2 ppm and finally, as the concentration of N₂ becomes 92.4%, NO_x emission becomes 140.2 ppm. The relationship between N₂ molar concentration in the combustion chamber and NO_x formation is nearly linear.

Thus, reducing the concentration of N_2 in the flue gas can help to decrease the NO_x produced. Additionally, it can be observed from Equation (15) that when N_2 concentration becomes zero, no NO_x will be formed at all. This means that using oxygen for combustion instead of air can eliminate NO_x formation. However, this will lead to increased operational expenses and reduced profit for the organization.

3.4 Effect of pressure NO_X emission

Although the importance of pressure on NO_x emission seems intangible, as there is no pressure component in Equation (15), higher compressor discharge pressure can increase the flame temperature and thereby increase the formation of NO_x .



Figure 5: Effect of N₂ Concentration on NO_x emission

From the factors observed, it is deduced that the most important parameter affecting NO_x formation is the combustor temperature.

4.0 CONCLUSION

A thermal equilibrium model for NO_x formation in natural gas-fired gas turbines has successfully been developed in this work. The close agreement between local gas turbine emissions data and the developed model confirms that thermal NO_x is the predominant formation mechanism in natural gas-fired gas turbine combustors. The main parameter that affects NO_x formation is temperature. As the combustion temperature reduces, NO_x emission significantly declines. However, low temperature leads to reduced cycle efficiency and power output. Therefore, there has to be a compromise between cycle efficiency and combustor outlet temperature. The models developed in this research can be a valuable tool in the design of effective NO_x pollutant prevention and control strategies as gas turbine operating conditions become more stringent. A careful study and simulation of the equation developed in this research-work can help designers and engineers determine optimum conditions for minimum pollutant emission while maintaining suitable operational efficiency.

NOMENCLATURE

A/F	Air to fuel Ratio
AMW	Average molecular weight (kg/kmol)
CEMS	Continuous emissions monitoring system
C _p	Specific heat capacity at constant pressure (kJ/kgK)
CO	Carbon monoxide
DLN	Dry Low NO _x
F/A	Fuel to air ratio
Н	Enthalpy (kJ)
Keq	Equilibrium constant
m	Mass flow rate (kg/s)
MW	Molecular weight (kg/kmol)
Ν	Number of moles (kmol)
NIPP	National Independent Power Project
NO _x	Oxides of nitrogen
Р	Pressure (bar)
PEMS	Parametric emissions monitoring system
ppm	Parts per million
ppmv	Parts per million, by volume
Т	Temperature (K)
UHC	Unburnt hydrocarbon
V	Volume (m ³)
W	Workdone (kJ)
У	Molar concentration (kmol/kmol)
Φ	Equivalence ratio
Δ	Change
ρ	Density (kg/m ³)

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