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1	Exergy and Energy Analysis of Organic Rankine Cycle Integration in the
2	Carbon Black Industry using Pinch Technology
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18 Abstract

19 Industrial Carbon black production is a petrochemical process that has high level of waste heat and 20 emissions. Main points of CB process include furnace and stack lines. Also, the use of different feedstocks can be effective in level of waste heat and amount of emission pollutants. So the main 21 objective of this research use from the pinch technology in CB process in order to minimize the 22 23 level of waste heat by utilization of waste heat recovery (WHR) applications for power generation. 24 By numerical investigation and modelling of WHR in furnace and stack points, can be defined best location for power generation in CB process. Moreover, through the analysis of Organic 25 26 Rankine Cycle (ORC) systems integrated with WHR from both energy and exergy perspectives, 27 second target to enhance their thermal efficiency. The results indicate that the presence of blowers on stacks leads to an increase in RoHR and RoHC. In order to determine the optimal location for 28 29 power generation cycle installation, an ORC energy and exergy analysis was conducted. The results showed that the energy and exergy values at the SLC stack were higher than those at the 30 31 HLC point. Also, numerical results showed the points that have suitable thermal efficiency and rate of exergy of WHR where have higher temperature gradient than other points. So SLC ($\dot{E}x_{WHR} = 166.7 \, kW$) and HLC ($\dot{E}x_{WHR} = 136.1 \, kW$) stacks integrated with blower are the optimal location for WHR utilization in the CB production process.

Keywords: Pinch Technology, Energy Losses, Organic Rankine Cycle, Waste Heat Recovery, Thermal Efficiency.

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41 Introduction

Increasing productivity and managing waste heat are major engineering challenges in petrochemical industries. Countries in the Middle East have a significant impact on the generation of energy sources. The availability and affordability of fossil fuels have made it feasible to operate petrochemical plants [1]. The main sources of heat production and CO2 emission are petrochemical and thermal power plants. Concerning the threats of global warming and climate change, there is a decline in heat management and an increase in CO2 emission [2,3].

One of the major petrochemical industries that have waste heat and production emissions is the 48 carbon black process. CB production is the primary material for tires, conveyor belt, cables, ink 49 and paint, rubber product and dry batteries [4,5]. In the CB process plant, 2 main points have high 50 level waste heat that include thermal furnace and stack lines. Due to the use from high viscosity 51 mineral oils and raw materials as a feedstock on CB process plant and feed gasification process 52 53 for carbon production, amount of waste heat from furnace and exhaust lines are too much [6]. For 54 the production of CB, need to provide gasification condition to make a mixture of carbon components. CB was produced after the steam flow passes through carbon catalyst and pyrolysis 55 unit. The type of furnace and quenching process affect the quantity and quality of carbon black 56 57 production [7,8]. In the carbon black industry, furnace are included a type of thermal cracker 58 furnace that consist of important elements such as the supplement and preheating feedstock unit, 59 evaporation or injection fuel system (fuel inlet), air injection and blowers elements, insulation wall, gasifier or furnace box element, pressure and temperature furnace box controlling system, and 60

61 exhaust unit. Olefin furnaces that use for ethylene production are suitable example from cracking furnace category. The Steam flow produced in the outlet of furnace box have 800 °C to 900°C 62 [9,10]. There are various approaches to optimize the chemical process and waste heat of cracking 63 furnaces. Thermodynamic and environmental approaches are among the most important of them. 64 Simulate thermo-chemical condition by mathematical methods are used to investigate the post-65 combustion products of these furnaces. Recent research tried to reduced CO₂ emission on thermal 66 cracking furnace by utilize LCA method integrated with exergy mapping information, 67 investigation of correlation between various thermo-chemical factors and use of equipment by 68 machine learning method [11–13]. Moreover use CFD simulation for optimize heat transfer on 69 furnace, reduce coke decomposition on preheating feed coil and use organic solvent for 70 regeneration carbon capture from post-combustion process as a renewable approach are newest 71 72 R&D field for thermal cracking furnace and olefin production unit [14,15].

Nomenclatur	e	Abbreviation	
C_p	specific heat $\left(\frac{kJ}{kg.k}\right)$	CB	Carbon Black
Ėx	rate of exergy (kW)	2E	Energy and Exergy
h	enthalpy $\left(\frac{kJ}{kg}\right)$	EPA	Environmental Protection Agency
Q_{in}	inlet heat (kJ)	ECO	Economizer
Q_{out}	outlet heat (kJ)	EVAP	Evaporator
Q_{hr}	heat released (kJ)	FAR	Fuel Air Ratio
Q_w	heat exchanged (kJ)	HLC	Hard Line Combustor
ṁ	mass flow rate (kg/h)	HRS	Heat Recovery System
₿ V _{fuel}	volumetric flow rate (fuel, $\frac{m^3}{min}$)	ORC	Organic Rankine Cycle
<i>V</i> _{air}	volumetric flow rate (air, $\frac{m^3}{min}$)	RoHR	Rate of Heat Released
р	pressure (kPa)	RoHC	Rate of Heat Capacity
Р	power (kW)	SLC	Soft Line Combustor
v	volume (m ³)	WHR	Waste Heat Recovery
u	Stoichiometric Ratio (carbon)	Greek s	ymbol
v	Stoichiometric Ratio (hydrogen)	arphi	Equivalence Ratio (fuel to air)
w	Stoichiometric Ratio (oxygen)	ρ	Density $(\frac{kg}{m^3})$
х	Stoichiometric Ratio (nitrogen)	η	Efficiency
у	Stoichiometric Ratio (sulfur)		

74 Due to CB process plant is similar to ethylene production, must be used new methods for optimize 75 waste heat [16]. Also the economic challenges and the use of processing equipment in macro-scale 76 dimensions as a limitation factors, it was suggested to define a mathematical model based on energy 77 perspective to minimize the amount of waste heat on CB process plant.

78 From energy management engineering perspective, one of the common methods for waste heat management in petrochemical plants is the use of pinch technology. Pinch Technology is a strategy 79 for managing costs, maximizing energy efficiency, and minimizing pollution impacts in energy 80 systems. Utilizing waste heat recovery (WHR) techniques in petrochemical plants lead to increased 81 82 thermal efficiency and reduce CO_2 emission [17,18]. Utilizing pinch technology in conjunction 83 with a waste heat recovery and power generation system boosts thermal efficiency and economic effectiveness in the petrochemical industry. Also, the use of pinch plants reduces waste water and 84 85 pollution impacts from the refining industry [19,20].

For the Petrochemical plant, The WHR can be used to optimize waste heat and reduce CO₂ 86 emissions [21]. The suitable cost-effective location for establish of waste heat recovery application 87 is where the level of emissions and waste heat is significant. In most petrochemical plants, the flare 88 gas is known as a high temperature area. Therefore, the use of the waste heat recovery application 89 in this location can be effective [22,23]. By utilizing of thermodynamic cycles, WHR can be used 90 to produce simultaneously heat and electricity. This simultaneous production is possible by 91 combining WHR application with thermodynamic power cycles. WHR establishes the Bryton and 92 93 Organic Rankine cycle (ORC) as main power coupled vapor thermodynamic cycles for boosting thermal efficiency [24]. The adaptability of WHR to different temperature conditions has led to 94 use as a suitable application for power generation. Classification of WHR based on temperature 95 96 range indicated that this technique is commonly used to improve thermal efficiency. WHR at high 97 temperature (more than 400°C), medium temperature (400°C - 100°C), and low temperature (less 98 than 100° C) [25]. A comparison between the temperature range of the WHR application and the maximum heat produced in the CB process plant indicates that if there is a need to recycle the 99 100 waste heat from each elements, it should be used high temperature WHR application on furnace, 101 stacks and other thermal equipment. Also use of many kinds of blowers as a factor for forced 102 intake air to the furnace and exhaust flow suction can be changed enthalpy. So the origin of waste heat source can be included many of the locations [26,27]. Utilizing a many kinds of cracking 103

furnaces or gasification systems in petrochemical plant that be integrated with WHR systems, for instance, is crucial [28,29]. Changes in the volumetric flow rate of supercritical H₂O and air intake in cracking furnace leads to impaired the stoichiometric equilibrium of the combustion reaction. The WHR system in the stack must include absorption equipment for preventing condensation of supercritical H₂O in power generation elements. Corrosion results from supercritical H₂O species an important challenge in the way of designing power generation equipment is CB process plant[30].

111 In a cement plant, using WHR to produce 80MW more power instead of 221,690 kg CO2/year demonstrated an increase in power output and a reduction in CO₂ emissions. In the cement unit, 112 113 the combination exergy-economic method used to WHR optimized the cost-benefit factor [31]. Increasing temperature and influence of heat and mass transport to discovering comfort location 114 115 for generation, it has required the use of a heat pump equipment in the ORC. In addition, linking the absorption elements with power generation cycle causes reduced latent evaporation enthalpy 116 117 of post - combustion production and leads to reduce the level of heat power regeneration. This condition causes reduce cost-effective criterion in petrochemical plants. The results of 2E analysis 118 119 and research to find suitable working fluid indicated that the optimal performance of the ORC depended on design of the cycle and enthalpy level investigation of working fluid characteristic on 120 121 the thermal efficiency of ORC and WHR demonstrated that waste gas can be used as a working fluid. So CO₂ emission that results from the consumption of light feedstocks can be used as a 122 123 suitable working fluid [32,33]. Consequently, using form supercritical gas phase CO₂, due to high level of specific heat, can lead to reduce environmental impact and waste heat. In addition to the 124 125 benefit of employing waste flue gas as a working fluid, is decreased corrosion effect in the stack and improved conditions for flue gas recycling. Additionally, the Brayton and refrigeration cycles 126 can be combined to increase the thermal efficiency of these systems [18,34]. 127

According to the characteristics that described for the CB process plant, optimizing level of waste heat is considered suitable plan for use of WHR application. As well as the use of ORC indicated this capability that can reduced the impact of environment pollution Simultaneously in CB process. The similarities between the olefin petrochemical process and CB plant thermal equipment caused that the investigations for reducing the waste heat of these plants carried out with the same procedure. Therefore, the use of industrial process models to solve environmental impacts, along with mathematical modeling based on numerical methods to optimization of waste heat is mentioned as the main innovation of this research. So the main objective of this study is to perform the exergy and energy analysis of a kind of the CB process plant. The basic focus was on improved thermal efficiency and reduce environmental impact of a furnace waste heat and stack lines in the CB plant. The investigations indicated impact of incorporating the WHR application in different production line scenarios, including the stacking process and post-filtering procedure. So tried to that incorporated energy and exergy analysis for WHR system in order to improve thermal efficiency and reduce environment impacts.

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143 Materials and Methods

Given the significance of power generation through heat recovery and the need to minimize 144 pollutant emissions in the CB process, it is crucial to establish a thermodynamic framework for 145 the CB process. The complexity of gasification phenomena in cracking furnace and other 146 production process components impedes Correct and complete comprehension from the effect of 147 thermal factors on the overall system efficiency [35]. To simplify the investigation of energy and 148 exergy, specific and waste heat of each elements must be analyzed. From a thermodynamic 149 approach, these parts were identified as critical locations for waste heat. So was tried to describe 150 the critical waste heat points in this section by definition diagram of the CB process plants. After 151 conducting a thermodynamic analysis on cracking furnace and stack lines, an equation was 152 153 developed to calculate thermal capacity. Eventually, with the support of energy and exergy analysis, it became possible to compute thermal parameters and determine accessible work. 154

155 *Identification of CB process plant and measurement instrument*

According to EPA standards, the manufacturing of CB (carbon black) is an environmentally harmful activity. This product is accompanied by numerous pollutants due to use gasification process on cracking furnace and use light hydrocarbons, raw materials and naphtha as feedstock [36]. Fig. 1 depicted the cracking furnace as hard line combustor (HLC) and the ducts connecting the combustor to the stack in the CB process.



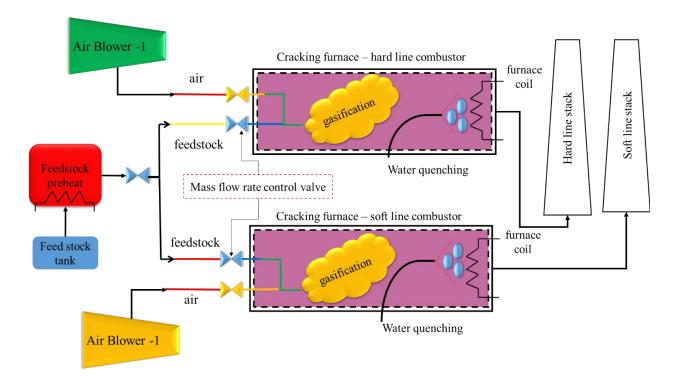
Fig. 1. Cracking furnace and ductwork connected to a furnace stack.

Typically, series or parallel cracking furnace arrangement are utilized in the CB process plant. 161 Based on range of equivalence ratio parameter, the air excess ratio is greater in parallel mode, and 162 complete combustion will occur in this furnace [37]. In series mode, however, thermal efficiency 163 is greater than in parallel, because waste gas from one of a furnace serves as feedstock for another. 164 165 In actuality, increasing volume fraction of CO in Post-combustion products indicates the lack of ideal combustion conditions for release maximum chemical energy from consumption of 166 feedstocks. So need to provide conditions to use waste gas as auxiliary feedstock in other upstream 167 furnaces. Accordingly, when the primary feedstock is heavy petrochemical or mineral products, 168 the configuration of CB process should be series arrangement [38]. Considering the arrangement 169 of furnaces, their performance and feedstock, the quantity of waste heat in both configurations 170 have high level, and the capacity to recycle the waste heat from furnaces and exhaust pipe lines 171 from stacks is sufficient to apply the WHR system. 172

For online controlling important factors on CB process used from electromagnetic and vortex flowmeters, piezoelectric pressure transducer, gas actuated thermometers and extractive gas analyzer. All of the measuring factors were monitored on controlling room and operators. Table 1 describe the location of sensors and accuracy of measurements. Due to continuous monitoring procedure on CB process, data acquisition carried out by determining the time step of half an hour. Then the enthalpy, mass rate of fluid, temperature and volume fraction of chemical compounds was obtained from Output log files.

Table 1. location of sensors in CB process and accuracy

Type of sensor	location	accuracy	
electromagnetic flowmeter	feedstock line, exhaust line	≤ 0.2%	
floren of a	blower, compressor, high	0.2%~0.5%	
vortex flowmeter	pressure air lines		
piezoelectric pressure	furnace, flare gas, high	$\leq 0.25\%$	
transducer	pressure lines		
gas actuated thermometers	furnace, flare gas, preheating	$\pm 1\%$	
(NTC/PTC)	feedstock lines		
extractive gas analyzer	furnace, flare gas	2% ~ 4%	



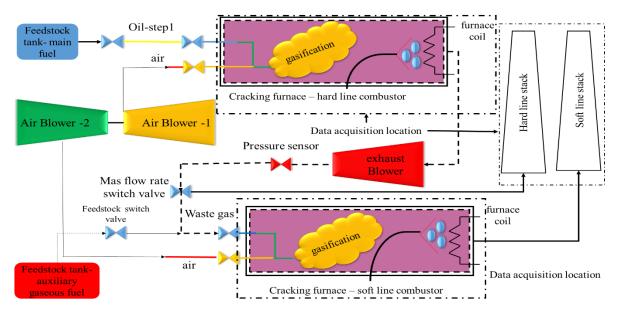


Fig. 2. Technical process diagram and configuration of carbon black plant . **a**. parallel configuration **b**. series configuration.

181 Thermochemical properties of Combustion phenomenon on CB production lines

According to Fig. 2, in order to produce CB of sufficient grade, used from oils that have high viscosity as feedstock. Complete combustion, on the other hand, consists of air fuel mixture as the reactant. Amount of mass fraction of combustion products depend on the equivalence ratio parameter. Generally, gasification process have produce many product compound. To create gasification conditions, must be increased temperature and reduce equivalence ratio. Therefore, it should be regarded a phenomenon of gasification to make it more comparable to the CB process. Eq. (1) outlines the chemical reaction for complete combustion under steady-state conditions [39].

$$C_{u}H_{v}O_{w}N_{x}S_{y} + \left(u + \frac{v}{4} - \frac{w}{2} + y\right)(O_{2} + 3076N_{2}) \rightarrow uCO_{2} + \frac{v}{2}H_{2}O + ySO_{2} + [3076\left(u + \frac{v}{4} - \frac{w}{2} + y\right) + \frac{x}{2}]N_{2}$$
(1)

189 That u, v, w, x and y shown the stoichiometric ratios of each component in chemical reaction.

Fuel equivalence ratio (φ) has define that the condition of mixture on cracking furnace is lean or rich. Eq. (2) describes equivalence ratio formula that can be calculated using mass flow rate of air for producing lean or rich burn mixture.

$$\varphi = \frac{\frac{(\dot{v}_{fuel})_{atr}}{(\dot{v}_{air})_{stoichiometric}}} (2)$$

193 That \dot{V}_{fuel} and \dot{V}_{air} are volumetric fuel and air ratio (m^3/min)

Using crude coal oil in the CB process and water quenching caused by increasing evaporated H_2O volume fraction in a part of furnace. Increasing evaporated H_2O volume fraction causes Disturbance of equilibrium on combustion reaction chain. As well as, the water quenching process has a major effect on heat and mass transfer because of the quickly phase changing. Therefore, heat transfer on firebox of cracking furnace consist of convection and radiation types. So used heat balance on the surface of reactor (2D) to describe heat transfer on cracking furnace by Eq. (3). [40]

$$\sum_{j=1}^{N} S_i S_j E_{r,j} + \sum_{j=1}^{M} G_j S_i E_{g,j} - \varepsilon_i A_i E_{w,i} + h_i A_i (T_{g,i} - T_{w,i}) = Q_{w,i}$$
(3)

That S_i and S_j are surface zone, $E_{r,j}$, $E_{g,j}$ and $E_{w,i}$ are black body emissive power of zone, G_j gas properties, ε_i emissivity, A_i area, h_i convective heat transfer coefficient, $T_{g,i}$ and $T_{w,i}$ are wall Temperature measured from different points of cracking furnace.

Because of the unsteady state condition on fire box of cracking furnace and difficulty of applying the formula to calculate heat transfer, used heat release rate (HRR) of combustion ralation by Eq. (4). HRR describes the rate of thermochemical energy exchange of feedstocks during the combustion process [41].

$$dQ_{hr} = \frac{k(T)}{k(T) - 1} p dV + \frac{k(T)}{k(T) - 1} V dp + dQ_w$$
(4)

That k is the specific heat ratio variable and dQ_w is the rate of heat exchanged by furnace wall temperature.

The heating value and equivalence ratio of commercial feedstocks used in the production of CB are important parameters for describing the lean and rich burning mixtures, as well as the amount of heat released during the combustion reaction. Table 2 explains the heating value and equivalence ratio of the fuels used as feedstock.

Type of fuel	arphi	Heat value $(\frac{MJ}{kg})$
Natural gas	0.7-1.4	42-55
Diesel fuel	0.66.2	42-46
Crude oil	1-1.56	42-47

Table 2. The heating value and equivalence ratio of feedstock fuels [42].

Bituminous coal	1.46-7.1	17.4-23.9
light naphtha	0.5	48.1

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In stack line, Heat transfer takes between the stack wall and the waste gas. So should be define enthalpy and entropy on whole domain. Eq. (5) used to calculation of specific heat coefficient, enthalpy and entropy of waste gas in stack line.

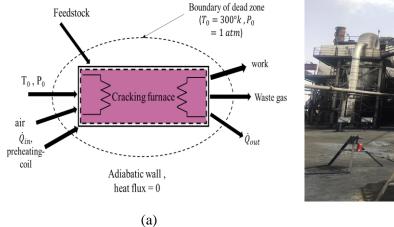
$$C_{P_{wg}} = AT^{6} + BT^{5} + CT^{4} + DT^{3} + ET^{2} + FT + G$$

$$h = \int_{T_{inlet}}^{T_{outlet}} C_{P_{wg}}(T) dT, s = \int_{T_{inlet}}^{T_{outlet}} C_{P_{wg}}(T) \frac{dT}{T}$$
(5)

That T_{outlet} and T_{inlet} are temperature of stack inlet and outlet, $C_{P_{wg}}$ specific heat coefficient of waste gas, A,B,C,D,E,F,G are fitting curve coefficient of waste gas.

219 Thermodynamic approach on CB process

To address the four locations of waste heat in the CB process plant, it is necessary to measure the mass flow rate of product species in the production line and the enthalpy at each point. Also should be determined the intended configuration of elements of CB process to beginning thermodynamic calculations. Therefore, series configuration of CB process equipment was chosen. In order to measure the mass flow rate, enthalpy and other specific of waste gases by sensors, Furnace and stack elements were considered. Fig 3 describe thermodynamic zone of critical element and points of measurement.





(b)

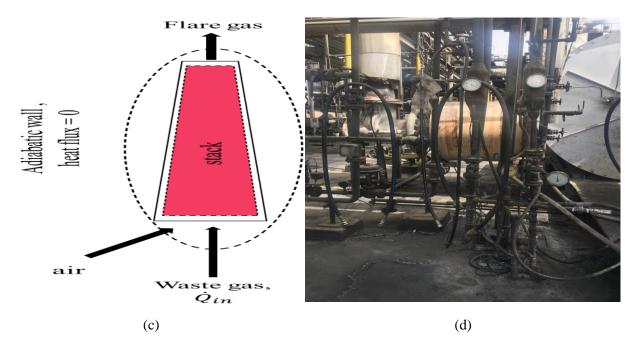


Fig. 3. Main points of CB process as thermodynamic and measurment zone. **a**. furnace system **b**. location of adjust sensors on furnace **c**. stack zone **d**. location of adjust sensors on stack

Due to the importance of temperature characteristics at each stage, it is necessary to examine the process from both an energy and exergy perspective. Subsequently, the WHR capacity should be calculated to determine the optimal location for WHR equipment in CB process lines. The method of reporting data and the configuration of combustors indicate that the SLC and SLC stack are preheating equipment for the HLC line. Therefore, should be analyze the energy and exergy of the HLC line.

Table 3. mass flow rate and thermodynamic parameters of waste gases of critical points

points	SLC	HLC	SLC stack	HLC stack
points	point 1 (kmol/h)	point 2 (kmol/h)	point 3 (kmol/h)	point 4 (kmol/h)
H2O	70.9	70	161	278.4
H2	27.1	24.1	61.5	96
N2	82.1	85.4	186.5	339.7
AR	1	1.1	2.4	4.2
CH4	1.2	0.6	2.8	2.5
СО	18.6	22.2	42.2	88.2
CO2	4.9	5.2	11.1	20.7

C2H2	0.5	1.4	1.2	5.7
Total	206.3	210	468.7	835.3
$ \rho_{actual}(rac{kg}{m^3}) $	0.5365	0.5731	0.5114	0.5463

Tables 3 and 4 shown the thermodynamic parameters of waste gases, mass flow rate, temperature,pressure, and enthalpy in critical points of CB process plant.

points SLC HLC SLC stack HLC stack Temperature (°C) 232 210 220 220 mass rate $\left(\frac{kg}{h}\right)$ 4441 4640 10051 18460 std volume rate 4622 4706 10506 18723 $\left(\frac{Nm^3}{h}\right)$ Pressure (kPa) 5 4.977 0.198 0.234 Enthalpy (Mkcal/h) 4.389 1.103

Table 4. Thermodynamic and initial conditions of waste gases on the each point.

According to the T-s diagram, waste heat source which has a high temperature gradient should be used to regeneration power. A high temperature gradient is the result of a large temperature difference between the cracking furnace as heat power source and exhaust line .So, heat transfer between lines and WHR system is based on temperature gradient. Fig. 4 shows the heat transfer for a sample WHR application integrated to a combined cycle power generation.

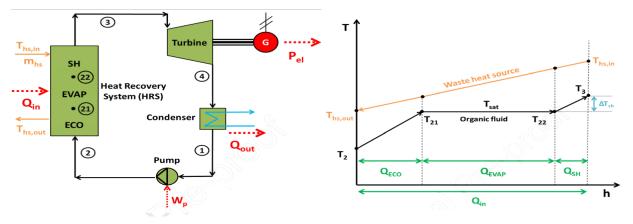


Fig. 4. T-s diagram for sample power generation cycle [43].

Calculate the real capacity of each line, which is the amount of heat exchanged into electricity,
using the T-s diagram. Therefore, should be compute energy balance and exergy indices to evaluate
WHR capacity. By utilizing a preheater, an economizer, or by recycling heat exchanger elements,
WHR can be used in ORC. Before conducting Energy and exergy study on ORC, must be
explained initial and boundary conditions. Table 5 outlined the region and initial condition of
ORC.

Table 5.	The initial	and boundary	conditions	of ORC.
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variable	value
<i>P_{in,WHR}</i> (kPa)	5000
<i>P_{out,condenser}</i> (kPa)	10
range of T_{in} WHR (°k), T_{state}	$450 < T_{in,WHR} < 550, 300$
Type of working fluid (real gas)	Steam
$C_{p \ steam}(rac{kJ}{kg.^{\circ}k})$	$1.926 \le C_p \le 1.984$

After defining initial and boundary conditions for implementation of ORC, began the energy and exergy investigation of an ORC by estimating the input heat available to the cycle. Each point's available input heat is equal to its heat loss. Therefore, Eq. (6) is utilized to calculate the rate of heat capacity (RoHC) at each site.

$$Q_{in,WHR} = m_{orc} \cdot c_{p,WHR} \cdot (T_{out,WHR} - T_{in,WHR})$$
(6)

That m_{orc} is the input mass on WHR element, h_{out} is the output enthalpy and h_{in} is the input enthalpy.

Gas turbine element on ORC is the power generator. So Eq. (7) describes the formula used to calculate output work and efficiency of the gas turbine.

$$w_{net,turbine} = m_{orc}. (h_{in,turbine} - h_{out,turbine})$$

$$h_{in,turbine} = h_{out,WHR}$$

$$\eta_{is,turbine} = \frac{h_{in,turbine} - h_{out,turbine}}{h_{in,turbine} - h_{out,turbine,is}}$$
(7)

- That $w_{net,turbine}$ is work produced from gas turbine, $\eta_{is,turbine}$ is the thermal efficiency of gas turbine in isentropic condition.
- 257 Other elements on ORC such as condenser and pump follow relations described in Eq. (8).

$$Q_{out,condenser} = m_{orc}. (h_{in,condenser} - h_{out,condenser})$$

$$h_{in,condenser} = h_{out,turbine}$$

$$w_{pump} = \frac{m_{orc}. (h_{out,pump} - h_{in,pump})}{\eta_{motor}}$$

$$h_{in,pump} = h_{out,condenser}$$
(8)

Thermal efficiency of ORC depends on the difference between power consumption and generation.
So, Eq. (9) describes thermal efficiency of ORC.

$$P_{net} = (\eta_{mc}). (w_{turbine}) - w_{pump}$$
$$\eta_{net,ORC} = \frac{P_{net}}{Q_{in,WHR}}$$
(9)

260 That η_{mc} is the electromechanically efficiency and $\eta_{net,ORC}$ is the thermal efficiency of ORC.

In order to calculate the thermal efficiency of a system, the thermal efficiency of WHR equipment must be defined. The temperature of waste gases is greater than the reference temperature; hence, this discrepancy can impact the thermal efficiency of WHR systems [44]. The thermal efficiency of WHR element and system will be described by Eq. (10).

$$\eta_{WHR} \approx \frac{T_{in,WHR} - T_{out,WHR}}{T_{in,WHR} - T_0}$$

$$\eta_{sys} = \eta_{net,ORC} \cdot \eta_{WHR}$$
(10)

That T_0 is the reference temperature, η_{WHR} is the thermal efficiency of WHR element and η_{sys} is the efficiency of system.

- 267 Exergy efficiency of ORC depends on temperature gradient of WHR elements and net power. So
- exergy of the input heat into WHR and Exergy efficiency of ORC can be describe by Eq. (11).

$$Ex_{WHR} = m_{WHR} \cdot c_{p,WHR} \cdot \left(T_{out,WHR} - T_{in,WHR} \right) - m_{WHR} \cdot c_{p,WHR} \cdot T_0 \cdot \ln\left[\frac{T_{in,WHR}}{T_{out,WHR}}\right]$$
(11)

$$\eta_{ex,ORC} = \frac{P_{net}}{Ex_{WHR}}$$

269

270 Because of the different values of $T_{out,WHR}$ and T_0 , $\eta_{ex,sys}$ can be described by exergy of input 271 heat into WHR as Eq. (12).

$$Ex_{input,WHR} = m_{WHR}. c_{p,WHR}. (T_{in,WHR} - T_0) - m_{WHR}. c_{p,WHR}. T_0. \ln[\frac{T_{in,WHR}}{T_0}]$$
$$\eta_{ex,sys} = \frac{P_{net}}{Ex_{input,WHR}}$$
(12)

272

273 **Results and Discussion**

To determine the optimal WHR, the thermodynamic cycle of the CB production process must be examined. Calculating rate of heat capacity (RoHC), energy and exergy analysis for WHR, and investigation of thermodynamic factors on the ORC are the objectives of this work.

277

278 Calculating rate of heat capacity (RoHC) on each point

Potential for Heat production on the CB process was evaluated using Eq. (5). Using this method, 279 280 an attempt is made to calculate heat generation potential based on the mass flow rate of species. 281 As well as, rate of heat capacity can be defined as heat utility of system. Therefore, RoHC changes depends on $C_{p,species}$. Results of RoHC levels in 4 points showed that the increase of species 282 concentration leads to RoHC increase. Whereas for better exhaust of waste gases must be used 283 blowers in the stacks. Using blowers on the stacks caused increase mass flow rate species 284 $(\dot{m}_{exhuast gases})$. So, the value of RoHC production in both SLC stack and HLC stack is more than 285 other points. In similar studies, heat utility and enthalpy are used as thermal parameters in order to 286 explain the heat potential of waste heat into petrochemical plant. The results of comparing studies 287

show that large dense of H₂O leads to increase the level of RoHC on stack lines. Also the effectiveness of using various kind of blowers in increasing RoHC in the exhaust line has. Therefore, the increase in RoHC in the stacks is the result of the increase in enthalpy due to the use of blowers [22,45,46]. Fig. 5 depicts the measurement of RoHC values for various waste gas species at four critical sites and the effect of volumetric and mass flow rates on RoHC.

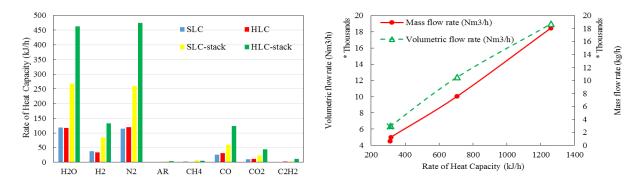


Fig. 5. Value of RoHC for different kinds of waste gases species and effect of volumetric and mass flow rate on the RoHC in 4 main points.

293 Most of the studies on WHR system's position in industrial line have been stated by installation WHR equipment where the higher temperature gradient leads to a more efficiency. Potential of 294 Heat production at 4 points depends on mass flow rate, temperature gradient and rate of volumetric 295 296 flow. Also, the literature review indicated that most petrochemical plants have thermodynamic efficiency in the high temperature range. However, the difference temperature between production 297 plant and exhaust lines are a about 20 to 60[16,29,31]. The effect of mass flow rate can also result 298 in modifications to the RoHC parameter. Thus, a comparison between the temperature gradient at 299 locations and the RoHC value can aid in determining the optimal location for installing a WHR 300 system. The value of RoHC and the magnitude of the temperature gradient were regarded as the 301 primary indicators for locating a good location to build a WHR system. According to this opinion, 302 the RoHC value was greatest for SLC and HLC stacks. But it was observed that the temperature 303

304 gradient was greater at the SLC and HLC stacks. Therefore, an examination of each point's energy and exergy should be conducted to determine the optimal location for WHR system installation. 305 Considering the decrease in temperature at the HLC stack due to the increase in mass flow rate, 306 307 the RoHC attained at the HLC stack was greater than at the HLC stack. The use of blowers for waste gas exhaust is one of the reasons why RoHC level is greater at stack. In contrast, the 308 309 temperature differential within the stacks does not alter significantly. Therefore, it is hypothesized that HLC and SLC stacks with a high level of RoHC. Fig.6 depicts the concentration of RoHC and 310 temperature gradient at four stages of the CB production process. 311

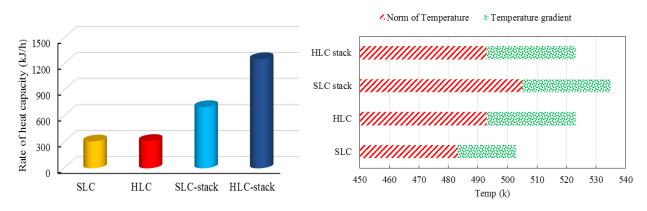


Fig. 6. RoHC and Temperature gradient on each point

312 Energy and exergy analysis for WHR

WHR system is utilized as a multi-component in the power generation cycle to recycle heat. Major WHR system components include the economizer, boiler, and heat pump [50]. If the designed WHR falls into high temperature ($T_{in} > 400(^{\circ}k)$) category and the working fluid is assumed saturated vapor steam, a comprehensible energy and exergy analysis can be presented. Table 6 demonstrates the results of WHR system energy and exergy analysis at 4 points.

Table 6. Energy and exergy analysis of WHR on each point.

points SLC HLC SLC stack HLC stack	:k
------------------------------------	----

T _{in,boiler} (°C)	210	220	232	220
mass rate $(\frac{kg}{h})$	4441	4640	10051	18460
volumetric flow rate $(\frac{Nm^3}{h})$	2950	3000	10506	18723
Actual density $(\frac{kg}{m^3})$	1.2426	1.2426	0.5114	0.5463
$Q_{in,boiler}$ (kJ)	701.2	746.8	802.4	746.8
$\eta_{boiler}(\%)$	88.67	89.25	89.88	89.25
$\dot{Ex}_{WHR}(kW)$	112.5	136.1	166.7	136.1

Heat exchanging at WHR was conducted by boiler. Then heat pump provides conditions to stabilize pressure and temperature that goes to turbine [51–53]. High temperature at the inlet of WHR directly effects exergy and thermal efficiency of boiler [54]. So, at the points which temperature levels effect on η_{boiler} . Therefore, SLC stack has had the highest temperature level and boiler efficiency. So, it can be stated that SLC stack can be the suitable spot for WHR system installation in CB production process.

Exergy analysis in thermal systems reveals the energy output capability of available energy. 324 Following the standard analytic exergy methods for IC engines, it is possible to determine the 325 available thermal potential in this instance. The results demonstrated that the SLC stack had 326 accumulated more exergy than other places. In order to increase WHR exergy at the SLC point, it 327 is advised that one circulation path be added from the turbine to the WHR system such that the 328 329 WHR temperature rises. Fig.7 shows the relation between temperature gradient, $\dot{Ex}_{boiler}, Q_{inlet, boiler}$ and η_{WHR} of the points. 330

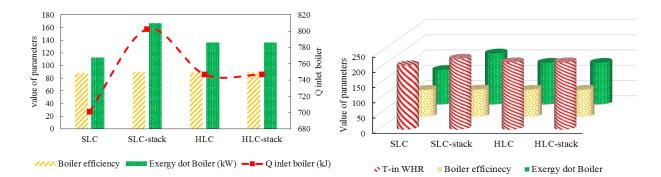


Fig. 7. Relation temperature gradient, boiler efficiency and Ex_{boiler} for describe potential of establishment of WHR from each point

331 Energy, exergy and efficiency analysis of ORC

WHR is installed on ORC to generate electricity. Therefore, energy and exergy analysis was utilized to examine the potential and efficiency of power generation. In order to get a comprehensive understanding arability of power generation at each point, should be studied WHR on ORC cycle. Hence, the results of ORC analysis at 4 points showed that SLC stack point has the highest η_{ORC} , η_{system} and also, the amount of $W_{turbine}$ at this point was higher than other points. High temperature at the inlet of WHR system at SLC stack point lead to higher η_{ORC} and η_{system} .

SLC HLC SLC stack HLC stack points 19.55 20.47 21.55 20.47 η_{ORC} (%) η_{system} (%) 17.33 18.27 19.37 18.27 $W_{turbine}(kJ)$ 142.1 157.9 157.9 178 $W_{pump}(kJ)$ 5.041 5.041 5.041 5.041 Mass fraction of condensation 23.58 24.83 26.32 24.83 (%)

Table 7. Energy and exergy analysis of ORC on the each point.

338

339 *Comparison of the results with literature study*

340 After determining the appropriate location of WHR application according to ORC and 2E analysis, a comparison should be conducted between the results obtained from other literature to investigate 341 the waste heat recovery capability in the CB process plant. For this, the common parameters 342 calculated in similar literatures, which describe the ability of the systems in heat generation and 343 waste heat recovery, should be compared with each other. For this purpose, three parameters of 344 345 temperature gradient, heat utility and η_{ORC} were considered. Also, the thermodynamic parameters and 2E analysis of SLC stack was used as the optimal location of the WHR application on the CB 346 347 process to compare with other results. Comparing the results showed that CB process plant at the SLC stack point has same temperature gradient as hot oil system [29]. However, it has a lower 348 temperature gradient than other similar investigations. Also, the level heat utility of the CB process 349 (sum of all values of heat rate capacity on 4 critical points) is lower than other research, which 350 indicates the changes in the input heat rate to ORC. However, η_{ORC} in CB process (at the stack 351 352 point) has been calculated higher than other research, which indicates the appropriate potential of 353 CB process plant in applying WHR application to other petrochemical plants. Table 8 shows the 354 evaluable parameters between relevant literatures and main research. These parameters are used 355 for joint evaluation of petrochemical plant and CB process.

Despite of the benefit mentioned about potential of power generation on CB process, maximum waste heat recovery can be achieved when the mass and volume rate of waste gas is in ideal state. Usually, due to the decrease in the performance of the blowers and the clogging of the coils inside the furnace, the mass and volume rate of the waste gas decreases and the assumption of optimal production deviates from the ideal form.

Table 8. Comparison thermodynamic parameters of SLC stack with other literatures.

production line	ref	ΔΤ	heat utility (all process)	η_{ORC} (%)
CB process plant	main research	30	~3 MW	21.55
hot oil system	[29]	30	~5 MW	18.9
cement plant	[31]	68	$4-9 \; MW$	18.81
Algerian petrochemical unit	[22]	100	~8.5 MW	15.8
petrochemical plant	[16]	45	10.27 MW	7.64

361

362 Conclusion

In this study, main objective was to assess the effectiveness of waste heat recovery (WHR) systems in locations where waste heat is generated during the CB process plant. Also aimed to quantify the amount of energy produced by level of RoHC (rate of heat capacity) parameter at each points. Based on the CB technical process diagram, there are four crucial waste heat locations: SLC, SLC stack, HLC, and HLC stack. The findings of this study demonstrate:

The RoHC achieved at SLC stack and HLC points was greater than at other points. The reason for this increase was the presence of large quantities of dense H₂O, as well as the presence of blowers for expelling waste gases.

- Increasing the temperature gradient at key points due to a rise in RoHC level.

- Exergy analysis of the WHR system revealed that the greatest amount of work, η_{boiler} and \vec{Ex}_{WHR} are available at the SLC stack ($\eta_{boiler} = 89.88\%$, $\vec{Ex}_{WHR} = 166.7 kW$). Also η_{boiler} and \vec{Ex}_{WHR} at critical points of hard line have same values ($\eta_{boiler} =$ 89.25%, $\vec{Ex}_{WHR} = 136.1 kW$). The reason for this topic was the higher level of $T_{in,boiler} = 232 \,^{\circ}$ C to the SCL stack than other points and finally the higher temperature gradient. ($|\Delta T_{inlet-outlet,boiler}| = 30$)

378 - Modeling ORC revealed that η_{ORC} and η_{system} at the SLC stack are higher than other 379 points. ($\eta_{ORC} = 21.55 \%$, $\eta_{system} = 19.37\%$)

- The results of the comparison of this study with similar literature showed that despite the
- lower heat utility level on CB process plant than the other petrochemical plants, but η_{ORC}
- at the SLC stack point is higher than similar thermal points, which indicates the high
- 383 potential of power generation in this plant.
- 384

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