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## Computer Assessment of $SO_2$ and $NO_x$ Emitted From Khoms Power Station in Northwestern Libya

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**Abstract:** Computer simulations of the combustion process at Khoms Gas & Steam Power stations in north western Libya reveal that  $SO_2$  and  $NO_x$  emissions exceeds four selected international standard limits. This study concludes that the operational procedures are inadequate.

**Keywords:**  $SO_2$ ;  $NO_x$ ; Hysys; Air pollutants; Emissions; Simulation; Libya.

### 1. Introduction

Emissions of  $SO_2$  and  $NO_x$  produced from natural gas and heavy fuel oil combustion in power stations are recognized as a public health hazard and a cause of degradation of surrounding environments. Several health problems such as respiratory disorders and allergies are attributed to such emissions [1]. Inhalation of  $NO_x$  interferes with the function of human respiratory system and worsens the health condition of asthma patients even at low concentrations [2, 3]. Increased  $SO_2$  levels in the atmosphere are blamed for degradation of agricultural productivity and death of some plants in early stages [4-6]. Similar impacts on human health and agricultural productivity are linked to high level of PMs dust in the atmosphere [1, 7]. This study aims to calculate the concentrations of emissions from both steam and gas power stations using advanced mathematical models.

#### 1.1. Types of Industrial Flue Gas Emissions and Their Sources

Stack emissions vary according to the type of industrial processes and used fuel. There are two types of emissions, particulate and gaseous:

First, gaseous emissions are products of fuel combustion that include sulfur oxides ( $SO_3$ ,  $SO_2$ ,  $SO$ ), hydrogen sulfide ( $H_2S$ ), nitrogen oxides ( $NO$ ,  $NO_2$ ,  $N_2O$ ), carbon oxides ( $CO$ ,  $CO_2$ ) and volatile organic compounds (*VOC's*). Second, particulate matter emissions are fine dust measured in micrometers that include cement dust and carbon particles emitted from steel plants and power plants as well as different types of heavy metals [9].

## 1.2. Emissions Covered by the Study

### 1.2.1 Sulfur Oxides ( $SO_x$ )

Sulfur oxides are emitted from sulfur containing fuels in a form of  $SO_2$  and  $SO_3$ . Sulfur dioxide dissolves in water vapor in the atmosphere yielding sulfite acid  $H_2SO_3$ . Sulfur trioxide is either emitted directly from the source or produced from the transformation of sulfur dioxide in the air. The occurrence of the sulfur dioxide is more common than other sulfur compounds in the lower atmosphere. Sulfur dioxide is a colorless gas with a foul odor and its presence in the surrounding air can be sensed by smelling at concentrations between 1000 to 3000  $\mu g/m^3$  [1].

### 1.2.2. Nitrogen Oxides ( $NO_x$ )

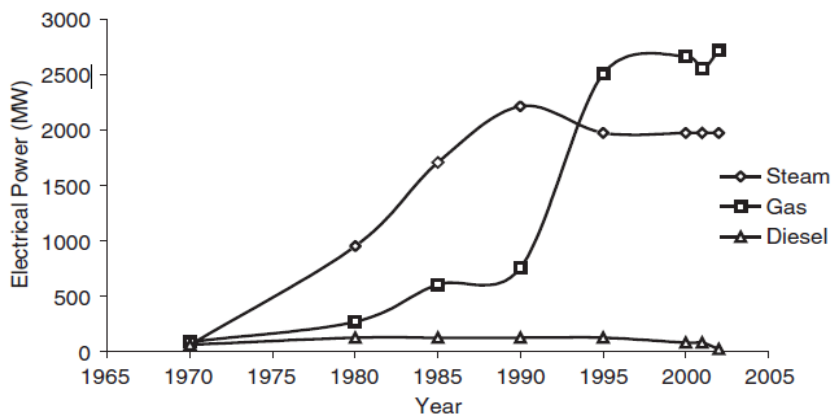
Nitric oxide ( $NO$ ) and nitric dioxide ( $NO_2$ ) are regarded as major pollutants in the lower atmosphere, in addition to nitrous oxide ( $N_2O$ ) that transforms into  $NO$  and  $NO_2$ . Nitric oxide is a colorless gas with a pungent odor, varies in color from orange yellow to reddish-brown and it is a powerful oxidizing agent converts in the air into nitric acid ( $HNO_3$ ).

Sources of  $NO_x$  are either natural such as volcanoes or industrial such as electric power stations, automobile engines, industrial boilers, burners, and factories producing nitrogenous compounds such as nitric acid. Nitrogen oxides emitted from industrial sources such as fixed industrial furnaces contribute about 30% of nitrogen oxides emissions, where 70% are attributed to power plants [1, 8].

## 2. Power Station Systems

Potential pollutant emissions from gas turbines/boilers include oxides of nitrogen ( $NO$  and  $NO_2$ , collectively referred to as  $NO_x$ ), carbon monoxide ( $CO$ ), unburned hydrocarbons ( $UHC$ , usually expressed as equivalent methane) and oxides of sulfur ( $SO_2$  and  $SO_3$ ). Unburned hydrocarbons are made up of volatile organic compounds (*VOCs*) which contribute to the formation of ground level atmospheric ozone, and compounds such as methane and ethane, that do not contribute to ozone formation. Natural gas combustion yields negligible amounts of  $SO_2$ ,  $UHC$  and  $PMs$ . Thus,  $NO_x$  and  $CO_x$  constitute the most pronounced products of natural gas combustion [10].

A progressive increase in electric power production in Libya over 32 years Fig.1 reflects a progressive increase in demand for electricity due to population growth and industrial expansions. Energy produced from Libyan stations comes from combustion of heavy oil, light oil, and natural gas. Combustion process of fuel is accompanied by increase emission rates of exhaust gases, such as,  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{CO}$ , dust, and  $\text{CO}_2$  correspond to increases in power generation [11].



**Fig 1.** Growth of electric power generations in Libya [12].

### 2.1. Modeling Process

Modeling is carried out by using Hysys v3.2 to calculate mass balances of compounds involved in chemical reactions. In order to control any chemical processes and relevant changes in combustion processes, it is necessary to study the state of incoming and outgoing compound flows [13, 14]. The objective of modeling is to find out how well a certain type of combustion chamber, boilers, turbines or compressors can describe a certain function in a process and a behavior of combustion process in a realistic way. Chemical analyses of fed fuel and excess air are essential for any simulation process in order to determine the chemical composition of emission gases.

Generally,  $\text{NO}_x$  emissions are generated during fuel combustion by oxidation of chemically-bound nitrogen in the fuel and by thermal fixation of nitrogen in the combustion air. The amount of thermally generated  $\text{NO}_x$  increases as flame temperature increases. Emissions of  $\text{SO}_2$  are generated from sulfur compounds in the fuel.

### 2.2. Gas Emissions Formation

#### 2.2.1. $\text{NO}_x$ Formation

There are two types of  $\text{NO}_x$  produced in the industrial process, thermal  $\text{NO}_x$  and fuel  $\text{NO}_x$  (chemical reactions are described by [9]). Combustion of oils containing significant amounts of fuel-bound nitrogen can produce up to 50% of the total  $\text{NO}_x$  emissions [15]. The most significant factors

influence  $NO_x$  formation are flame temperature and the amount of nitrogen in the fuel. Other factors affecting  $NO_x$  formation are excess air level and combustion air temperature.

The  $NO_x$  production rate falls sharply as either the combustion temperature decreases, or as the fuel-air ratio decreases, due to an exponential temperature effect. Therefore, an introduction of a small amount of any diluents into the combustion zone can decrease the rate of thermal  $NO_x$  production [10].

### 2.2.2. $SO_2$ Formation

Sulfur compounds are present in liquid fuels specially heavy fuel oil. As a result of combustion, sulfur in fuel evaporates in the burning zone as  $SO_2$ . A higher sulfur content can result in an increased  $SO_2$  emission with the exit gases.

## 2.3. Types of Used Fuels

### 2.3.1 Natural Gas

In recent years, natural gas has become the most favored fuel due to its lower sulfur content. The main components of natural gas are methane, ethane and hydrocarbons as shown in Table.1. Some natural gas may also contain up to 10% inert gases such as carbon dioxide, nitrogen and helium. Sulfur presence in natural gas occurs in a form of hydrogen sulfide [9].

**Table 1.** Natural gas composition supplied to Khoms Gas station[16]

<i>Comp.</i>	<i>Unit</i>	<i>Value</i>
$N_2$	<i>mol.%</i>	0.593
$CO_2$	<i>mol.%</i>	2.023
$CH_4$	<i>mol.%</i>	86.482
$C_2H_6$	<i>mol.%</i>	10.392
$C_3H_8$	<i>mol.%</i>	0.496
$i-C_4H_{10}$	<i>mol.%</i>	0.014
<b>Total</b>	<i>mol.%</i>	<b>100</b>
<i>M.Wt.</i>	--	18.282
<i>Density</i>	<i>kg/Nm<sup>3</sup></i>	0.77519
<i>T.S.</i>	<i>g/Nm<sup>3</sup></i>	0.0009

### 2.3.2. Heavy Fuel Oil

The chemical composition of heavy fuel oil supplied to Khoms steam power station is shown in Table 2 [16].

**Table 2.** Heavy fuel oil composition supplied to Khoms steam power station [16]

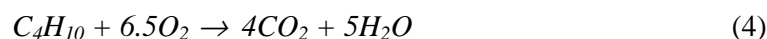
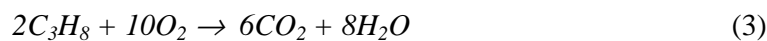
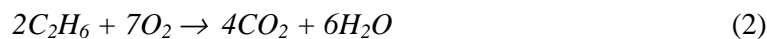
Specification	Unit	Value
Carbon Content	wt. %	86.6
Hydrogen content	wt. %	12.8
T.S. content	wt. %	0.32
Water content		Traces
T.N. Content	wt. %	0.17
Total		99.89
Heating Value	kcal/kg	10037.25
API	--	35
Density	kg/m <sup>3</sup>	847.6

#### 2.4. Combustion Reactions and Pollutants Formation

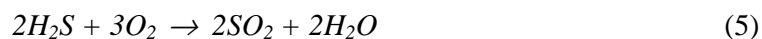
The amount of combustion gases generated from the same amount of thermal units of natural gas is 18.5% and 12.2% higher than that generated from coal and fuel oil respectively [9]. Higher volumes of combustion gases released from natural gas combustion are attributed to air requirement. Combustion of fuel oil requires lesser amounts of air than natural gas.

##### 2.4.1. Combustion of Natural Gas

The main reactions associated with natural gas combustion (Table.1) are as follows [9];



With a conversion rate of 100% at operating conditions [9]; and side-reactions;



such that  $H_2S$  is fully converted at given operating conditions [3].



where only 0.15% of the nitrogen contained in injected air is converted to NO [3].

##### 2.4.2. Combustion of Heavy Fuel Oil

Carbon and hydrogen present in heavy fuel oil are fully converted into  $CO_2$  and  $H_2O$  at operating conditions;





such that all nitrogen compounds in the fuel are converted into  $NO_x$ , where only 0.3% of nitrogen in injected air is converted into  $NO_x$  according to Eqn. (6) [13].

All amount of sulfur compounds are converted into  $SO_2$  as shown in Eqn.(9);



### 2.5. Simulation Process and Operating Conditions

Simulation of the combustion processes for both stations are based on the operating condition using HYSYS v3.2. Building a simulation model requires knowledge of process details and sufficient information regarding design and operation [13]. The following data for the gas and steam power stations correspond to steady state conditions.

#### 2.5.1. Steam Power Station

The station is located 7 km east of Khoms in a coastal farming strip inhabited by about 100,000 people.

Design efficiency: 120 MW\*4 units= 480 MW [17]

Operating efficiency: 100 MW \* 4 units= 400 MW [18]

Type of fuel: Heavy fuel oil/light fuel oil [17]

Capacity of the boiler: 375 Ton/hr [17]

Operating temperature: 1050°C [18]

Thermal efficiency of each unit: 31.67% [18]

Actual excess air: 15% [18]

Relative Humidity: 60% [18]

#### 2.5.2. Gas Power Station

The station is located next to the steam power station.

Design efficiency: 150 MW\*4 units= 600 MW [17]

Operating efficiency: 120 MW\*4 units= 480 MW [18]

Type of fuel: Natural gas [17]

Capacity of the air compressor: 485 Ton/hr [17]

Operating temperature: 1050°C [18]

Thermal efficiency of each unit: 34.8% [18]

Actual excess air: 32% [18]

Relative Humidity: 60% [18]

### 3. Results and Discussion

HYSYS simulation of each station reveals that the estimated and the actual thermal efficiencies are equal and provides estimates of emission concentrations of  $SO_2$  and  $NO_x$ . Tables (3 & 4) contain the results against the standard limits of four international codes, American (USEPA), Canadian (CEPA), European (ECE) and Saudi (KSA).

The (+) sign represents a percentage by which an emission rate of each gas exceeds a certain standard limit, where the (-) sign represents a percentage by which an emission rate falls below a standard limit.

Nitrogen oxides and Sulfur dioxide emitted from the steam power station exceed all the standard limits set by the USEPA, CEPA, ECE and KSA several times corresponding to standard deviations ranging from 261.13% (ECE) to 6,360.83% (CEPA) for  $NO_x$  and from 50.07% (ECE) to 4,3674.78% (CEPA) for  $SO_2$ .

**Table 3.** Estimated  $NO_x$  &  $SO_2$  emissions from Khoms steam power station vs. four international standard limits [18-22]

Pollutants	Standards	USEPA	CEPA	ECE	KSA
$NO_x$	<i>Unit</i>	<i>lb/MW.hr</i>	<i>g/GJ</i>	<i>mg/m<sup>3</sup> (E.G.)*</i>	<i>lb/MBtu</i>
	<i>Standard limit</i>	1.3	50	200	0.3
	<i>Estimated value</i>	2.56	3,230.414	722.265	7.51
	<i>Deviation %</i>	<b>+1,869.23</b>	<b>+6,360.83</b>	<b>+261.13</b>	<b>+2,403.33</b>
$SO_2$	<i>Unit</i>	<i>lb/MW.hr</i>	<i>kg/MW.hr</i>	<i>mg/m<sup>3</sup> (E.G.)*</i>	<i>lb/MBtu</i>
	<i>Standard limit</i>	0.9	4.6	300	2.3
	<i>Estimated value</i>	16	2,013.64	450.2106	4.679
	<i>Deviation %</i>	<b>+1,677.78</b>	<b>+4,3674.78</b>	<b>+50.07</b>	<b>+103.43</b>

\* E.G. : *Emitted Gases*

Nitrogen oxides emitted from the gas power station follow a pattern similar to  $NO_x$  emission rates from the steam power station exceeding all the standard limits by differences correspond to standard deviations within 1,866.67% (ECE) to 34,995.25% (CEPA) for  $NO_x$ .  $SO_2$  emissions are negligible as natural gas contains only traces of  $H_2S$ .

The excessive  $NO_x$  and  $SO_2$  emission from both stations during the steady state operating conditions reveal that combustion in both stations is achieved under poor operating conditions of large amounts air input exceeding the optimum amounts of excess air (10%) [15].

**Table.4** Estimated  $NO_x$  &  $SO_2$  emissions of Khoms gas power station vs. four international standard limits [18-22]

Pollutants	Standards	USEPA	CEPA	ECE	KSA
$NO_x$	<i>Unit</i>	<i>lb/MW.hr</i>	<i>g/GJ</i>	<i>mg/m<sup>3</sup> (E.G.)*</i>	<i>lb/MBtu</i>
	<i>Standard limit</i>	1.3	40	150	0.3
	<i>Estimated value</i>	111	14,038.1	2,950	32.6233
	<i>Deviation %</i>	<b>+8,438.46</b>	<b>+34,995.25</b>	<b>+1,866.67</b>	<b>+10,774.43</b>

\* E.G. : *Emitted Gases*

A comparison of results Tables (3 & 4) indicate that the amount of  $NO_x$  emitted from the gas station is about 4 times greater than that emitted from the steam station.

Under stable meteorological condition, high concentration of  $SO_2$  and  $NO_x$  emissions can be serious occupational health hazards. Short term exposures (e.g., less than three hours) to low level of  $NO_2$  may decrease lung function in individuals with preexisting respiratory illnesses. Long-term exposures well above ambient  $NO_2$  levels may cause irreversible changes in lung structure [23]. Furthermore,  $NO_x$  tend to react with ammonia and water droplets in the atmosphere to form nitric acid and other chemicals that can interfere with the respiratory processes and damage lung tissues. Particles inhaled deeply into the lungs can cause or aggravate respiratory conditions such as bronchitis and emphysema. Sensitive groups such as asthmatics, children, elderly and heart and lung patients are recognized as risk groups if exposed to  $SO_2$ . Longer-term exposures to high levels of  $SO_2$  gases and related particles are regarded as a cause of respiratory illnesses and aggravation of heart patients conditions [24].

#### 4. Conclusion

Excessive high rates of  $NO_x$  emitted from the gas power station cannot be attributed to the chemical composition of natural gas. Emissions of  $NO_x$  from both power stations can mainly be attributed to large quantities of excess air exceeding the optimum values. When natural gas is the fuel high rates of emissions should not occur and high rates of  $NO_x$  cannot be linked to the fuel composition. Sulfur dioxide emissions are largely attributed to the combustion of HFO.

An increased demand on natural gas in power generation without responsible operational procedures, highlight a possible serious impact on the surrounding environment. It can be concluded that deficient operation is to blame for the present excessive emissions and any related environmental can sequence.



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