

UTILIZING CHEMICAL ADDITIVES TO REDUCE THE SIDE EFFECTS CAUSED BY COMBUSTION OF FUEL OIL

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Abstract

Syrian fuel oil is most common of its contents of sulphur and vanadium, i.e. 4.5% and 120 ppm respectively and during its combustion, sulphur will be converted to sulphur dioxide SO₂. In some of the boiler parts such as superheater, reheater and air heaters, some of the sulphur dioxide will be catalyzed by Vanadium to sulphur trioxide SO₃. In both cases this causes severe corrosion and deposits in addition to air pollution. To meet stringent emission standards stipulated by regulatory agencies, fuel oil is required to bring down its content of sulphur or it must be treated during its combustion. The present work aims to highlight the side effects caused by fuel oil combustion in addition to investigate the influence of special types of chemical additives in order to reduce these effects. Solids contents (ash, soot, cenosphere) as well as gas emissions produced from Zara Thermal Power Station (ZTPS), which is operated using fuel oil or sometime nature gas, have been determined. The station consists of three units with maximum capacity of 660MW. The results show that the station produces about 15 ton SO₂/hr and about 4 ton solids/day in addition to corrosion problems at several parts of the boiler and chimney. By utilizing continuous combustion-unit and fuel oil as fuel to this unit, we could apply several chemical additives such as Cu, Mn, Mn+Cr and Mn+Cu+Cr at different concentrations of 100, 175 and 250 ppm. There were worth noting results of using these additives in reducing gas emissions (SO_x, CO).

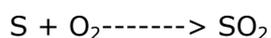
Key words: fuel oil; chemical additives; sulphur; vanadium; combustion.

1. Introduction

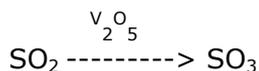
Fuel oil is a mixture of hydrocarbons containing a variety of organic compounds. Sulphur is the third most abundant element after carbon and hydrogen in fuel oil, and it is an undesirable component because it forms Sulphur dioxide SO₂ during fuel oil combustion, a part of this dioxide will be converted to Sulphur trioxide SO₃ in the boiler superheater and reheater and in both cases this causes severe corrosion and deposits. To meet stringent emission standards stipulated by regulatory agencies, fuel oil is required to bring down the sulphur content or it must be treated during its combustion. The combustion of sulphur compounds are not only causing corrosion but also contributing considerably to acid rains and air pollution^[1-4].

Various heterocyclic sulphur compounds such as naphthothiophene (NTH), benzothiophene (BTH) and its derivatives and dibenzothiophene (DBT) and its derivatives can be detected in fuel oil^[5].

In addition to Sulphur, other impurities can be existed in fuel oil like nitrogen, oxygen, water, ash, salts and different metals (V, Ni, Fe)^[6,7]. Syrian fuel oil is suffering from both environmental and technical problems as a result of its high content of sulphur, vanadium (4.5%, 120 ppm respectively). During combustion, the whole chain of events begins with the levels of sulphur content found in the fuel oil, the sulphur reacts with oxygen as:



The oxidization of sulphur dioxide to sulphur trioxide is naturally exothermic and occurs at high temperature flame where atomic oxygen is present.



Post combustion, in areas where the temperature falls below 482°C, Sulphur trioxide will react with water vapor to produce sulphur acid vapors



The sulphur acid vapors are carried off in the gas stream to the stack, and by doing so they begin to cool down rapidly. When the flue gas temperature falls to 140-160°C it reaches the dew point, this is the point where sulphur acid vapor will condensate to moisture on the surface of solid metal components such as an economizer, air heaters and stack components^[8,9].

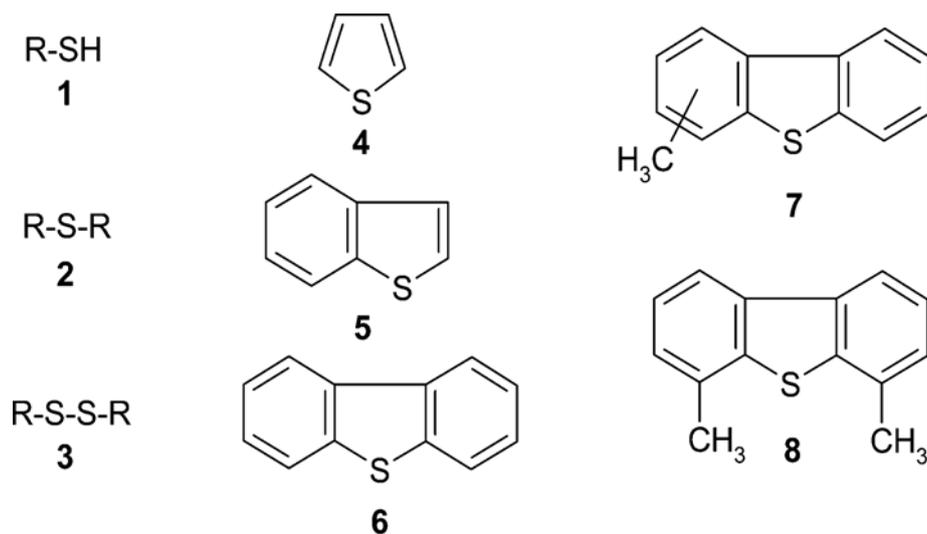


Fig. 1 Typical organosulphur compounds in fuel oil

1-thiols, 2-thioethers, 3-disulfides, 4-thiophene, 5-benzothiophene BT, 6-dibenzothiophene DBT, 7-methyldibenzothiophenes (MDBT), 8- 4,6-dibenzothiophene(4,6-DMDBT)

2. Applied methods to reduce the side effects caused by fuel oil

During the last three decades, big attention has been given to the desulphurization of oil and its derivatives like fuel oil since exhaust gases containing SO_x are a major cause of air pollution and acid rain. We can divide these methods to three categories:

- 1- The first interests to reduce sulphur before fuel oil combustion.
- 2- The second interests to reduce side effects after fuel oil combustion.
- 3- The third interests to reduce side effects during fuel oil combustion.

2.1 Applied methods to reduce sulphur before fuel oil combustion

- A. Hydrodesulphurization (HDS)^[10-14] is the most common technology used by refineries to remove sulphur from intermediate streams. This catalytic process is carried out by treating the fuel with hydrogen under severe operating conditions including the operating temperature between (200–450°C), and operating pressure of 30-100 bar. However, HDS has several disadvantages like energy intensive, costly to install and to operate, and does not work well on refractory organosulphur compounds like DBT.
- B. Extractive desulphurization^[15-18] is another alternative concept that is carried out at or around ambient temperature and pressure and without the need for hydrogen. However, this technology is not practical.
- C. Biodesulphurization (BDS)^[19-25] is often considered as a potential alternative to the conventional deep HDS processes used in refineries. In this process, bacteria remove organosulphur from petroleum fractions without degrading the carbon skeleton of the organosulphur compounds. During a BDS process, alkylated dibenzothiophenes (C_x -DBTs) are converted to non-sulphur compounds. BDS offers mild processing conditions and reduces the need for hydrogen. Both these features would lead to high energy savings in the refinery.

There are other methods to reduce sulphur in fuel oil such as treatment with acidic solutions, thioles oxidation and basic treatment^[26-27].

2.2 Applied methods to reduce side effects after fuel oil combustion^[28]:

- A- Exhausts gas purification.
- B- Exhausts gas dispersion.

2.3 Applied methods to reduce side effects during fuel oil combustion

A. Combustion water-in-oil emulsion^[29-30]: One of the successful technologies to optimize combustion is the production and the firing of stable water-in-oil emulsion. It allows a remarkable reduction of Solid-NO_x-SO₃ emissions by a complete combustion. A typical oil droplet has a diameter of 100-150 μm as shown below (fig.2). With the emulsification unit, the droplet has a diameter of (4-6 μm). Without water-in-oil emulsion, the droplets are not completely burned and a certain percentage of the fuel remains in a form of unburned carbon. With water-in-oil emulsion, there is a secondary micro explosion of the water droplets which fragments the oil droplets in thousands of tiny oil particles. Thus the combustion is almost complete, without remaining unburned carbon.

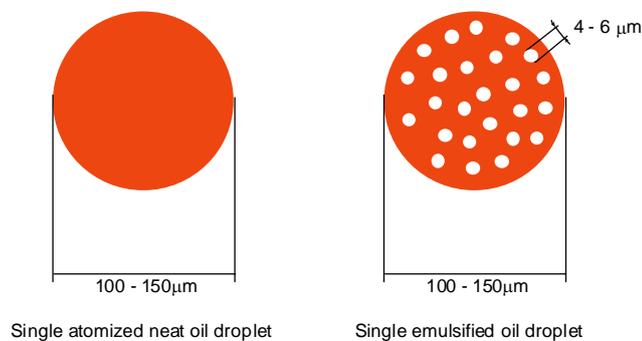


Fig.3- Vanadium oxides and its melting points

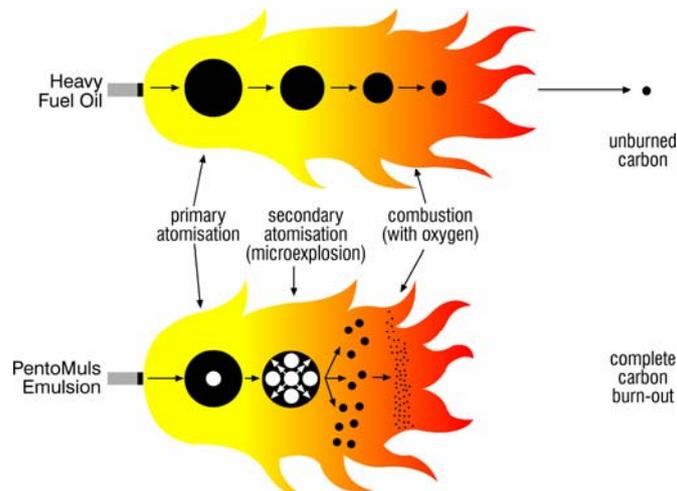


Fig.2: Combustion with and without water-in-oil emulsion

B- Fuel oil treatment by chemical additives^[31-37]

Some of metals oxides are added to fuel oil as chemical additives to improve combustion and decrease corrosion. Syrian fuel oil has high levels of vanadium, sodium and sulphur so it has a high degree of slag components and that will lead to formation a corrosive slag (high temperature corrosion) in superheaters and reheaters. When excessive amounts of excess air are available for the formation V₂O₅ and when furnace temperature exceeding (1100°F) is achieved, the slag (rang of compositions of Na₂O*V₂O₅) forms liquids expands considerably (fig.3) and they stick to the surfaces of the boiler tubes were they can cause corrosion problems and also insulate the tubes and thus resulting in bad efficiency and less availability of the boiler. Chemical additives such

as MgO reacts with these compositions which make them have higher melting point (fig.4) so that they leave the combustion chamber as dry particles. In addition the additive reacts with sulphur trioxide and that decreases the formation of sulphur acid and consequently decreasing in air heaters and chimney (low temperature corrosion).

Fuel oil has long hydrocarbon molecules which requires a longer time to burn completely so fuel oil combustion will produce too much soot in the furnace. Chemical additives act as a catalyst and scientists say that additives lower the ignition point on soot with 200 - 400°C. Another result obtained by burning the soot instead of producing soot in a boiler is that the boiler walls get cleaner and heat transfer is more efficient, consequently the overall boiler efficiency increases. The oil companies say that 1 mm of soot on the boiler walls lowers the boiler efficiency with over 2 percent. We can abbreviate advantages of chemical additives in these points:

- To eliminate high & low temperature corrosion, deposits and fouling.
- To reduce solid & SO₃ emissions and acid smut fall-out.
- To increase boiler efficiency.
- To reduce soot-blowing, cleaning and thereby increasing the availability of boiler for production.

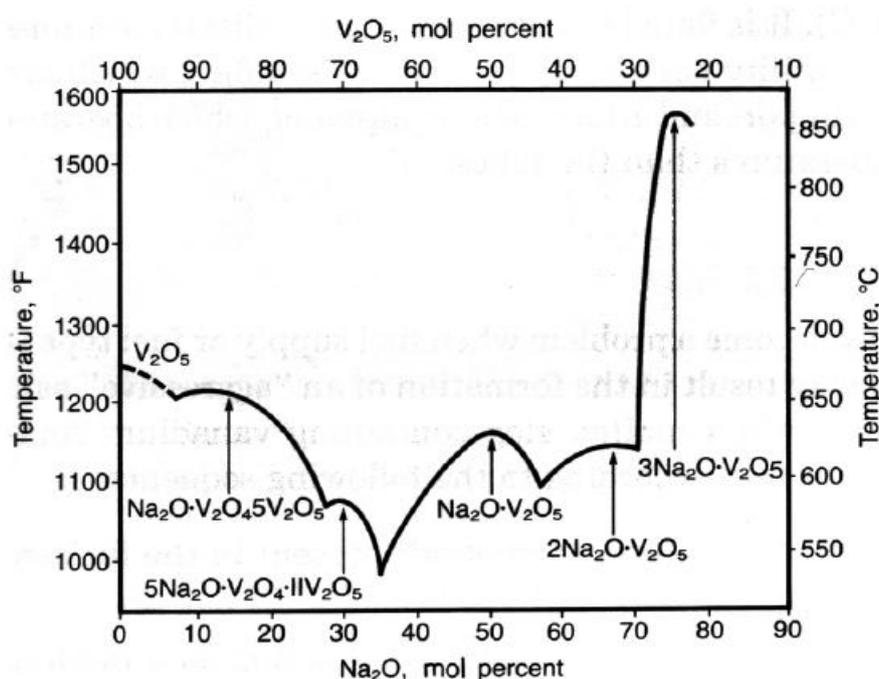


Fig.3- Vanadium oxides and its melting points

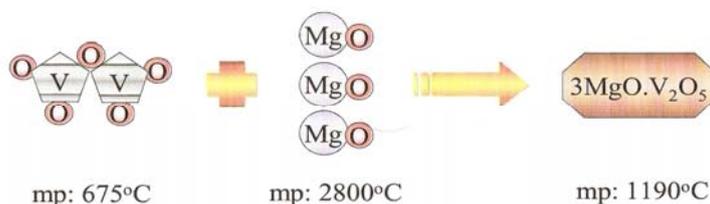


Fig.4- Reaction between magnesium oxide and vanadium oxide

3. Materials and instruments

3.1 Chemicals

Fuel oil was obtained from Homs refinery. All other chemicals were of analytical grade or better.

3.2 Instruments

Petrotest CIA2 (for flashing point). Germany, Bomb Calorimeter, PARR 1356, USA, Universal Saybolt viscometer, Rex. C410 . USA, Dry Test Gas Meter. DC-2 .Shina Gawa

Cor. Japan., Horiba- portable gas analyzer PG-250, Japan, Dustac Sampler Okano works, Ltd. .ESA-701 . Japan, Gas analyse Computer-95\CD .Japan, Continuous combustion-unit, P.A.Hilton Ltd. Engineers. Hants.England.

4. Results and Discussion

We can divide our work in this study to tow parts. The first part is to determine solid and gas emissions from Zara thermal power station (ZTPS), while the second one is to study the effect of some chemical additives on fuel oil combustion by utilizing continuous combustion-unit.

4.1 Determination of chemical and physical properties of fuel oil

Physical and chemical properties of fuel oil which is used in (ZTPS) are listed in Table 1 :

Table 1. fuel oil specification

Analysis	Unit	Result	Method
Specific density @15°C	g/cm ³	0.98	ASTM D-1298
Flashing point (open cup)	°C	175	ASTM D-92
Viscosity @ (50°C)	cst	240	ASTM D-445
Sulphur (S)	%	4.5	ASTM D-1552
Vanadium (V)	ppm	120	UOP-391
Nitrogen (N)	%	0.4	UOP-348
Ash	%	0.1	ASTM D-482
Water & Sediment	%	0.5	ASTM D-95

4.2 Determination of the exhausts gas from (ZTPS)

By utilizing gas analyzer (Horiba) , we measured the concentration of exhaust gases for unit -2 , when it is operated by fuel oil as fuel then when it is operated by nature gas as fuel ,and in the same operation conditions at loading 220 MW .(see table 2) .

Table 2. Exhaust Gases concentration in (ZTPS)

Pollutant	Concentration (when utilization gas as fuel)	Concentration (when utilization fuel oil as fuel)
SO ₂	-	1 800 ppm
CO ₂	11 %	10.3 %
CO	-	28 ppm
NO ₂	125 ppm	225 ppm

Note: The values in table (2) are the average ones and at normal operational conditions, the divergence of these values will not exceed 10% .

4.3 Determination of the solids emissions produced from ZTPS

By using Dastac device , we determined stack gas flow, its velocity, its content of dust(ash, cenosphere, soot) and predominant conditions inside stack. Moisture ratio : $X_w = 15.8\%$, concentration of dust at normal conditions: $M_{dust} = 0.073 \text{ g/ m}^3\text{N}$. From the Dustac report (fig.3): $Q'_N = 835849 \text{ Nm}^3/\text{h}$. Then, quantity of solids emissions from every unit for every day is: $Q_{dust} = M_{dust} \times Q'_{Nt} \times 24 = 0.073 \times 835849 \times 24 = 1464 \text{ Kg/day}$.

4.4 Exhaust gases quantity produced from fuel oil combustion

By conversion the volume concentration in table (2) to wt. concentration, table (3) can be reported:

Table 3. Exhaust Gases concentration in (ZTPS)from fuel oil combustion (mg/m³N)

Pollutant	Concentration, mg/Nm ³
SO ₂	5 143
CO ₂	202 321
CO	35
NO ₂	462

Gases flow at normal conditions (fig. 3) is: $Q_N = 973049 \text{ Nm}^3/\text{hr}$. Then, from table (4) and gases flow, we obtained exhaust gases quantity: $m_{\text{SO}_2} = 5143 \times 973049 = 5004 \text{ kg/hr}$, $m_{\text{S}} = 0.5 \times m_{\text{SO}_2} = 2502 \text{ kg/hr}$ (eq. 1), $m_{\text{CO}_2} = 197 \text{ ton/hr}$, $m_{\text{CO}} = 34 \text{ kg/hr}$, $m_{\text{NO}_2} = 450 \text{ kg/hr}$.

Q^*N	: 835849	m^3/h	Q_N : dry exhaust gas flue at normal conditions
Q_N	: 973049	m^3/h	Q_N : wet exhaust gas flue at normal conditions
r	: 0.812	kgf/m^3	r : gas density at practical conditions
N_2	: 86.38	%	r_0 : gas density at practical conditions
O_2	: 3.33	%	q_1 : gas flow average in Dastac
CO_2	: 10.29	%	q_m : set point of gases flow
CO	: 28	PPM	V : gas vilosity inside cheminy
r_0	: 1.255	kgf/m^3	θ_m : gas temperature inside Dastac
q_1	: 10.1	L/min	θ_s : gas temperature inside cheminy
q_m	: 10.2	L/min	V_s : draft gas volum of cheminy in work conditions
v	: 19.9	m/s	V'_N : draft gas volum of cheminy in normal conditions
θ_m	: 42	$^\circ\text{C}$	V_m : draft gas volum of cheminy in Dastac conditions
θ_s	: 126	$^\circ\text{C}$	
h	: 22.6	mmH_2O	
P_s	: -17	mmH_2O	
P_a	: 720	mmHg	
U_s	: 0.2954	m^3	
U^*N	: 0.1642	m^3/N	
U_m	: 200.154	L	

Fig.(5):photo copy at dustac report about epidemic conditions in chimney

4.5 Sulphur balance in the furnace

Sulphur concentration in fuel oil is 4.5%, and fuel oil flow is 56 ton/hr then sulphur input to furnace is $S_{\text{in}} : S_{\text{in}} = 2520 \text{ Kg/hr}$. From equation (1), we found that the sulphur output from furnace was $S_{\text{out}} : S_{\text{out}} = 2502 \text{ Kg/hr}$. Then , sulphur remain in furnace $S_{\text{rem}} : S_{\text{rem}} = S_{\text{in}} - S_{\text{out}} = 18 \text{ Kg/hr}$.

Some of this remaining sulphur converts to sulphuric acid which caused series corrosion problem in furnace components . (see figure 6)



Figure 6. Chimney wall corrosion of unit -2 at (ZTPS) (15-7-2008)



Figure 7. Continuous combustion-unit

5. Continuous combustion-unit

This unit looks like small boiler (fig.7), it is used to study several liquid fuel combustion and to study the effect of chemical additives on the combustion. Butane gas is always companion with liquid fuel during operating this unit.

Note : because of this unit is not equipped with heater , it is difficult to use absolute fuel oil as fuel in this unit (fuel oil needs to be heated to $110 \text{ }^\circ\text{C}$ before combustion).for that reason, we prepared fuel consisting of (60% fuel oil and 40% diesel oil) as a fuel to this unit, and this mixed fuel is used at all of the following experiences. Because of the target of this study is to compare between chemical additives and not to determine the absolute values of exhaust gas, it is possible to generalize our results at absolute fuel oil.

5.1 Comparison between liquid fuel combustion and gas fuel combustion

Exhaust gases are determined by utilizing (gas analyse Computer-95\CD) . Work conditions and results are shown in table (4).

Table 4. comparison between liquid fuel combustion and gas fuel combustion

	Liquid fuel	Gas fuel
Gas fuel flow, kg/hr	0.5	4
Liquid fuel flow, kg/hr	6	0
Exhaust gas temperature , °C	460	440
Cooling water temperature, °C	48	45
H ₂ S ppm	1	0
CO ppm	2 004	3
SO ₂ ppm	11	0
NO _x ppm	0	0

6. Study the effect of chemical additives on fuel oil combustion

We used in this study different metal oxides witch are diluted in naphtha at concentration of 10% v/v, then before combustion the additives were mixed with fuel oil at different concentration (100,175,250) ppm. Chemical additives, which are used , are:

- 1- Copper oxide (10% v/v in naphtha).
- 2- Manganese oxide (10% v/v in naphtha).
- 3- Manganese and Chrome oxides (10% v/v in naphtha).
- 4- Copper and Manganese and Chrome oxides (10% v/v in naphtha).

Tables (5,6,7) show results which are represents in figures (8,9).

Table 5 . Fuel oil combustion with (100 ppm) of different additives

Chemical additives	Concentration ppm			Exhaust gas temperature	Cooling water temperature
	NO _x	SO ₂	CO		
Without	0	11	2004	460°C	48°C
Cu	0	5	2190	450°C	50°C
Mn	0	6	1480	450°C	53°C
Mn+Cr	0	6	1083	460°C	51°C
Cu+Mn+Cr	0	0	300	450°C	50°C

Table 6 . Fuel oil combustion with (175 ppm) of different additives

Chemical additives	Concentration ppm			Exhaust gas temperature	Cooling water temperature
	NO _x	SO ₂	CO		
without	0	11	2004	460 °C	48 °C
Cu	0	3	1080	460 °C	51 °C
Mn	0	5	1520	450 °C	51 °C
Mn+Cr	0	6	981	460 °C	50 °C
Cu+Mn+Cr	0	0	165	460 °C	51 °C

Table 7 . Fuel oil combustion with (250 ppm) of different additives

Chemical additives	Concentration ppm			Exhaust gas temperature	Cooling water temperature
	NO _x	SO ₂	CO		
Without	0	11	2004	460°C	48°C
Cu	0	0	284	460°C	50°C
Mn	0	6	1601	450°C	47°C
Mn+Cr	0	5	968	470°C	50°C
Cu+Mn+Cr	0	0	74	460°C	53°C

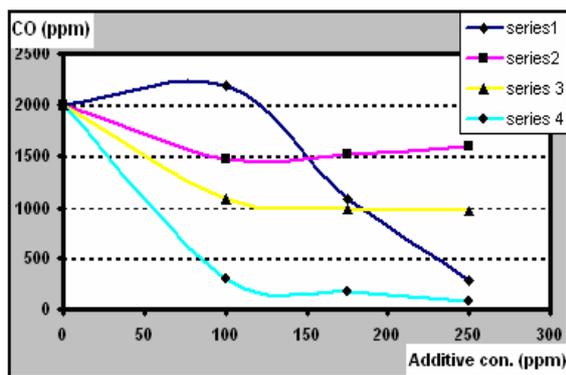


Fig 8. Chemical additives effect on emission of gas CO Series 1. Cu, Series 2. Mn, Series 3. Mn+Cr Series 4. Cu+ Mn+Cr

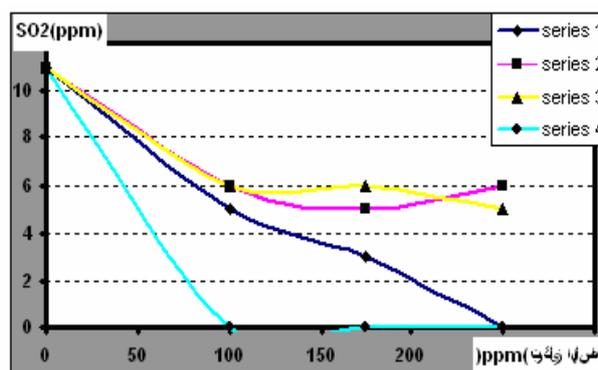


Fig 9. Chemical additives effect on emission of gas SO₂ Series 1. Cu, Series 2. Mn, Series 3. Mn+Cr Series 4. Cu+ Mn+Cr

7. Conclusion

1. Syrian fuel oil has a high content of Sulphur and Vanadium (4.5%, 120 ppm respectively), and that cause serious corrosion and pollution problem during its combustion. Our study, which is applied at Zara thermal power station ZTPS (operated by fuel oil with capacity 660 MW), show that the station produces about 15 ton SO₂/hr and about 4 ton solids/day.
3. By utilizing continuous combustion-unit and fuel oil as fuel to this unit , we applied several chemical additives (Cu , Mn , Mn+Cr , Cu+Mn+Cr) at different concentrations (100,175,250) ppm, there were clear effects of this additives in reducing gas emissions (CO , SO₂).
4. Figures (8, 9) show that elimination ratio of (CO, SO₂) did not effect seriously by increasing concentration of (Mn , Mn+Cr).
5. By adding (Mn) elimination ratio of (CO, SO₂) reaches to (20%, 45% respectively) at 250 ppm.
6. By adding (Mn+Cr) elimination ratio of (CO, SO₂) reaches to (52%, 55% respectively) at 250 ppm.
7. Figures (8,9) show that elimination ratio of (CO, SO₂) increases by increasing concentration of (Cu). It reaches to (86%, 100% respectively) at 250 ppm.
8. Additive (Cu+Mn+Cr) affect very well at emissions of (CO, SO₂). It eliminates absolutely (SO₂) at all added concentrations . And elimination ratio of (CO) reaches to (96%) at 250 ppm.
9. It is of crucial important to find absolute methods to eliminate sulphur from fuel oil before its combustion specially in developing biodesulphurization to become practical method.

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