Evaluation of the Environmental Impact of CO₂ Flare Gas Emission for three hydrocarbon Gases by Using Exergy

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Abstract—Serious global environmental problems are created by carbon dioxide emission such as global warming. The effect of CO_2 emission on the environment can be evaluated by using Exergy. The degree of deviation of a system from the environmental state can be measured by Exergy. A system is deviating when its composition, pressure & temperature are different from those of the environment. The difference can be measured by the Exergy discharge of CO_2 .

In this paper, the Exergy analyses were used as a quantitative method to compare the carbon dioxide emission on three hydrocarbon fuels, which were methane, ethylene and propane. The affect of flame temperature and excess air on the emission Exergy of ${\rm CO}_2$ were studied.

Results showed that is sensitive to excess air and flame temperature. Also results showed that the environmental impact of carbon dioxide (higher emission Exergy) increases with increasing the ratio of (C/H).

Index Terms—Emission, exergy, environmental impact, carbon dioxide.

I. INTRODUCTION

Global warming has become an issue of concern because of its negative effects on the environment. The main cause of Global warming is the release of greenhouse gases to the environment. Human activities, mainly burning of fossil fuels are increasing the atmospheric concentrations of greenhouse gasses. The resulting enhanced greenhouse effect is likely to cause global warming and climate change [1]. Carbon dioxide is one of the major greenhouse gases and part of its emissions released through flare gases. The flared gas is the gas burnt off as unusable waste gas or flammable gas, which is released by pressure relief valves during unplanned over-pressuring of plant equipment. It burns through a gas flare on Oil gathering centers and refineries (see schematic diagram of gas flare in Fig.1). In oil gathering centers the main purpose of gas flaring is to act as a safety device to protect oil and effluent water tanks from over-pressuring due to unplanned upsets. Whenever the tank is over-pressured, pressure relief valves automatically releases gas (and sometimes also liquids). The released gases and/or liquids are burnt as they exit the flare chimney. The size and brightness of the resulting flame depend upon the amount of released flammable material. In order to keep the flare system functional, a small amount of gas is continuously burnt, like a pilot light, so that the system is always ready for its primary purpose as an over-

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pressure safety system [2].

Flaring is a high-temperature oxidation process used to burn combustible components, mostly hydrocarbons, of waste gases from industrial operations. Natural gas, propane, ethylene, propylene, butadiene and butane constitute > 95% of the waste gases flared. In complete combustion (no excess air), gaseous hydrocarbons react with atmospheric oxygen to form carbon dioxide (CO_2) and water. The impact of carbon dioxide (CO_2) on environment was calculated by using Exergy.

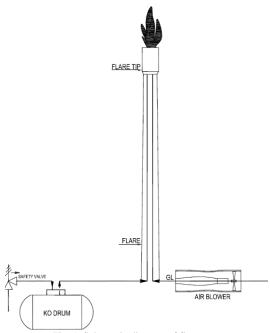


Fig. 1. Schematic diagram of flare gas.

II. EMISSION EXERGY AND ENVIRONMENT

Exergy is the maximum amount of work that can be produced by a stream of matter, heat or work as it comes to equilibrium with environment. Exergy is a useful concept that could use for analysis different kind of industry [3]. Exergy is a measure of the potential to cause change of the system or flow, as a result of not being completely in stable equilibrium with environment. Exergy is a meaningful and useful indicator of the potential for environmental impact [4], [5]. Emission Exergy is accounts for waste energy going directly to the environment.

In literature, some authors defined the emission exergy to include the physical Exergy and mixing Exergy [6], while other defined it to include only mixing Exergy [7]. In this paper Emission Exergy is divided into two Components: physical and mixing Exergies. Physical exergy is the maximum work resulting from the temperature & pressure

of the substances measured with respect to the temperature & pressure of the environment. The mixing Exergy is that portion of chemical Exergy, which is due only to material changes in composition with respect to the environment.

The environment is just a atmosphere model of finite extent at constant temperature, pressure and composition. The values of temperature, pressure and composition used in this research as environmental reference for carbon dioxide (environmental state) as follows:

- Reference Temperature is 25°C
- Reference Pressure is 1 atm
- Reference Composition is as shown in Table below [8]

Substance	Mole Fraction, $y_{i,00}$
CO ₂	0.0003

By choosing the above environmental state for carbon dioxide at atmosphere, it can be applied to account the deviation between carbon dioxide exhausted from flare and environment state, which a measure of the pollution to the environment.

III. EXERGY MODELS OF HYDROCARBON FUELS

In this paper a comparison between three hydrocarbons fuels, namely methane, ethylene and propane in terms of environmental impact were studied. The difference between the exhausted carbon dioxide from flare for three mentioned fuels in terms of temperature and composition will be calculated by Exergy with respected to the state of carbon dioxide at environmental state. The Exergy model in this research for fuel combusted at atmospheric pressure is as follows:

$$\begin{aligned} \Psi_{\text{CO}_{2}} &= y_{\text{CO}_{2}} * \left[\left(\bar{h}_{@T_{f}} - \bar{h}_{@T_{o}} \right) - T_{o} \left(\bar{s}_{@T_{f}} - \bar{s}_{@T_{o}} \right) \right] \\ &+ y_{\text{CO}_{2}} \bar{R} T_{o} ln \left(\frac{y_{\text{CO}_{2}}}{y_{i,oo}} \right) \end{aligned}$$

Now the chemical equations for each fuel will be presented at 0%, 25%, 50% & 100% excess air in addition to Exergy calculation:

1) Methane

 Methane with 0% excess air (complete combustion). The chemical reaction occurred in the combustion chamber and the CO₂ Exergy are as follow, respectively

$$\begin{aligned} \text{CH}_4 + 2(\text{O}_2 + 3.76\text{N}_2) &\to \text{CO}_2 + 2\text{H}_2\text{O} + 7.52\text{N}_2 \\ \Psi_{\text{CO}_2} &= 0.0952 * \left[\left(\bar{h}_{@T_f} - \bar{h}_{@T_o} \right) - T_o \left(\bar{s}_{@T_f} - \bar{s}_{@T_o} \right) \right] \\ &+ 0.0952 \bar{R} T_o ln \left(\frac{0.0952}{y_{l,oo}} \right) \end{aligned}$$

Methane with 25% excess air

$$CH_4 + 2.5(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 0.5O_2 + 9.4N_2$$

$$\Psi_{\text{CO}_{2}} = 0.0775 * \left[\left(\bar{h}_{@T_{f}} - \bar{h}_{@T_{o}} \right) - T_{o} \left(\bar{s}_{@T_{f}} - \bar{s}_{@T_{o}} \right) \right] + 0.0775 \bar{R} T_{o} ln \left(\frac{0.0775}{y_{i,oo}} \right)$$

• Methane with 50% excess air

$$\begin{aligned} \text{CH}_4 + 3(\text{O}_2 + 3.76\text{N}_2) &\to \text{CO}_2 + 2\text{H}_2\text{O} + \text{O}_2 + 11.28\text{N}_2 \\ \\ \Psi_{\text{CO}_2} &= 0.0654 * \left[\left(\bar{h}_{@T_f} - \bar{h}_{@T_o} \right) - T_o \left(\bar{s}_{@T_f} - \bar{s}_{@T_o} \right) \right] \\ &+ 0.0654 \bar{R} T_o ln \left(\frac{0.0654}{v_{\text{CO}_2}} \right) \end{aligned}$$

Methane with 100% excess air

$$\begin{aligned} \text{CH}_4 + 4(\text{O}_2 + 3.76\text{N}_2) &\rightarrow & \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{O}_2 + 15.04\text{N}_2 \\ \\ \Psi_{\text{CO}_2} &= 0.0499 * \left[\left(\bar{h}_{@T_f} - \bar{h}_{@T_o} \right) - T_o \left(\bar{s}_{@T_f} - \bar{s}_{@T_o} \right) \right] \\ &+ 0.0499 \bar{R} T_o ln \left(\frac{0.0499}{y_{i,oo}} \right) \end{aligned}$$

- 2) Ethylene
- Ethylene with 0% excess air (complete combustion). The chemical reaction occurred in the combustion chamber is

$$\begin{aligned} C_2 H_4 + 3(O_2 + 3.76 N_2) &\rightarrow 2 C O_2 + 2 H_2 O + 11.28 N_2 \\ \Psi_{CO_2} &= 0.1309 * \left[\left(\bar{h}_{@T_f} - \bar{h}_{@T_o} \right) - T_o \left(\bar{s}_{@T_f} - \bar{s}_{@T_o} \right) \right] \\ &+ 0.1309 \bar{R} T_o ln \left(\frac{0.1309}{y_{i,oo}} \right) \end{aligned}$$

Ethylene with 25% excess air

$$C_2H_4 + 3.75(O_2 + 3.76N_2) \rightarrow 2CO_2 + 2H_2O + 0.75O_2 + 11.28N_2$$

$$\begin{split} \Psi_{\text{CO}_2} &= 0.1061 * \left[\left(\bar{h}_{@T_f} - \bar{h}_{@T_o} \right) - T_o \left(\bar{s}_{@T_f} - \bar{s}_{@T_o} \right) \right] \\ &+ 0.1061 \bar{R} T_o ln \left(\frac{0.1061}{y_{i,oo}} \right) \end{split}$$

• Ethylene with 50% excess air

$$\Psi_{\text{CO}_{2}} = 0.0892 * \left[\left(\bar{h}_{@T_{f}} - \bar{h}_{@T_{o}} \right) - T_{o} \left(\bar{s}_{@T_{f}} - \bar{s}_{@T_{o}} \right) \right] + 0.0892 \bar{R} T_{o} ln \left(\frac{0.0892}{y_{i,oo}} \right)$$

 $C_2H_4 + 4.5(O_2 + 3.76N_2) \rightarrow 2CO_2 + 2H_2O + 1.5O_2 + 16.92N_2$

• Ethylene with 100% excess air

$$C_2H_4 + 4.5(O_2 + 3.76N_2) \rightarrow 2CO_2 + 2H_2O + 3O_2 + 22.56N_2$$

$$\begin{split} \Psi_{CO_2} &= 0.0677 * \left[\left(\bar{h}_{@T_f} - \bar{h}_{@T_o} \right) - T_o \left(\bar{s}_{@T_f} - \bar{s}_{@T_o} \right) \right] \\ &+ 0.0677 \bar{R} T_o ln \left(\frac{0.0677}{y_{i,oo}} \right) \end{split}$$

- 3) Propane
- Propane with 0% excess air (complete combustion). The chemical reaction occurred in the combustion chamber is

$$\begin{split} C_{3}H_{8} + 5(O_{2} + 3.76N_{2}) &\rightarrow 3CO_{2} + 4H_{2}O + 18.8N_{2} \\ \Psi_{CO_{2}} &= 0.1163 * \left[\left(\bar{h}_{@T_{f}} - \bar{h}_{@T_{o}} \right) - T_{o} \left(\bar{s}_{@T_{f}} - \bar{s}_{@T_{o}} \right) \right] \\ &+ 0.1163 \bar{R} T_{o} ln \left(\frac{0.1163}{y_{i,oo}} \right) \end{split}$$

• Propane with 25% excess air

$$C_3H_8 + 6.25(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 1.25O_2 + 23.5N_2$$

$$\begin{split} \Psi_{\text{CO}_2} &= 0.0945 * \left[\left(\bar{h}_{@T_f} - \bar{h}_{@T_o} \right) - T_o \left(\bar{s}_{@T_f} - \bar{s}_{@T_o} \right) \right] \\ &+ 0.0945 \bar{R} T_o ln \left(\frac{0.0945}{\gamma_{i,oo}} \right) \end{split}$$

• Propane with 50% excess air

$$C_{3}H_{8} + 7.5(O_{2} + 3.76N_{2}) \rightarrow 3CO_{2} + 4H_{2}O + 2.5O_{2} + 28.2N_{2}$$

$$\Psi_{CO_{2}} = 0.0796 * \left[\left(\bar{h}_{@T_{f}} - \bar{h}_{@T_{o}} \right) - T_{o} \left(\bar{s}_{@T_{f}} - \bar{s}_{@T_{o}} \right) \right]$$

$$+0.0796 \bar{R}T_{o} ln \left(\frac{0.0796}{y_{i,oo}} \right)$$

Propane with 100% excess air

$$C_3H_8 + 10(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 5O_2 + 37.6N_2$$

$$\begin{aligned} \Psi_{\text{CO}_2} &= 0.0605 * \left[\left(\bar{h}_{@T_f} - \bar{h}_{@T_o} \right) - T_o \left(\bar{s}_{@T_f} - \bar{s}_{@T_o} \right) \right] \\ &+ 0.0605 \bar{R} T_o ln \left(\frac{0.0605}{y_{i,oo}} \right) \end{aligned}$$

IV. RESULTS AND DISCUSSIONS

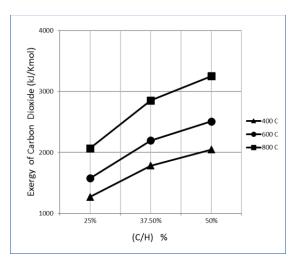


Fig. 2. Exergy of carbon dioxide versus (C/H) at different flame temperatures.

The effect of ratio of carbon on Exergy of carbon dioxide at different flame temperatures is shown in Fig. 2. The results are obtained at humidity ratio of 60% and excess air of 0%. The fuel assumed to be at the ambient conditions of 25°C and 1 atm. As is shown in Fig. 2, the Exergy of carbon increases with the increase in amount of $\left(\frac{c}{\mu}\right)$. The Exergy of

carbon dioxide increases with the increase of flame temperature.

The effect of flame temperature on Exergy of carbon dioxide for three hydrocarbon fuels namely; methane, ethylene and propane is shown in Fig. 4. The results are obtained at humidity ratio of 60%, excess air of 0% and flame temperature with values of 400 °C, 600 °C & 800 °C. The fuel assumed to be at the ambient conditions of 25 °C and 1 atm. As it is shown in Fig. 3, the Exergy of carbon increases with the increase of flame temperature for the three hydrocarbon fuels. This is because the increase of the flame temperature leads to flare gases with high temperature to be wasted; which means high Exergy of carbon dioxide.

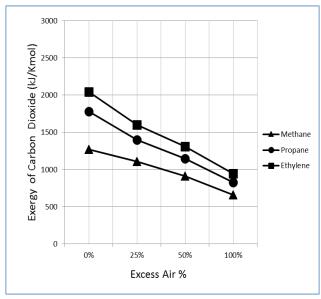


Fig. 3. Exergy of carbon dioxide versus excess air for three hydrocarbon fuels.

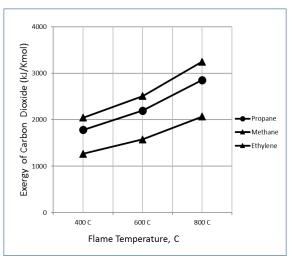


Fig. 4. Exergy of carbon dioxide versus flame temperature for three hydrocarbon fuels.

V. CONCLUSION

The present research investigate the environmental impact of three hydrocarbon fuels; namely methane, ethylene and propane. The environmental impact of these fuels were calculated based on Exergy analysis. The results direct the attention to that the environmental impact of fuel is minimized as the carbon to hydrogen ratio decreases. Also, results showed that the Exergy of carbon dioxide increases

with increasing flame temperature and decreases with increasing excess air. We included that, it is good environmentally to combust hydrocarbon fuel with low ratio of $\left(\frac{C}{H}\right)$ and high percentage of excess air.

NOMENCLATURE

\overline{R}_{u}	Molar universal gas constant, kJ kmol ⁻¹ K ⁻¹
\overline{h}	Molar specific enthalpy, kJ kmol ⁻¹
- S	Molar specific entropy, kJ kmol ⁻¹ K ⁻¹
T_f	Flame Temperature, °C
T_o	Environment Temperature, °C
y_{co_2}	Mole fraction of carbon dioxide
$\left(\frac{C}{H}\right)$	Carbon to Hydrogen ratio
ψ_{co_2}	Discharge Exergy of CO ₂

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