Enriched Oxygen for Crude Oil Preheating in Petroleum Refining

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Abstract

The crude distillation unit is one of the energy-intensive processes in the refinery. This is because of the crude preheater that suffers from excessive energy loss due to the use of air in the combustion furnace. Alternatively, fuel combustion by enriched oxygen can improve heat efficiency, minimize fuel consumption and reduce emissions. In this paper, enriched oxygen has been simulated by UniSim for preheating Kuwaiti crude in one of the distillation columns in the Clean Fuels Project. Results show that the use of 30 mol% of concentrated oxygen reduced fuel consumption by 5%. Carbon dioxide emissions were also minimized by 22,240 tons per year. A membrane system made from perfluoropolymer was simulated for the production of 5,298 tons of enriched oxygen (per day) and it required an area of 39,000 m^2 with a capital investment of 6.9 million $.

1. Introduction

Combustion is the reaction of fuel with oxygen to generate heat. Air is usually used as a source of oxygen because it is readily available. However, air contains only 21 mol% of oxygen and the balance is nitrogen. Meanwhile, the use of enriched oxygen (containing more than 21 mol% of oxygen) is proven to improve combustion efficiency and reduce fuel consumption [1]. This is because higher oxygen concentration will increase the flame temperature [2]. Furthermore, because enriched oxygen contains less amount of nitrogen, the emissions of harmful gases such as nitrogen oxides and carbon monoxide can be minimized [3].

In the petroleum industry, combustion is used for heating feedstocks and to provide the energy for the process [4]. For example, the steam methane reforming process, which produces hydrogen from methane and water, requires a high temperature to initiate the endothermic reaction [5]. Some processes need the heat to convert water into steam to operate utilities such as boilers. Enriched oxygen can be also used to regenerate the catalyst from the fluid catalytic cracking (FCC) process by burning off the deposited coke on the catalyst surface [6]. The enriched oxygen accelerated the regeneration rate of the catalyst [7]. Furthermore, enriched oxygen can be employed in the Claus process to convert hydrogen sulfide into solid sulfur by oxidation [8]. The sulfur capacity of the process was significantly increased when concentration oxygen was used [9].

Figure 1 shows the energy consumption of various units in the refinery and it is obvious that the crude distillation unit consumes the most energy. The unit consists of energy-intensive utilities such as heaters, boilers, coolers, and condensers. The furnace (fired heater) which preheats the crude prior to the distillation process is considered as one the highest energy consumer, not only in the distillation process but in the whole refinery [10]. This is because the furnace is used to heat a large amount of crude oil (hundred thousand barrels) from 200–280 to 350–390°C [11]. Furthermore, the furnace suffers from excessive energy loss due to the

generated entropy of the combustion reaction [12]. However, it was found that the use of enriched oxygen can reduce energy loss and consequently improve combustion efficiency [13]. Figure 2 shows the energy loss of various equipment of the distillation process.

Currently, there are three commercialized technologies for oxygen production such as cryogenic distillation, pressure swing adsorption (PSA), and membranes. In cryogenic distillation, the air is cooled down to an extremely low temperature of −175°C in which oxygen will be liquefied [14]. In PSA, air will pass through a bed of zeolite in which nitrogen will be adsorbed while oxygen will pass due to the adsorption and molecular sieving properties of zeolite [15]. In membranes, the separation mechanism is based on the solution-diffusion model in which oxygen dissolves and diffuses through the polymer [11]. The polymer contains voids that act similar to physical pores but they differ as their location and size can change depending on the operating conditions [16]. In terms of oxygen quality, of 99.99 mol%. PSA can produce oxygen with purity up to 95 mol% oxygen.
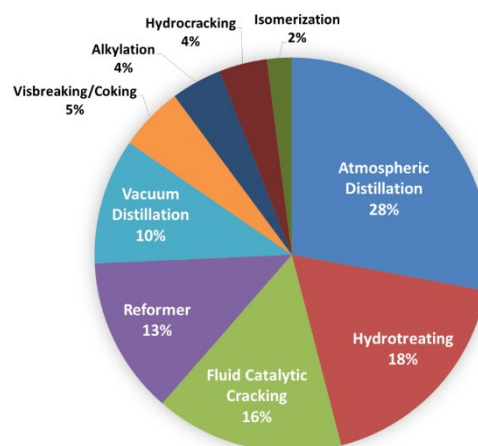

Figure 1. Different refinery units and the total energy consumption [17].

However, the membranes are only capable of producing oxygen up to 40 mol% oxygen. In terms of cost, the membranes have the lowest capital and operating costs compared to PSA and cryogenic distillation. The reason for this is that the membranes do not have mechanical parts and have a continuous life of nearly five years. Furthermore, the membranes are energy-efficient units as they operate at ambient temperature. Table 1 compares the three technologies for oxygen enrichment from technical and economic points of view.

In this paper, the furnace of the crude distillation unit was simulated in UniSim with the use of enriched oxygen. The study was to calculate the fuel reduction as a function of oxygen content in the feed. Carbon dioxide concentration in the flue gas was determined as well. The simulation was performed based on one of the crude distillation units available at the Clean Fuels Project which processes 255,000 barrels per day of Kuwait exported crude. The membrane system has been selected for the simulation due to its low capital and operating costs as indicated in Table 1. For most industries, enriched oxygen with 30 mol% oxygen is preferable because it does not require major process modification due to safety issues with enriched oxygen.
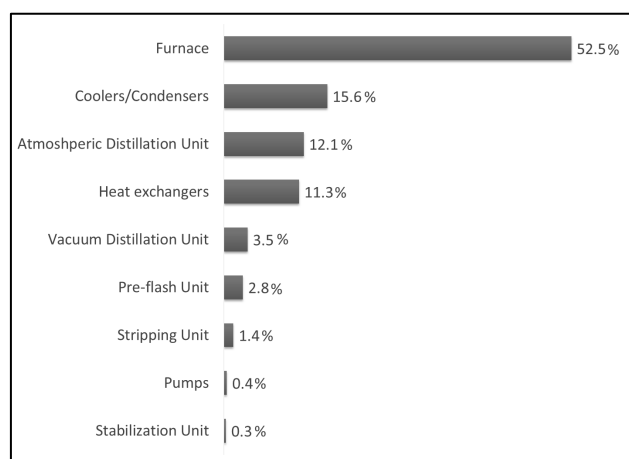

Figure 2. Energy loss of various units of the atmospheric crude distillation process.

Table 1. Commercialized technologies for oxygen enrichment [18-20].

Technology	Benefits	Capital Cost ($/ton)	Operating Cost ($/ton)
Cryogenic Distillation	• 99.99 mol% O_2 purity. • Liquefied O_2 for easier storage.	25,000 – 525,000	39
Pressure Swing Adsorption (PSA)	• 95% O_2 purity. • Operates at ambient temperature. • Better stability to feed impurities.	13,000 – 70,000	26
Membranes	• Low capital and operating costs. • Continuous life of five years. • Operate at ambient temperature. • Best reliability and turndown.	11,000 – 27,000	23

2. Methodology

Honeywell UniSim was used to simulate the performance of the furnace of the atmospheric distillation unit. Kuwait exported crude entered the furnace at 220°C then exit at 370°C. The flue gas temperature was maintained at 380°C. The operating conditions of the furnace are given in Table 2. The fuel is assumed to be natural gas containing 83 mol% methane (full composition is given in Table 3). Adjust functions in UniSim were used to calculate the required flowrates of fuel and air based on an oxygen excess in the flue gas of 2 mol%. This concentration is used industrially to ensure complete oxidation of the fuel [21]. Oxygen concentration was then varied from 21 to 100 mol% and the fuel consumption was determined. Fuel reduction was calculated by comparing the enriched oxygen stream to air. The molar concentration of carbon dioxide in the flue gas was monitored as well. The process flow diagram of the simulation case is given in Figure 3.

Table 2. Operating conditions used in the simulation of the crude distillation furnace.

Property	Condition
Crude Flowrate	255,000 barrels per day
Crude Inlet Temperature	220°C
Crude Outlet Temperature	370°C
Crude Feed Pressure	5 bar
Fuel Gas Temperature	25°C
Fuel Gas Pressure	1 bar
Enriched Oxygen Pressure	1 bar
Enriched Oxygen Temperature	25°C
Flue Gas Temperature	380°C
Excess Oxygen in Flue Gas	2 mol%

Table 3. Composition of natural gas used in this study.

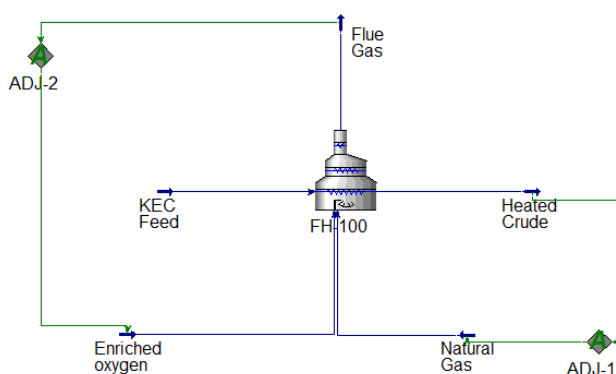| Component	Mole Fraction (%)
Methane (CH_4)	87
Ethane (C_2H_6)	9
Propane (C_3H_8)	2
Butane (C_4H_{10})	1
Nitrogen (N_2)	1

Figure 3. UniSim process flow diagram for the simulation of the fired heater for Kuwait crude oil heating before the atmospheric distillation unit.

3. Results and Discussion
3.1 Fuel Savings and CO₂ Emissions

Fuel reduction in the fired heated of the crude distillation unit is plotted as a function of oxygen concentration in Figure 4. It is clear that fuel-saving increases exponentially bounded with the oxygen content. At the region of 20 to 40 mol% oxygen, the fuel-saving function is almost linear and the saving is noticeable. This zone is also favorable for the refinery as no major process modification will be required for the integration of enriched oxygen stream [22]. Above 40

mol% of oxygen, the effect of enriched oxygen becomes less effective on fuel saving. For example, for a stream containing 40 mol% oxygen, a fuel saving of 8% can be achieved however, if pure oxygen was is used, a maximum saving of only 12% can be accomplished.

The other aim of this study is to monitor the carbon dioxide content in the flue gas as a function of oxygen concentration. Figure 5 shows that the molar concentration of carbon dioxide rises significantly with oxygen content. For example, when air is used, the molar concentration of carbon dioxide is 9% but it increases to 16% when a stream containing 40 mol% oxygen is fed. Pure oxygen produces a flue gas containing 34 mol% carbon dioxide which is nearly four times the concentration when air is used. It is expected from these numbers that carbon dioxide emissions are higher due to the increase in molar concentration. To investigate more, the molar flow of carbon dioxide was determined for air and enriched oxygen. The air gives a carbon dioxide flowrate of 1072 kmol h^{-1} while the enriched oxygen stream of 40 mol% oxygen produces 989 kmol h^{-1}. This tells that actually there is a reduction in carbon dioxide emission by 8% despite the increase in the molar concentration in the flue gas from 9 to 16%. This is because the enriched oxygen reduced the required amounts of the feed stream while maintaining the flue gas with 2 mol% excess oxygen. When pure oxygen is used, a maximum carbon dioxide reduction of 12 mol% can be achieved as given in Figure 5. For a stream containing 30 mol% oxygen, it is estimated that carbon dioxide emissions in the flue gas will be minimized by 22,240 tons annually.
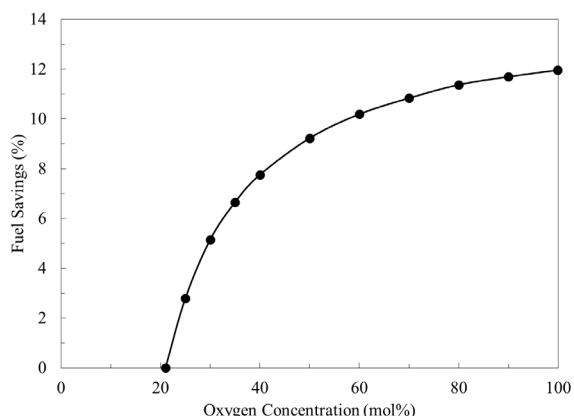

Figure 4. Fuel savings by utilizing enriched oxygen for the crude distillation preheater of one of the Clean Fuels Project refineries.
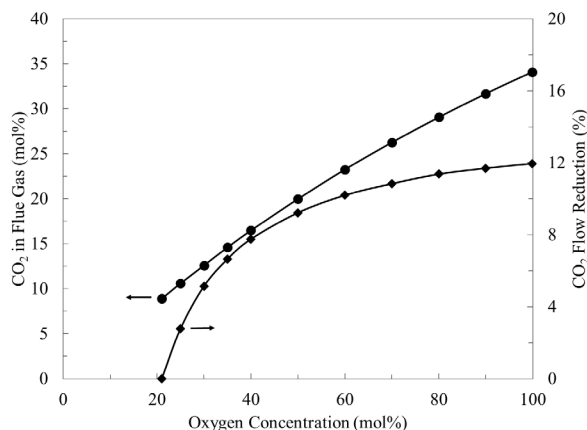

Figure 5. Reduction of CO$_2$ emissions from crude distillation preheater with the use of enriched oxygen.

3.2 Membrane Process

A commercial perfluo-polymer membrane with oxygen permeance of 1200 gas-permeation unit (GPU) and oxygen-to-nitrogen selectivity of 3 was considered in this study [7]. The membrane system was simulated in UniSim to produce oxygen with 30 mol% in purity. Unfortunately, UniSim does not have an integrated unit for gas-separation membranes. Therefore, the unit was modeled using a component splitter and a spreadsheet. The membrane module was assumed to have a spiral wound structure. Mass balance across the membrane can be applied by:

$$x_F n_F = y_P n_P + x_R n_R \tag{1}$$

where n is the number of moles (kmol h^{-1}), x_F is the mole fraction of oxygen or nitrogen in the feed, x_R is the mole fraction in the reject, and y_P is the mole fraction in the product. The previous equation can be rewritten as:

$$y_P n_P = x_F n_F - x_R n_R = QA(\overline{xP_F - yP_P}) \tag{2}$$

where Q is the permeance (GPU), A is the membrane area (m^2), and the last term is the trans-membrane pressure difference. P_F is the feed pressure while P_P is the product pressure (bar). Assuming a cross-flow pattern, the pressure difference across the membrane can be determined by [23]:

$$(\overline{xP_F - yP_P}) \cong \left[\frac{x_F - x_R}{\ln\left(\frac{x_F}{x_R}\right)} \right] P_F - y_P P_P \tag{3}$$

The membrane is solved then using the adjust functions in UniSim and the following equations:

$$\sum_{i=1}^{n} x_F = 1 \; ; \; \sum_{i=1}^{n} x_R = 1 \; ; \; \sum_{i=1}^{n} y_P = 1 \tag{4}$$

First, the stage-cut in the product (θ) is guessed:

$$\theta = \frac{y_P n_P}{x_F n_F} \tag{5}$$

After that, x_R and x_P are simultaneously solved and the stage-cut is re-calculated based on the permeance by:

$$\theta_{Calc} = \frac{QA(\overline{xP_F - yP_P})}{x_F n_F} \tag{6}$$

The guessed value is then changed until Eq. (9) and (10) are equal with an error less than 0.001.

For the membrane process, air was first compressed to 4 bar but due to the Joule-Thomson effect, the stream was heated to 214°C. Accordingly, a cooler was employed to decrease the air temperature back to 25°C. The product stream from the membrane system was then fed to the furnace for fuel combustion. The operating conditions for the membrane process are given in Table 4. Figure 6 shows the solved UniSim flowsheet for the production of 247 tons per hour of enriched oxygen (30 mol%). The calculated membrane area is 39,000 m^2 with a compressor power of 24,930 kW. oxygen. Based on these data, the membrane capital and operating costs can be estimated (neglecting cooler and labor costs). Currently, the membrane skid is sold
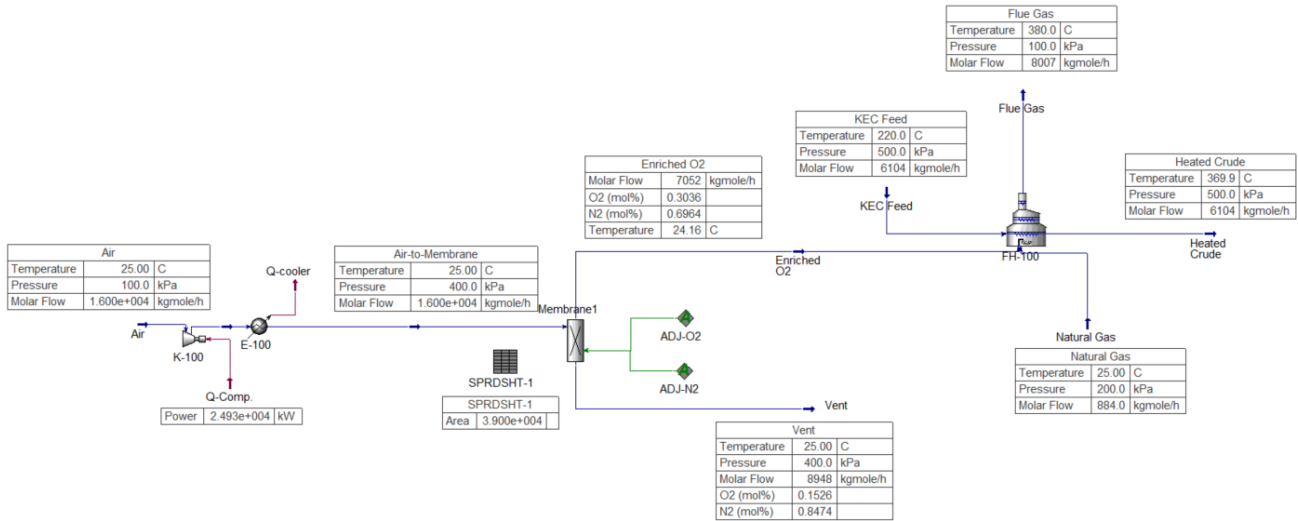
Figure 6. UniSim simulation for the production of enriched oxygen (30 mol%) for crude oil pre-heating in one of the distillation columns in the Clean Fuels Project.

for 50$ per m^2 and therefore, the skid will cost 1.9 million $. The air compressor is estimated to cost 200$ per kW so the compressor price is 5.0 million $. This gives a total capital cost of 6.9 million $. The operating cost is based on the maintenance and utility bills. It is assumed that the maintenance bill is 5% of the capital cost while the utility bill is calculated from the Kuwait electricity tariff of 0.0015$ per kW. Thus, the annual operating cost is 0.6 million $. It should be noted that the enriched oxygen (30 mol% oxygen) reduced fuel consumption by 5% and this can result in a saving of 0.7 million $ using a current natural gas price of 2.73$ per MMBTU. Therefore, the fuel savings can be used to pay the operating cost of the membrane. The capital investment of 5.0 million $ for the membrane system for five years is still beneficial as it reduced carbon dioxide emissions by 22,240 tons annually. After five years, the membrane skid needs to be replace and the cost is expected to be 50% of the capital investment. Summary of the economic evaluation is given in Table 5.

Table 4. Operating conditions for membrane simulation for the production of 30 mol% oxygen.

Property	Condition
Air Feed Pressure	4 bar
Feed Temperature	25°C
Retentate Pressure	4 bar
Retentate Temperature	25°C
Product Pressure	1 bar
Oxygen Permeance*	1200 GPU
Nitrogen Permeance*	400 GPU

*Reference [7]

4. Conclusions

Combustion with enriched oxygen is beneficial in terms of better heat efficiency and fuel consumption. In refineries, combustion is required to heat streams and provide the energy for the process. The fired heater of the crude distillation unit is one of the energy-intensive utilities due to the high-energy input. The heater also suffers from excessive energy loss due to the use of air in the combustion reaction. In this work, enriched oxygen has been used, instead of air, to simulate the fired heater performance. UniSim has been used to calculate the fuel savings and the carbon dioxide content in the flue gas. Results show that the fuel reduction

Table 5. Estimation of capital and operating costs of the membrane system for the production of 30 mol% oxygen for crude oil preheating.

Parameter	Value
Capital Cost	
Membrane skid cost (MS)	50$ per m^2
Membrane Area	39,000 m^2
Compressor Cost (C)	200$ per kW
Compressor Power	24,900 kW
Total Capital Cost (MS+C)	6,930,000 $
Annual Operating Cost	
Utility (U)	0.0015$ per kWh
Maintenance (MT)	5% capital cost
Total Operating Cost (U+MT)	673,686$

increases exponentially bounded with the oxygen content. The maximum achievable fuel saving was 12% when pure oxygen was implemented. However, carbon dioxide molar concentration in the flue gas increased remarkably to 34 mol%. Interestingly, the molar flowrate of carbon dioxide was still reduced by 12%, compared to air, due to the lower flowrate of the enriched oxygen stream. In petroleum refinery and other industries, an enriched oxygen stream with 30 mol% is more favorable as it does not require major process modification to meet safety requirements. The membrane system was selected in this study compared to other technologies due to the low capital and operating costs. It was estimated that an area of 39,000 m^2 of perfluoropolymer membrane is needed to produce 247 tons of oxygen (per hour) with 30 mol% in purity. The capital cost of the system is expected around 6.9 m$ while the operating cost will be covered by the fuel-saving. Though, the capital investment of the membrane system can run for five years with the reduction of carbon dioxide by 22,240 tons per year.

Nomenclature

θ	Stage cut
A	Membrane area (m^2)
n	Molar flowrate (kmol h^{-1})
P	Pressure (bar)
Q	Permeance (GPU)
x	Mole fraction
y	Mole fraction in the product

Subscripts

F	Feed
R	Reject
P	Product

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