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**MSc Oil and Gas Process Systems Engineering  
Approaches and Design for Zero-Flaring in Refineries**

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Athens, March, 2021

## ΔΗΛΩΣΗ ΣΥΓΓΡΑΦΕΑ ΜΕΤΑΠΤΥΧΙΑΚΗΣ ΕΡΓΑΣΙΑΣ

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«Είμαι συγγραφέας αυτής της μεταπτυχιακής εργασίας και ότι κάθε βοήθεια την οποία είχα για την προετοιμασία της, είναι πλήρως αναγνωρισμένη και αναφέρεται στην εργασία. Επίσης, οι όποιες πηγές από τις οποίες έκανα χρήση δεδομένων, ιδεών ή λέξεων, είτε ακριβώς είτε παραφρασμένες, αναφέρονται στο σύνολό τους, με πλήρη αναφορά στους συγγραφείς, τον εκδοτικό οίκο ή το περιοδικό, συμπεριλαμβανομένων και των πηγών που ενδεχομένως χρησιμοποιήθηκαν από το διαδίκτυο. Επίσης, βεβαιώνω ότι αυτή η εργασία έχει συγγραφεί από μένα αποκλειστικά και αποτελεί προϊόν πνευματικής ιδιοκτησίας τόσο δικής μου, όσο και του Ιδρύματος.

Παράβαση της ανωτέρω ακαδημαϊκής μου ευθύνης αποτελεί ουσιώδη λόγο για την ανάκληση του πτυχίου μου».

Ο Δηλών



## ABSTRACT

Gas flaring is the controlled high temperature oxidation process used to burn waste gases containing combustible components. It is unfortunately responsible for severe environmental and health problems and in this paper we will present various methods to minimize that impact. Initially, we will describe the gas flaring equipment setup and process and present the aforementioned health and environmental issues. We will then analyze the various flare gas reduction methods used in oil refineries categorized by their type of implementation. Flare gas collection and compression, gas to liquid technology, gas to solid technology, energy production, flaring reduction in operation and flaring reduction in maintenance.

*Keywords:* Gas Flaring, Gas Flaring Impact, Flared Gas Reduction, Flare Gas Recovery Systems

## ΠΕΡΙΛΗΨΗ

Η καύση απαερίων μέσω πυρσού είναι η ελεγχόμενη διεργασία οξείδωσης σε υψηλή θερμοκρασία που χρησιμοποιείται για την καύση των απαερίων που περιλαμβάνουν εύφλεκτα συστατικά. Δυστυχώς, ευθύνεται για πολλά προβλήματα στην υγεία και το περιβάλλον και σε αυτή τη διατριβή θα παρουσιάσουμε διάφορες μεθόδους ώστε να αντιμετωπιστούν τα προβλήματα αυτά. Αρχικά, θα περιγράψουμε τη διάταξη και τη λειτουργία του εξοπλισμού καύσης των απαερίων και θα παρουσιάζουμε τα προαναφερόμενα θέματα υγείας και περιβάλλοντος. Σε συνέχεια, θα αναλύσουμε τις διάφορες μεθόδους μείωσης απαερίων που χρησιμοποιούνται στα διυλιστήρια πετρελαίου κατηγοριοποιημένα σύμφωνα με τον τύπο εφαρμογής. Συλλογή και συμπίεση απαερίων, τεχνολογία αερίου σε υγρό, τεχνολογία αερίου σε στερεό, παραγωγή ενέργειας, μείωση απαερίων στη λειτουργία και μείωση απαερίων στη συντήρηση.

*Λέξεις - Κλειδιά:* Καύση απαερίων μέσω πυρσού, επίδραση καύσης απαερίων, μείωση απαερίων, Συστήματα Ανάκτησης Απαερίων

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## GLOSSARY OF TERMS AND ACRONYMS

CDM	United Nations Kyoto Clean Development Mechanism
CH <sub>4</sub>	Methane
C <sub>2</sub> H <sub>4</sub>	Ethylene
CHA	Chabazite
C <sub>3</sub> H <sub>3</sub> N <sub>3</sub>	Triazine
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
DSC	Dry Screw Compressor
FGRS	Flare Gas Recovery System
FSC	Flooded Single or Dual Screw Compressor
F-T	Fischer-Tropsch Synthesis
GGFR	The World Bank Global Gas Flaring Reduction Partnership
GMI	Global Methane Initiative
GTE	Gas to Ethylene
GTL	Gas to Liquid
GTS	Gas to Solid
HCHO	Methanol
H <sub>2</sub> O	Water
HONO	Nitrous Acid
HP	High Pressure Steam
H <sub>2</sub> S	Hydrogen Sulfide
ktCO <sub>2</sub> e	Kiloton of CO <sub>2</sub> equivalent
LNG	Liquefied Natural Gas
LP	Low Pressure Steam
LPG	Liquefied Petroleum Gas
LRC	Liquid Ring Compressor
MP	Medium Pressure Steam
MSR	Methane Steam Reforming
NDCs	Nationally Determined Contributions
NGH	Natural Gas Hydrates
NO <sub>2</sub>	Nitrogen Dioxide
NO <sub>3</sub> <sup>-</sup>	Nitrate Ion

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NOAA	U.S. National Oceanic and Atmospheric Administration
O <sub>3</sub>	Ozone
ORC	Organic Rankine Cycle
PAHs	Aliphatic and Polycyclic Aromatic Hydrocarbons
PG	Polymer Grade
PRICO	Poly Refrigerant Integrated Cycle Operation
RC	Reciprocating Compressor
SMR	Single Mixed Refrigerant
SO <sub>2</sub>	Sulfur Dioxide
SO <sub>4</sub> <sup>2-</sup>	Sulfate Ion
SOFC	Solid Oxide Fuel Cell
SRC	Steam Rankine Cycle
SRU	Sulfur Recovery Unit
SVC	Sliding Vane Compressor
TPD	Tons Per Day
UNFCCC	United Nations Framework Convention on Climate Change
VHP	Very High Pressure Steam
VIIRS	Visible Infrared Imaging Radiometer Suite
WGS	Water Gas Shift

## CHAPTER 1: INTRODUCTION

Gas flaring is the controlled combustion of volatile, combustible, waste gases from oil refineries. It is now recognized as a significant health and environmental problem. As a result, various international agreements, as the Paris Climate Agreement developed by the United Nations, have been achieved in order to mitigate, if not eliminate this issue. That means that the oil refineries must prioritize the flaring reduction, even if that means impacting their economic profit.

The purpose of this paper is to present various flare gas reduction methods to satisfy the increased environmental demands and create an overview of the gas flaring in oil refineries according to the following:

- Gas flaring definition
- Flame system description in oil refineries
- Health and environmental impacts
- Various flare gas recovery and reduction methods



## **CHAPTER 2: GAS FLARING**

Gas flaring is the controlled high temperature oxidation process used to burn waste gases containing combustible components, such as volatile organic compounds, methane, carbon monoxide and hydrogen, which are not possible to be processed for sale or use because of operational or economic reasons. Some of these reasons are the gases marginal rates, the high field development cost and space limitations. The waste gases which are generated in a petroleum refinery during normal operation and process upset conditions are collected in piping headers and delivered to a flare system composed of multiple flares for safe and efficient disposal. The flare gas originates from various sources, such as blowdown systems, exhaust of utilities, safety valves connections and vent connections. The combustion of the waste gases takes place at a remote and usually elevated location with the use of an open flame in ambient air using a specially designed burner tip, auxiliary fuel, and, in some cases, assist gases like steam or air to promote mixing for nearly complete (e.g.,  $\geq 98\%$ ) destruction of the combustible components. The combustion performance depends on the ratio of steam assist to flare gas, the flare gas heating value, the wind speed conditions and the waste gas exit velocity (Sorrels, Coburn, 2019).

Flares are safety devices and their main role is to prevent the release of unburned gas to atmosphere and its combustion or even explosion if it reaches an ignition source outside the plant. There are two levels of flaring. The first is flaring that occurs during an emergency. This can be a very large flow of gases that must be destroyed before they cause a significant safety event. The maximum flare gas flow that can be treated by a flare is its hydraulic capacity. Examples of emergency flaring include:

- Excess fuel gas production creating fuel gas imbalance
- Fuel gas quality issues like low calorific value or high sulfur content
- Equipment failure
- Process upset
- Fire, natural disaster, malevolent actions, loss of utilities

The second level of flaring is the treatment of waste gases generated during normal operation, including purge gas and planned decommissioning of equipment. Examples of flare gas sources during regular operation include:

- Sampling purges

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- Analyzer purges
- Safety valves leakage
- Seal pots vents from pump seals
- Vents of low pressure vessels and tanks when atmosphere release is not allowed due to environmental protection
- Small operation actions and maintenance procedures
- Vents of low pressure equipment like tower overhead systems
- Loading and unloading operations
- Planned maintenance including process unit startup and shutdown and various turnaround events

There are many reasons forcing flare gassing during maintenance activities. The most common of them are indicated below:

- The flare gas compressors do not have the necessary capacity to recover the flare gases
- The flare gases have high nitrogen or hydrogen content or insufficient heating content to satisfy the required quality of fuel gas unit
- Fuel or hydrogen gas overproduction that cannot be negated by the active users
- Nitrogen, hydrogen or steam purge during shutdown
- Replacement catalyst conditioning with sulfur compounds that can create flare gases with excess hydrogen sulfide content
- The startup of high pressure vessels that must be pressurized slowly to avoid potential for damage that results to the recovery of high temperature inert gases

If the flare gas is not flared and is recovered unchecked to the fuel gas unit it can cause many significant issues:

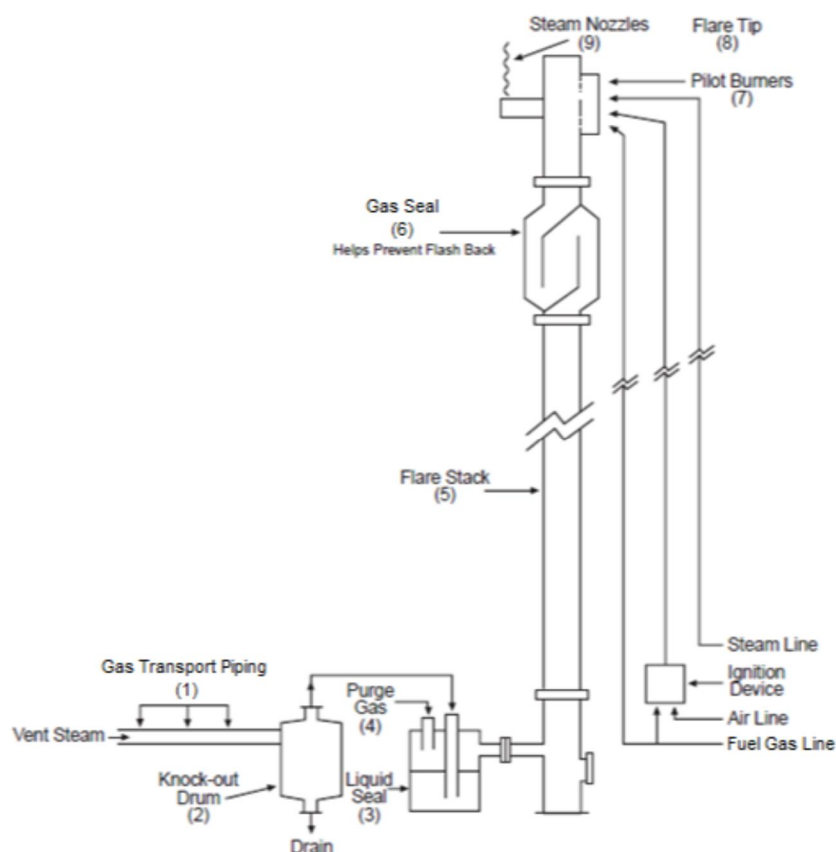
- A low heating value fuel gas can cause unstable operation and flameout
- A fuel gas with not appropriate molecular weight can affect the performance of the flare gas compressors and increase their temperature over their design value
- Low heating fuel gases with high nitrogen content can increase the formation of nitrogen oxides

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- The presence of high steam content can increase the inlet temperature of the compressors and overheat them to the point of emergency shutdown
- Steam presence can overflow the knock out drums and increase sour water formation (Valero Refining Company – California, 2010)

## CHAPTER 3: FLARE SYSTEM DESCRIPTION

A complete diagram of a steam assisted elevated smokeless flare system, the most commonly used at petroleum refineries, is shown in Figure 1. It consists of flare header (also referred to as gas transport piping), utilities (fuel, steam, and air), piping from the base up, knock out drum, liquid seal, flare stack, gas seal, burner tip, pilot burners, steam jets, ignition system, and controls (Sorrels, Coburn, 2019).



**Figure 1:** Overall flare stack system in a petroleum refinery (Sorrels, Coburn, 2019)

### 3.1 GAS TRANSPORT PIPING

Flare gas is sent from the various facility release points to the flare location through the gas transport piping, also referred to as flare header. The piping is usually schedule 40 carbon steel and is designed to minimize pressure drop. Valves utilization should be kept to an absolute minimum and should be sealed open. Pipe layout is designed to avoid any potential dead legs and liquid traps. Flare sweep gas is introduced into the header to maintain a constant gas flow and as a result to prevent oxygen buildup

in the flare header and oxygen backflow into the flare tip that could cause the formation of explosive mixtures.

### **3.2 KNOCK OUT DRUM**

Any liquid that may be included in the flare gas or that may be created due to condensation in the flare header is removed by a knock out drum. The knock out drum is generally either a horizontal or vertical vessel located at or close to the base of the flare or a vertical vessel located inside the flare stack base. The liquid removal is required as liquid presence can extinguish the flame or cause irregular combustion and smoking. Furthermore, a potential spray of burning liquids can land to the ground and create a safety hazard.

### **3.3 LIQUID SEAL OR FLAME ARRESTOR**

The flare gas, downstream of the knock out drum, usually passes through a liquid seal before going to the flare stack to be burned. This seal prevents flame flashback in the flare stack caused by low vent gas flow. The liquid level of this seal can also preserve a positive pressure on the flare header and acts as a mechanical damper on any explosive shock wave that may occur in the flare stack. In addition to this, there are many other devices that can act as a replacement or a supplement to the liquid seal, such as flame arrestors and check valves. The prevention of flashback in the flare stack can also be aided by the use of sweep or purge gas.

There are two types of flame arrestors: deflagration flame arrestors and detonation flame arrestors. Deflagration flame arrestors are designed to prevent the propagation of fire and detonation flame arrestors are designed as an explosion safety measure. Both types of arrestors manage to extinguish the flame front as it attempts to pass through them with the use of a metal matrix that dissipates the thermal load.

### **3.4 FLARE SWEEP OR PURGE GAS**

The total flare gas flow must remain in a high enough volume in order to prevent oxygen reverse flow into the flare or flare header that can result to explosive mixture formation. One of the factors that mitigate this safety problem is the use of flare sweep

or purge gas. Those gases are usually natural gas or process gas and sometimes inert gases, such as nitrogen or carbon dioxide.

Flare sweep gas is injected to the farthest upstream point in the flare header to ensure a constant, positive flow in the header and to protect the header from oxygen buildup. When there is no liquid seal, the flare sweep gas flows all the way up to the flare tip and is burned and disposed to the atmosphere. In the presence of a liquid seal, the flare sweep gas is typically recovered and reused.

Flare purge gas is injected between the liquid seal and the flare tip to prevent oxygen reverse flow and infiltration into the flare tip. That means that flare purge gas is used for flares that operate mainly with a liquid seal, such as emergency flares and flares with a FGRS. If there is no liquid seal, flare purge gas is not needed and is replaced by the flare sweep gas.

### **3.5 FLARE STACK**

The role of the flare stack is to elevate the flare and locate it at appropriate distances so that it will ensure the safety of the surrounding personnel and facilities.

### **3.6 GAS SEAL**

One additional measure that prevents the air infiltration is the installation of a gas seal in the flare gas. There are various types of gas seals such as flare seal, stack seal, molecular seal, labyrinth seal and gas barrier. The gas seal is installed just below the flare tip to restrain air from entering the flare stack and the flare header. In addition to this, some seal types, acting as orifices in the top of the stack, achieve the reduction of the required sweep or purge gas flow when there is no flare gas to dispose. These types of seals are referred as internal gas seal, fluidic seal and arrestor seal.

### **3.7 PILOT BURNERS**

The pilot burners, which are located around the outer flare tip perimeter, provide a stable and continuous ignition source in order to assure the safe and uninterrupted combustion of all the waste gas, including the flare sweep or purge gas, that is sent to

the flare. The pilot burners can be actuated either manual or automatic. The automatic systems are usually based on a flame detection device that utilizes a thermocouple, an infrared sensor or an ultraviolet sensor. Usually, the flame detection is achieved with a standard thermocouple located at the end of a pilot tip. If the thermocouple detects a below the set point temperature it indicates the pilot failure and the required corrective measures will restore the continuous pilot flame.

### **3.8 FLARE TIP**

The role of the flare tip is to achieve an environmentally satisfying flare gas combustion, flame stability, ignition reliability and noise suppression taking into consideration the minimum and maximum flare system capacity. The flame stability can be improved by the installation of flame holder retention devices inside the flare tip inner circumference. With the flame holders aid, a stable flame can be preserved for flare gas exit velocity range of 0.3 to 180 m/sec. The maximum flare tip flow depends on the flare header pressure ability to overcome the total system pressure drop and the flare gas velocity is normally designed not to exceed half the sonic velocity.

### **3.9 STEAM NOZZLES**

The flare flame receives the required for combustion oxygen from the surrounding atmosphere. In some cases, the high flare gas flow does not allow the proper mixture and combustion with the air oxygen by just a simple gas diffusion. As a result, high velocity steam injection nozzles are installed around the outer perimeter of the flare tip in order to increase gas turbulence in the flame boundary zones and combustion air suction and to improve mixing. In case the flare stack has a large enough diameter, the steam can be injected concentrically into the flare tip.

The injection of steam into a flare flame can also reduce smoke formation, mainly due to three effects. The steam minimizes polymerization by separating the hydrocarbon molecule and forms oxygen compounds that are combusted at a reduced rate and temperature preventing cracking and polymerization. Furthermore, water vapors react with the carbon particles to form carbon monoxide, carbon dioxide, and hydrogen thereby reducing the amount of carbon that cools and forms smoke. Finally,

steam reduces the temperature in the flame core and causes the suppression of thermal cracking. The smokeless capacity of the flare depends on the physical limitation on the quantity of steam that can be delivered and injected into the flare. Smokeless capacity is the higher gas volume that can be combusted in the flare without any signs of smoke. Usually, the smokeless capacity is less than the stable flame capacity of the burner tip.

The main steam usage disadvantage is the increase in cost and noise. The noise increase is caused due to the high-frequency jet noise of the steam injection. Small multiple steam jets and, if necessary, acoustical shrouding can mitigate the noise problem. Excess steam usage increases the operating cost and causes poor flare combustion efficiency. Steam injection can be controlled manually and automatically. Manually, the operator observes the flare directly or through a monitor and adjusts steam injection rate in order to prevent smoke formation. Automatically, the steam flow adjustment is realized by infrared sensors that sense flare flame characteristics. The most accurate automatic control method is based on flare gas flow and flame radiation or net heating value monitoring.



## CHAPTER 4: REFINERY FLARE GAS QUANTITY AND COMPOSITION

Flare gas composition and properties vary considerably in every case as it depends on the equipment and utilities which are connected to the flare networks. There is also great variation in flare networks pressure and temperature. For example, in Tables 1, 2 we present the flare gas composition and physical properties of three oil refineries in Iran (Amidpour, Karimi, Joda, 2018).

**Table 1:** Flare Gas Composition (Mole Percent)

<b>Components</b>	<b>Tabriz</b>	<b>Tehran</b>	<b>Bandar Abbas</b>
Methane	10	19.16	17.0
Ethane	30	9.24	3.3
Propane	2	12.56	4.5
i-Butane	5	3.74	1.5
n-Butane	5	5.86	1.5
i-Pentane	-	1.86	-
n-Pentane	-	1.1	0.4
n-Hexane	-	0.54	-
Oxygen	-	1.32	-
H <sub>2</sub> S	5	2.82	0.7
CO <sub>2</sub>	-	-	0.4
H <sub>2</sub> O	-	0.04	-
Hydrogen	43	36.72	70
Nitrogen	-	5.04	0.7

**Table 2:** Flare Gas Physical Properties

<b>Physical Property</b>	<b>Tabriz</b>	<b>Tehran</b>	<b>Bandar Abbas</b>
Mass Flow (kg/hr)	630	1,370	4,391
Molar Flow (kgmole/hr)	31.7	59.4	450
Temperature (°C)	80	46	35
Pressure (kPa)	100	96	99

## **CHAPTER 5: ENVIRONMENTAL IMPACTS**

Gas flaring presently causes serious energy and environmental problems and has a considerable impact on local population health as many toxic compounds like CO<sub>2</sub>, CO, NO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S and benzene are released. In 2012, global gas flare emissions stood for more than 50 % of the annual Certified Emissions Reductions issued by the projects registered under the United Nations Kyoto Clean Development Mechanism (CDM).

Nowadays, most FGRS have been installed taking into account the economic benefit only. In order to provide a short investment payback period, the systems are designed to collect most, but not all, of the flare gas and in normal operating conditions. The waste gas flow is rarely higher than the normal operating one and is not economically wise to take that case into account. However, the continuous increasing global environmental awareness and the implementation of Kyoto protocol by most of its member countries will inevitably result to the prohibition of gas flaring. As a result, refinery practices and processes must undergo significant changes according to environmental and not economic criteria.

This effort is being assisted by the United Nations' Clean Development Mechanism which offers 'Certified Emissions Reductions' and provides flaring and venting reduction projects. One of these assisted projects are The World Bank Global Gas Flaring Reduction (GGFR) Partnership and the Global Methane Initiative (GMI). In addition to this, the World Bank introduced the "Zero Routine Flaring by 2030" Initiative to bring together governments, oil companies and development institutions who recognize the unsustainable flaring situation and agree to work on the elimination of routine flaring until 2030. According to this Initiative, the endorsing oil companies will reap various benefits.

- Improved resource management due to increased and sustained effective monetization of hydrocarbon resources.
- Environment-friendly oil production and reduced carbon footprint.
- Global recognition of the company being a responsible oil producer with strong environmental stewardship.
- Regional impact by demonstrating leadership and setting an example for others to follow, thereby impacting flaring practices at other oil companies.

Network advantages as the company connects to a network of leading oil-producing countries and companies that sets a de facto new global industry standard for gas flaring. This will provide companies valuable opportunities to exchange knowledge and experience, and to interact with the world's leading multilateral financial institutions.

## 5.1 RESIDENTS HEALTH IMPACT

A list of all the flare pollutants and their effect on residents' health is presented in Table 3.

**Table 3:** Pollutants of flare and their health effect (Barati, Pirozfar, 2019)

Chemical name	Health effect
Ozone in land	Low density: Eye stimulation. High density: Respiratory problems.
Sulphide hydrogen	Low density: Eye and nose irritation which results in insomnia and headache.
Nitrogen oxides (NO <sub>x</sub> )	Low density: Lung irritation, decrease lung function, increase susceptibility to allergens for asthmatics. High density: It results in meta-haemoglobins which prevents from absorption of oxygen by blood.
Carbon monoxide	Headache, nausea, weakness, potential long-term health effects
Particles matter	Accumulation of dust in pulmonary system causing pneumoconiosis, cancer and heart attack possibility.
Dioxide of sulfur	Respiratory system irritation and airway obstruction resulting in asthma and bronchitis aggravation.
Alkanes: Methane, Ethane, propane	Low density: Swelling, itching and inflammation. High density: Eczema and acute lung swelling.
Alkenes: Ethylene, Propylene	Weakness, nausea and vomit.
Benzene	Leukemia, aplastic anemia, pancytopenia, leukocytes, thrombocytes
Toluene	Potent central nervous system toxicant leading to narcosis, in coordination, emotional liability, and subjective symptoms such as headache and fatigue.
Xylenes	Unequivocal developmental toxins, leading to delayed development, decreased fetal body weights and altered enzyme activities
Styrene	Irritant of the skin, eyes, and mucous membranes and a central nervous system depressant

Naphthalene	Destroying the membrane of the red blood cells with the liberation of hemoglobin, irritating the eyes
Formaldehyde	Irritation of lungs and mucous membranes, cause to naso/pharyngeal cancers and possibly leukemia

## 5.2 GREENHOUSE EFFECT

Carbon dioxide emissions from flaring, which are by products of the combustion of fossil fuels, have high global warming potential and contribute to climate change. In addition to this, flares emit methane, which has about 25 times greater global warming effect than carbon dioxide on a mass basis. It is also more prevalent in flares when they operate at lower efficiency. Therefore, CH<sub>4</sub> and other volatile organic compounds must also be considered regarding climate change.

In order to mitigate greenhouse effect, the United Nations developed the Paris Climate Agreement, under the United Nations Framework Convention on Climate Change (UNFCCC), that came into force on November, 2016. Under this Agreement, specific actions and targets were set by the member countries that are referred as Nationally Determined Contributions (NDCs). The NDCs are divided into two categories. The unconditional NDCs which the countries have undertaken voluntarily without requiring any financial and technical assistance and the conditional NDCs that can be realized with external assistance.

The global results on various flaring emissions versus NDC targets are presented in Table 4. The results originate from gas flare estimates from satellite data collected by the U.S. National Oceanic and Atmospheric Administration's (NOAA) Visible Infrared Imaging Radiometer Suite (VIIRS). Flare quantities are divided into three categories, upstream, downstream and industrial flaring. Upstream flaring occurs in or near oil and gas wells. Downstream flaring is based on oil and gas refineries. Industrial flaring is the sum of the remaining operational flaring sites.

**Table 4:** Global results comparing gas flaring to NDC reduction targets (Elvidge, Bazilian, Zhizhin, Ghosh, Baugh, Hsu, 2017)

Global emissions (ktCO <sub>2</sub> e)	45,366,440
Conditional %	9.35%
Unconditional %	33.80%

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Conditional reduction target (ktCO <sub>2</sub> e)	4,243,761
Unconditional reduction target (ktCO <sub>2</sub> e)	15,335,069
Total NDC reduction target (ktCO <sub>2</sub> e)	19,578,831
Total flaring (ktCO <sub>2</sub> e)	285,347
% of Total NDC target for total flaring	1.46%
% of Unconditional NDC target for total flaring	1.86%
Upstream flaring (ktCO <sub>2</sub> e)	258,579
% of Total NDC target for upstream	1.32%
% of Unconditional NDC target for upstream	1.69%
Downstream (ktCO <sub>2</sub> e)	23,953
% of Total NDC target for downstream	0.12%
% of Unconditional NDC target for downstream	0.16%
Industrial flaring (ktCO <sub>2</sub> e)	2,814
% Total NDC for industrial flaring	0.014%
% Unconditional NDC for industrial flaring	0.018%

The collected data indicate that upstream flaring accounts for 90.6% of the total global gas flaring, the downstream one for 8.4% and the remaining 0.99% is the industrial percentage. The total gas flaring emissions of 285,347 ktCO<sub>2</sub>e represent 1.86% of the unconditional NDC goal and 1.46% of the total NDC target. This means that downstream flaring covers a very small percentage of the NDC targets and oil refineries an even smaller one.

Below, various figures present national results for the countries with the most significant gas flaring contribution.

### Top 20 Flaring Countries

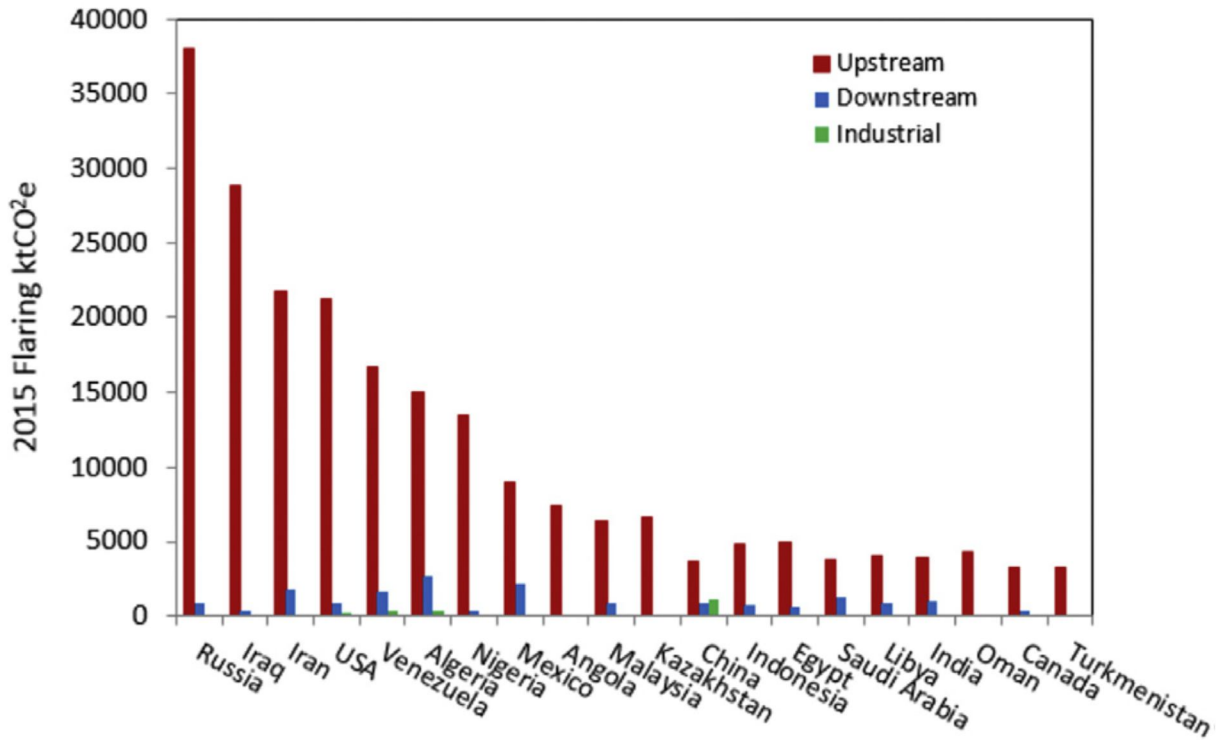


Figure 2: Total 20 countries for total gas flaring in 2015 (Elvidge et al, 2017)

### Percent of Unconditional NDC from Downstream flaring

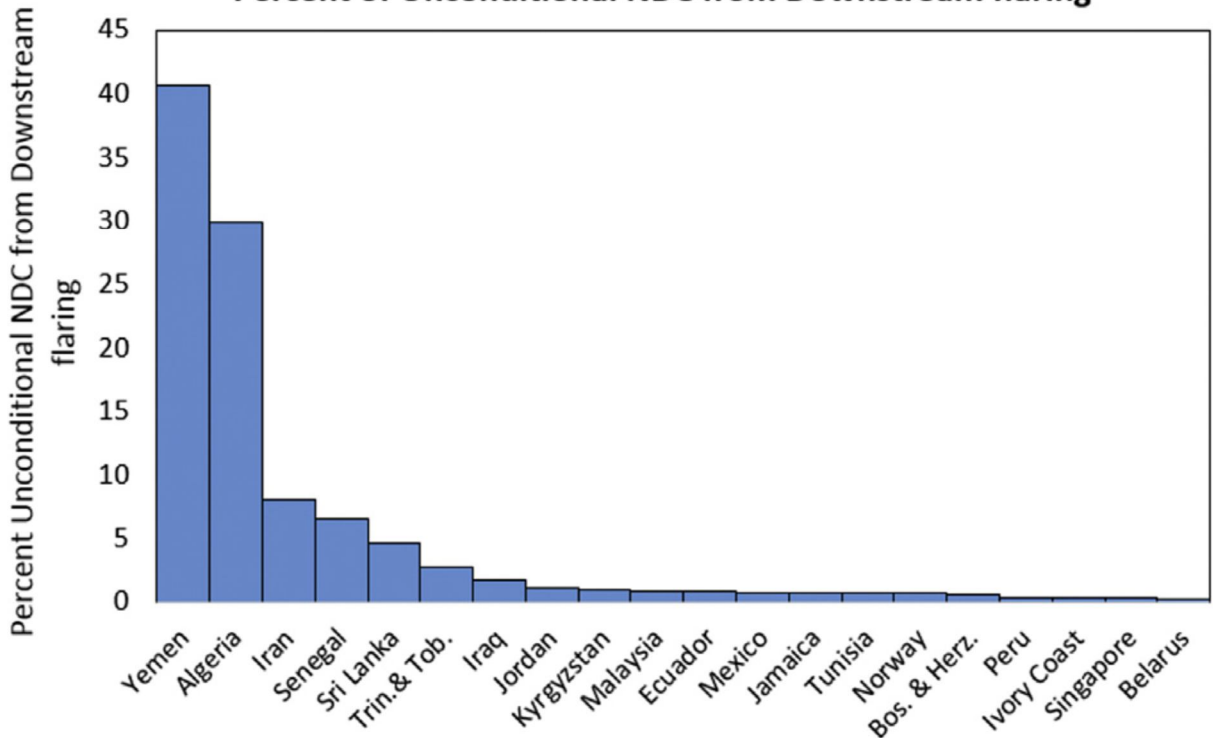
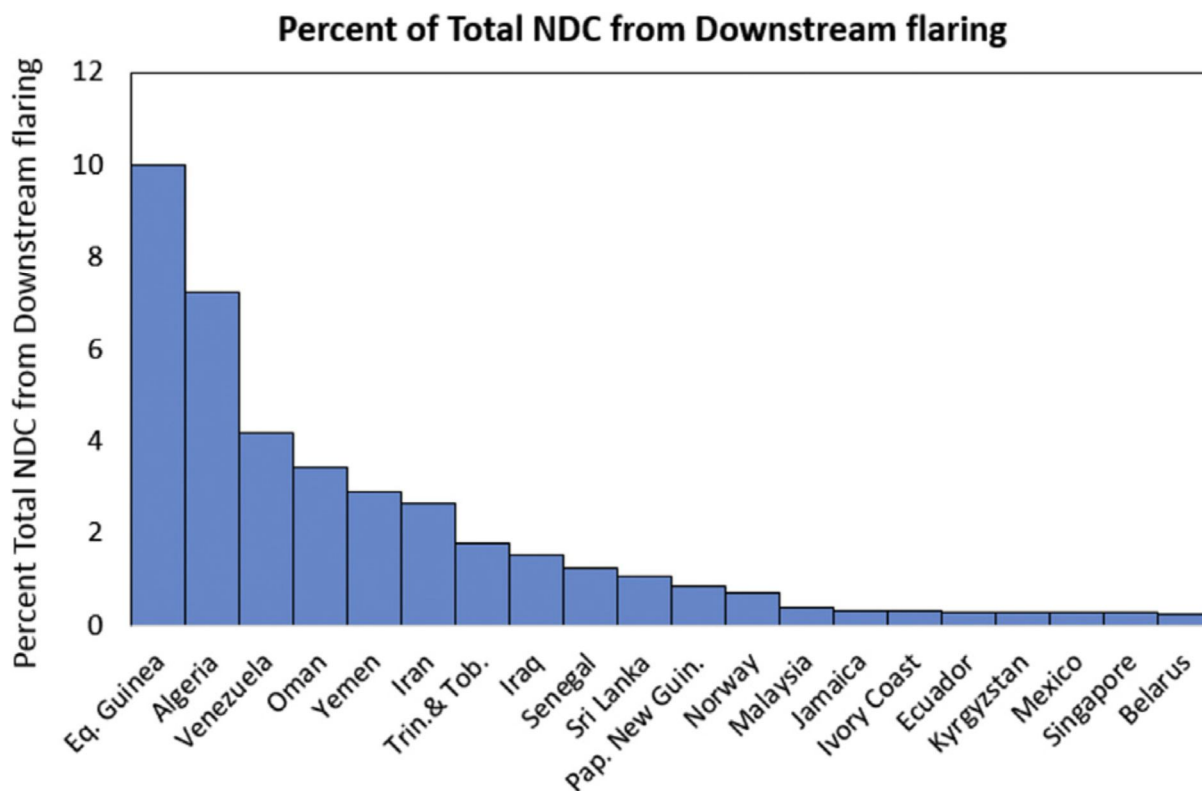


Figure 3: Percent of the unconditional NDC target that could be met with reductions in downstream flaring - top 20 countries (Elvidge et al, 2017)



**Figure 4:** Percent of the total NDC target that could be met with reductions in downstream flaring - top 20 countries (Elvidge et al, 2017)

### 5.3 ACIDITY IMPACT

When flare gas is burned into the atmosphere it can cause acid rain due to increased  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations, especially in humid environments. The acid rain is corrosive and causes damage to the environment, the vegetation and surface water. It can cause serious health problems such as skin cancers and lesions via dermal exposure. It can also cause a deteriorating effect on the refinery facilities and equipment (Soltanieha et al, 2016).

### 5.4 PHOTOCHEMICAL OZONE FORMATION

The photochemical oxidation of volatile organic compounds and carbon monoxide in the presence of nitrogen oxides and sunlight causes the formation of ozone at the ground level of the troposphere. High concentrations of ground-level tropospheric ozone damage vegetation, human respiratory tracts and manmade materials through reaction with organic materials. The Second Texas Air Quality Field Study was conducted in Houston in August and September 2006 in order to provide a better

understanding of atmospheric chemical processes was conducted. The study found evidence for the importance of short-lived radical sources such as HCHO and HONO in increasing O<sub>3</sub> formation. Those pollutants that were produced in flares from local refineries and petrochemical facilities could increase peak O<sub>3</sub> by approximately 30 ppb (Soltanieha et al, 2016).

## **5.5 AGRICULTURE IMPACT**

Most petroleum contaminants end up at soil and sediments. The aliphatic and polycyclic aromatic hydrocarbons (PAHs) which contain two to five aromatic circles pose a significant risk because of their mutagenic and carcinogenic properties and tendency to accumulate in organic tissues due to their lipophilic character and electrochemical stability (Soltanieha et al, 2016).

## **5.6 INCREASE IN REFINERY MAINTENANCE COST**

In addition to this, a flare disposing mainly unprocessed gas may constitute a significant overall particulate emissions factor. The untreated gas can also increase the maintenance cost due to condensation, fouling, corrosion and abrasion. Fouling can be created by the build-up of paraffin wax and asphaltine deposits, corrosion due to the presence of hydrogen sulfide, moisture, or some air and abrasion due to the combination of high flow velocities with debris, dust and other impurities presence in the piping (Emam, 2015).

## **5.7 COMBUSTION EFFICIENCY IMPACT**

The flare generated emissions quantity is mainly controlled by the combustion efficiency of the flare, namely, the percentage of hydrocarbon converted to carbon dioxide. The flare combustion efficiency depends from various factors such as heating value, gas velocity inside the flare and meteorological conditions which effect the size of the flame. Flares have highly variable efficiencies between 62 - 99 %, but when they are properly maintained and operated they can achieve a minimum combustion efficiency of at least 98%. In order to increase the combustion efficiency, a turbulent



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mixture of flare gas and steam or air is created to maximize the contact between carbon and oxygen. In case the turbulent mixture is created by air, there is a significant possibility for various implications on emissions. The combination of nitrogen found in the air and of high combustion temperatures favor the formation of thermal nitric oxide. On the other hand, the use of excess air may lead to reduced production of carbon monoxide but also leads to increased heat loss (Emam, 2015).

## CHAPTER 6: GAS FLARING REDUCING AND RECOVERY

Taking into account the various environmental and economic problems that are created due to the emissions of flare gas, the utilization of flare gas recovery systems (FGRS) is absolutely necessary in order to reduce the final emitted quantity. With the use of FGRS we can achieve reduction in noise and thermal radiation, operating and maintenance costs, air pollution and gas emission.

There are many methods which result in flare reduction and recovery flaring and they are summarized below (Barati, Pirozfar, 2019), (Soltanieha et al, 2016), (Hajizadeh, Mohamadi-Baghmolaei et al, 2018):

- **Collection, compression, and injection/reinjection**
  - a. into the refinery pipelines
  - b. collection and delivery to a nearby gas-gathering system
  - c. shipping the collecting flared gas to treatment plants before subsequent use
  - d. using as a feedstock for petrochemicals production
  
- **Gas-to-Liquid (GTL)**
  - a. converting to liquefied petroleum gas (LPG)
  - b. converting to liquefied natural gas (LNG)
  - c. converting to chemicals and fuels
  
- **Gas-to-Ethylene (GTE)**
  
- **Gas-to-Solid (GTS)**
  - Converting to Natural Gas Hydrates (NGH)
  
- **Fuel utilization**
  - Use of flared gas as fuel for the production of heat or electricity

Based on economic criteria, the decision of flaring or processing the gas depends on gas prices. If there is a certainty that gas sale will remain profitable for a satisfying time period, the necessary infrastructure could be built for gas processing and transportation. Based on technical criteria, the implementation of FGRS faces numerous challenges due to the vast variability of flow rate and composition of flare gas.

In case of very high flare gas yield, the preferred option is gas to liquid (GTL) conversion or liquefied natural gas (LNG) production in order to increase the value of the gas and to facilitate the fuel transport to distant markets. The main disadvantage of these methods is the enormous investment cost and that is the reason why it is considered only in case of large flare gas quantities.

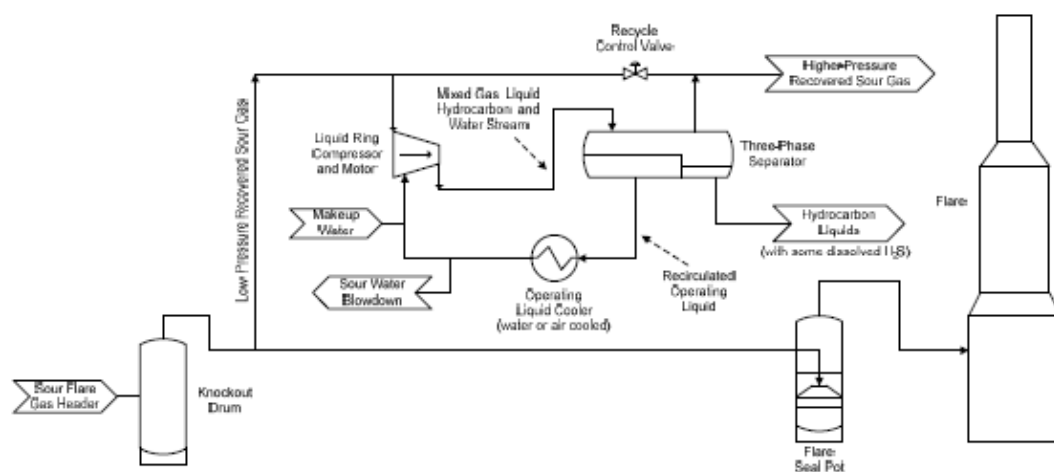
In case of high hydrogen sulfide concentration, several plants prefer the reinjection of the flare gas as it is more cost efficient than sulphur removal.

There is also the option of electricity generation using flare gas as fuel but its economic feasibility depends by the electricity needs of the plant.

## CHAPTER 7: GAS FLARING COLLECTION AND COMPRESSION

### 7.1 FLARE GAS RECOVERY USING COMPRESSOR

One of most common methods to reduce flare gas emissions is the collection and compression of flare gas in order to be transported and be processed in a suitable form for sale. This is achieved by the use of a gas compression and recovery system (FGRS) and a general view is presented on Figure 5. The flare gas which is collected from flare header is headed to the FGRS entering the knock out drum and then a liquid seal vessel. With the use of a compressor, the flare gas is discharged from the liquid seal vessel into a liquid separator. The separated liquid, through a heat exchanger, returns back to the service liquid inlet on the compressor. The dry gas is directed to the desired plant spot, usually the plant fuel gas header. The compressor recycle valve set point preserves the flare gas header under continuous positive pressure. The liquid seal drum is the safety measure in case of excess flare header flow as the higher pressure will break the liquid seal and allow the excess flare gas to be disposed and burned at the flare. The compressed gas which is collected from the FGRU will be used as feed for various processes or as fuel, depending from the design and the needs of the refinery.



**Figure 5:** Flare Gas Recovery System (McIntush, Mamrosh, Jones, Beitler, 2016)

### 7.2 FGRS DESIGN CRITERIA

#### 7.2.1 Sizing

The main FGRS design factor is the flare gas load. FGRS are rarely designed for emergency cases. In order to reduce cost, the selected FGRS capacity satisfies a normal flare rate, above which gas is flared. Their purpose is to comply with the

relevant laws and regulations during their normal operation. In order to minimize the disposed flare gas, the FGRS are designed to operate at the double to triple normal operating flare gas flow (Enayati Sangsaraki, Anajafi, 2015).

### **7.2.2 Liquid Seal Drum**

The main safety risk of using a flare gas recovery system is the air ingress into the flare header due to the compressor suction. This could cause the creation of a flammable gas mixture inside the system which can be ignited by the flare pilots. Seal drums will cause the buildup of flare header pressure and prevent air leakage into the flare system due to compressor shutdown or flare gas overload. The FGRS must operate within a very narrow pressure spectrum of 5 - 13 cm of water to 25 – 30 cm of water.

The liquid seal vessels used in FGRS are also called “deep liquid seals” with seal water depth of 0.7 meters or more. This depth is sufficient to provide adequate pressure control range for FGRS operation and to handle any flow changes from the normal operation to any emergency condition. Typically, the liquid seal drum is installed downstream of the knock out drum that is usually positioned near the flare stack base.

One additional liquid seal drum design factor that must be taken into account is the formation of unwanted seal fluid waves that can cause operating problems. These problems may include vibration, suction pressure instability and cyclic flare flame puffing. These problems can be resolved by the proper design of the drum internal structure. Water is not the only acceptable seal fluid as there are other fluids, such as stove oil and glycol water mixtures, that are used as possible alternatives. The main criteria of the fluid selection are freeze protection in cold climates, hydrocarbon and water separation, implications of carryover, cost, availability, and disposal.

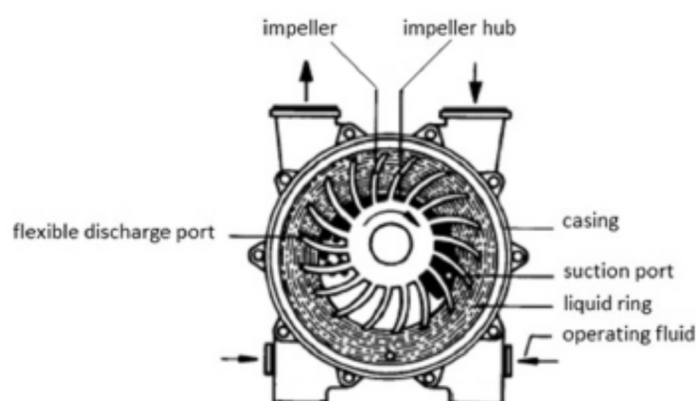
### **7.2.3 Compressor**

The most important equipment item of the FGRS is the compressor. The selected compressor technology greatly affects many important FGRS properties like initial capital, dimensions and operating and maintenance costs. There are various compressor types, depending of the refinery needs and capabilities, such as dry screw compressors (DSC), sliding vane compressors (SVC), reciprocating compressors (RC), liquid ring compressors (LRC) and oil injected or flooded single or dual screw compressors (FSC). The most common compressor types in refineries are the LRC and RC.

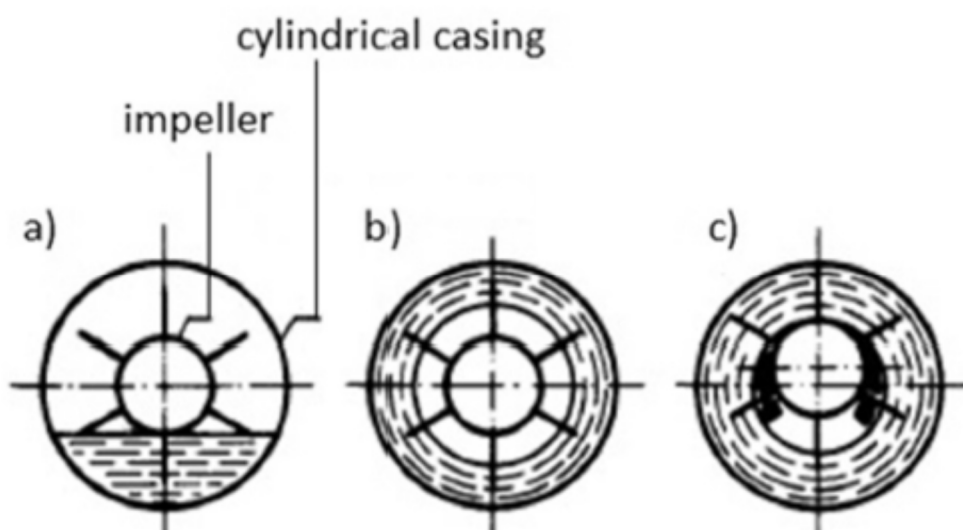
The liquid ring compressor (LRC) is a rotary volumetric machine that compresses the flare gas using water or amine as a secondary fluid. Amine is preferred in case of sour flare gas in order to remove the undesired hydrogen sulfide from the flare gas.

LRC consists on an axial impeller which is enclosed in the external case of the compressor. The flare gas is compressed and directed from the inlet port to the discharge port due to the impeller circular motion using of a number of blades positioned on the impeller. The flare gas is confined by the blades and the liquid fluid. This method can achieve high compression ratios, usually up to 1:31 between the suction and the pressure sides (Comodi et al, 2016).

Fig. 6 illustrates the parts of the liquid ring compressor and Fig. 7 its working principle.



**Figure 6:** Section of a Liquid Ring Compressor (Comodi et al, 2016)



**Figure 7:** Liquid Ring Compressor Working Principle (Comodi et al, 2016)

The impeller is installed eccentrically inside the circular casing, which is partly filled with liquid (Fig. 7a). The blades positioned on the impeller are radially or forward facing. When they are forward facing, higher liquid ring speed and compression are achieved. A liquid seal is formed at the external part of the cylindrical case due to the centrifugal forces that are caused by the rotation of the impeller (Fig. 7b). As the impeller is installed eccentrically, the space between the impeller and the liquid ring has a crescent shape (Fig. 7c). The impeller blades divide this crescent shaped space into several smaller ones. The flare gas enters the compressor through one of the divided spaces facing the suction port. The rotation movement of the impeller moves the flare gas to the smaller volume of the crescent shaped section causing its compression and final exit through the discharge port. The secondary liquid not only causes the compression of the gas but also its cooling negating the temperature increase during the compression stage.

The LRCs offer some additional benefits. They have a rugged construction and they are resistant to liquid slugs and dirty gas fouling. In addition, they can easily be used in case of two-phase flow, which is usually the case. It is also unlikely to enter into surge mode.

Their main disadvantage is that the rotating operation increases maintenance cost and noise levels. Their efficiency is low and their discharge pressure is low. In case of amine liquid ring, an interconnecting system must be installed to deliver amine to an amine washing column and then return the clean amine to the liquid ring.

The RCs advantage is their simple design which makes them more affordable to purchase and maintain. They can also operate with a wide range of compositions. Their main disadvantage is that they represent a significant risk since they can exceed their design pressure and lead to an explosion. Piston compressors are available with a variety of cylinder and stages number. Increasing the number of cylinders leads to increased flow while increasing the number of stages leads to higher pressure. The gas compressed in the cylinder in the first stage is cooled in the intermediate cooler and then compressed to the final pressure in the second stage.

Centrifugal compressors have lower maintenance requirements however they are less suitable for a wide variety of fluids.

Rotary screw compressors are cost effective but less reliable (Valero Refining Company – California, 2010).

#### **7.2.4 Compressor Control**

The conventional compressor control strategy is based on maintaining the suction pressure constant by adjusting the discharge flow of the compressor. A suction pressure of about 70 mbarg is sufficient to prevent air ingress and low enough to allow for the proper relief valves operation. As mentioned before, the suction pressure depends on the seal liquid height in the liquid seal drum. The pressure control measurement should be located in the compressor suction drum. This control signal initiates a recycle spillback to the compressor suction drum in order to preserve the required suction pressure. On the other hand, for equipment protection, an automatic emergency shutdown system should be incorporated, properly designed for the specific machine, components, and operating philosophy.

#### **7.2.5 Flare Gas Composition**

One more important design factor is the flare gas composition. Significant molecular weight variation can overload and damage the compressor and increase the compressed gas discharge temperature beyond the design one. As a result, special care is required to maintain the gas composition to the designed range in order to allow the compressor to operate as intended.

#### **7.2.6 FGRS Capacity**

The flare gas flow rate widely varies throughout the normal operation of the refinery. In order to minimize flare gas disposal and recover at least 90% of the flare gas flow the FGRS must be designed for a flow about 2 to 3 times higher than the average normal flare flow. Additionally, it must be designed taking into account the normal range of flare gas molecular weight. It is not required to consider the rare operating conditions during an upset or a turnaround.

When flare gas flow exceeds the design flow of FGRS, the flare header pressure increases to the point of the liquid seal back pressure. At that point, the flare gas surplus will pass through the liquid seal drum and will be end up in the flare to be burned. On the other hand, if the flare gas flow is lower than the design one the FGRS capacity adjusts to a turndown condition. This adjustment is realized by shutting down compressors or by the discharged flare gas diversion back to the suction header with



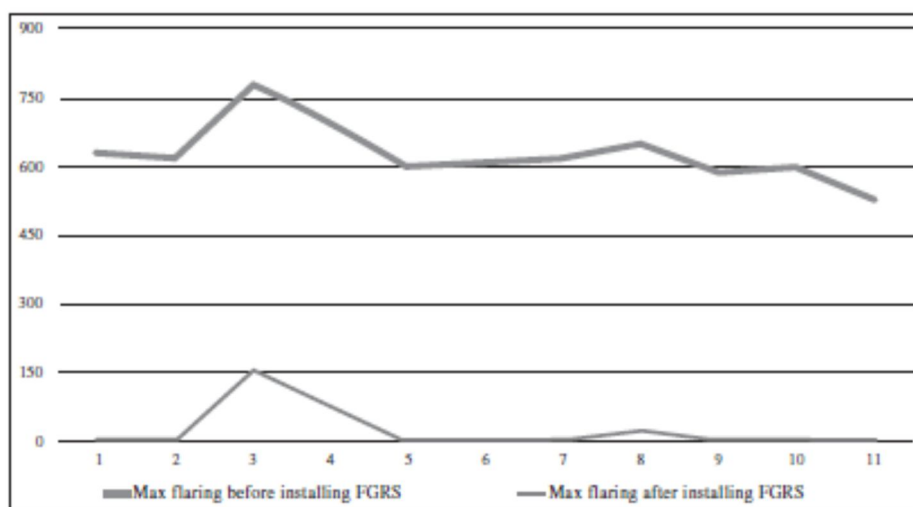
the use a recycle control valve or by the compressor speed reduction. These adjustments are automatic requiring minimal direct operator intervention.

### 7.2.7 FGRS Implementation Examples

The use of FGRS in refineries offers various advantages. In Dushanzi-China, the local oil refinery managed to recover 60 MMBTU/hr of flare gas. The atmospheric emissions were annually reduced by about 32.5, 176.8 and 67,000 metric tons of nitrogen oxides, carbon monoxide and carbon dioxide respectively. On top of that, the overall light, noise and thermal radiation were reduced benefitting the safety and the environment. Finally, the recovery and exploitation of flare gas provides significant economic benefit. Assuming a recovered flare gas value of \$ 5.00/MMBTU and a FGRS full capacity operation the total annual gain shall surpass \$ 5,000,000. As a result, the payback period of the total FGRS capital is estimated to less than nine months.

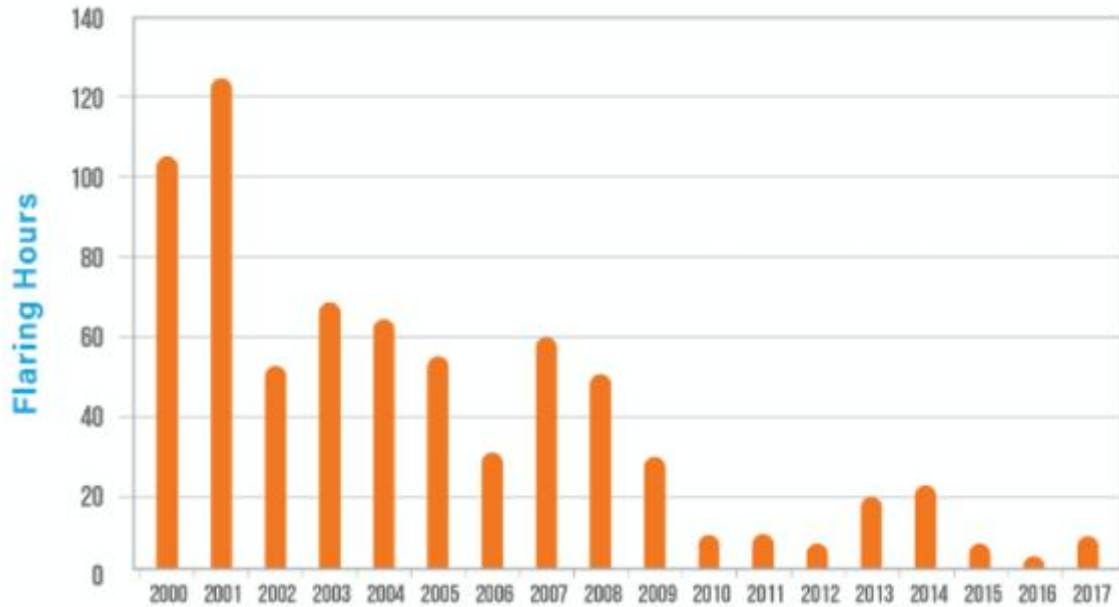
An oil refinery in Suez, Egypt managed to reduce the annual carbon dioxide emissions by about 163,000 t and the total flare gas emissions by about 94% and to recover FGRS capital cost in about two years.

A case study by Zadakbar et. al. of using FGRS in Tabriz Petroleum Refinery in Iran, with a nominal capacity of 80,000 barrels per day, including two LRC, two horizontal three phase separators and two water coolers indicated that a decrease of 85% of flare gas emissions and a 20-month payback period will be achieved, assuming the recovery of 630 kg/hr flare gas as fuel gas. The drastic flaring reduction is shown in figure 8.



**Figure 8:** Max. Monthly flaring before (up) and after (down) Tabriz Oil Refinery FGRS Installation (kg/h) (Zadakbar et al., 2008)

In Flint Hills Resources' Pine Bend Refinery in Rosemount, Minnesota the implementation of FGRS has dramatically reduced the annual number of flaring hours (Fig. 9).



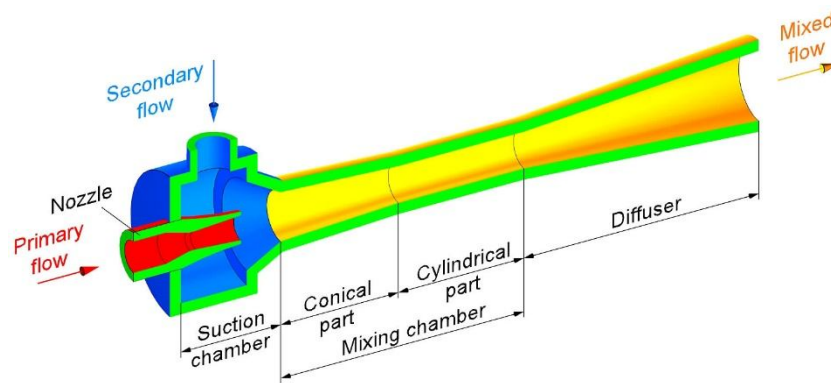
**Figure 9:** Flint Hills Resources' Pine Bend Refinery Annual Flaring Hours (American Fuel & Petrochemical Manufacturers, 2020)

### 7.3 FLARE GAS RECOVERY USING EJECTOR

Ejectors can also be used at FGRS as they are simple, reliable and cost, space and energy efficient. Their investment payback period ranges from few weeks to a few months. Ejector is a very simple device based on Bernoulli's principle. If no work is added to a flowing frictionless fluid, the sum of its potential, kinetic and pressure energy remains constant at all points along the streamline. As a result, an increase in its velocity results in a decrease in its pressure and vice versa. Based on this principle, the ejector uses a high pressure fluid to achieve the entrainment and the pressure increase of flare gas to an intermediate pressure between the two initial ones (Sonawat, Samad, 2012).

A single stage injector is presented on Figure 10. It consists of a driving nozzle, suction nozzle, mixing chamber and diffuser. The high pressure fluid (also called primary, motive, power or driving fluid) enters the driving nozzle where its kinetic energy is increased at the expense of its pressure energy. The significant pressure drop

of the driving fluid creates a low pressure spot in front of the driving nozzle that causes the entrainment of the flare gas, which is called secondary, suction or low pressure fluid, into the ejector. The two fluids mix together in the mixing chamber and energy is transferred from the high pressure fluid to the low pressure one causing the high pressure fluid deceleration and flare gas acceleration. The mixture pressure increases in the mixing chamber and further increases in the diffuser due to its velocity decrease. As a result, the ejector entrains the flare gas and compresses it to an exit pressure higher from its suction one and lower from the driving fluid one.



**Figure 10: Ejector**

If the mixture exit pressure is not high enough to allow for the recovered gas transportation, multiple ejectors can be used in series. The discharged mixture of the first ejector acts as the suction fluid of the additional ejector and this practice continues until the discharge pressure reaches the desired value. The driving fluid may originate from high pressure compressors, high pressure pipelines and first stage separators. The driving fluid is usually gas because even a small amount of flare gas requires a high driving liquid flow rate resulting in high economic cost.

The advantages of ejector use in FGRS are:

- The simplicity of the ejector which makes it easy to install and operate, safe and reliable.
- The operation and maintenance cost is lower as there are no moving parts.
- Its capital investment is low and provides a high return rate with a short payback period.
- They offer zero emissions operation.
- They produce low noise levels.

The disadvantages are:

- The improper mixing and frictional losses result to low efficiency between 26-33%.
- Operating conditions are not stable.
- The large driving flow rate that is required to compress and recover a small amount of flare gas.
- The difficulty to achieve accurate and reliable design of the FGRS.
- They do not offer gas washing treatment.

The ejector performance is mainly affected by its geometric, flow and fluid parameters.

The key geometric parameters are:

- The area ratio which is the ratio of the driving nozzle to that of the mixing chamber.
- The mixing chamber diameter and length.
- The setback distance which is the distance between the driving nozzle exit to the mixing chamber entrance.

The improper mixing of the two fluids and the formation of a recirculation region near the entrance of the mixing chamber are the main reasons that cause the loss of efficiency in the ejector. An increased mixing chamber length can reduce the losses by providing an optimized mixing. The recirculation region formation and its effect on the ejector efficiency can be prevented by reducing the setback distance or by increasing the area ratio. Finally, increase in the mixing chamber diameter to length causes increase in flow rate recovery and boosting effect decrease.

The key flow parameters are:

- The compression ratio, which is the ratio of outlet pressure to the secondary fluid pressure.
- The entrainment ratio, also named flow or discharge ratio, which is the suction nozzle flow rate to driving nozzle flow rate ratio.

An increase in compression or in entrainment ratio increases the low pressure fluid pressure boost.

There are various fluid parameters that affect the ejector performance. However, the viscosity of the two fluids is the most significant as its increase causes an efficiency

reduction due to increased frictional and momentum losses. To overcome this problem, a longer mixing chamber is required to improve the mixing.

In addition to this, the amount of liquid must not be more than 2% by volume in gas in any of the two fluids as it will reduce the ejector efficiency. To avoid this effect, separators are used to reduce liquid intake and maximize the ejector performance.

Finally, the ejectors must operate strictly according to their design conditions as a minimal high pressure fluid pressure reduction leads to their problematic operation.

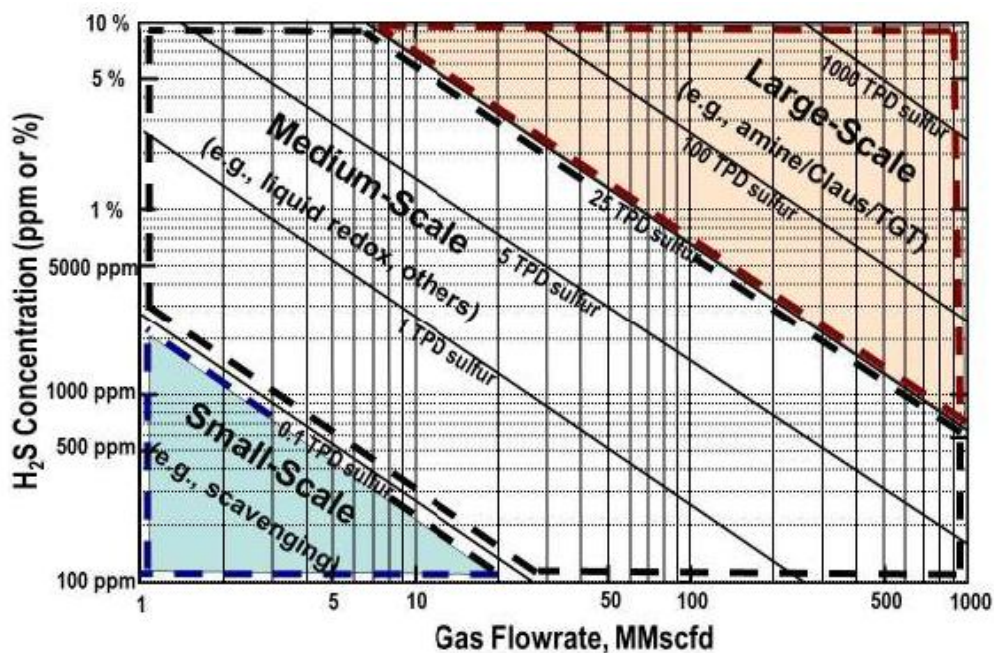
#### **7.4 ALTERNATIVES TO FGRS FOR SOUR GAS**

When FGRS is exposed to sour gas service, the capital, operating and maintenance cost raises considerably in order to provide consistent, safe and reliable operation. The recovered gas can also affect negatively the gas treating system. For example, if the recovered sour gas contains oxygen it will cause amine degradation and amine system corrosion. To resolve these issues, alternative hydrogen sulfide treating technologies should be considered thanks to their economic benefit (McIntush, Mamrosh, Jones, Beitler, 2016).

The removal of hydrogen sulfide from gas streams can be achieved with a large number of technologies based mainly on the hydrogen sulfide concentration and not the gas flow rate alone. Figure 11 below demonstrates the various methods categorization.

In case of large scale treating of more than 25 tons of sulfur per day, the amine / Claus process combination with a tail gas treating unit is used for complete sulfur recovery. For sulfur loads between 0.1 to 25 TPD other continuous applications are used, like liquid redox processes. Finally, for small sulfur loads, lower than 0.1 TPD a different method called “scavengers” is usually applied. Scavengers are non regenerable chemicals that operate in a semi batch mode. This method may have high chemical operating cost due to its semi batch mode but its lower capital cost and operating complexity make it more suitable than the ones applied at larger scales.

The most common technologies that are used for the sulphur removal from the flare gas in small scale are caustic treating, solid scavenging and liquid scavenging.



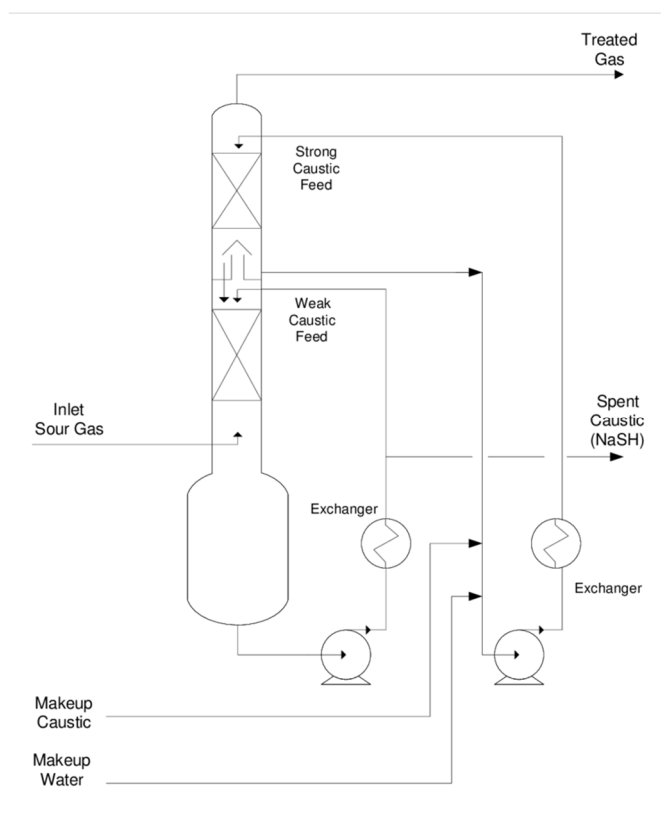
**Figure 11:** Technology Selection for H<sub>2</sub>S Removal (McIntush, Mamrosh, Jones, Beitler, 2016)

#### 7.4.1 Caustic Treating

The caustic treating method is used in small scale applications for the sulfur removal from the flare gas with the use of sodium hydroxide solutions. It can also find use in medium applications if there is a market for the sodium hydrosulfide solution that is produced during this process. If the caustic is not regenerated, it is referred as “scavenger”. The sodium hydroxide reacts with the hydrogen sulfide and forms a liquid mixture of dissolved sodium hydrosulfide and sodium sulfuret solutions and with carbon dioxide, if present, to form sodium bicarbonate and sodium carbonate. The problem with carbon dioxide presence is higher caustic use and potential carbonate salt precipitation. At moderate pH values, sodium hydrosulfide and sodium bicarbonate are the main products and at highly alkaline pH, sodium sulfuret and sodium carbonate respectively. Caustic treating can be performed continuously or in a semi batch mode with various equipment choices like packed and trayed towers, sparged tanks, in line and Venturi contractors.

The continuous caustic scrubber is preferred when our main concern is the caustic use minimization. In this design (Figure 12), the scrubbing tower is configured with two separated recirculating loops of caustic solution. The top loop is fed by a fresh caustic solution supply, operates at a high pH and its role is to maximize hydrogen sulfide removal efficiency. The caustic solution overflows from the top section to the

bottom one. The bottom section pH is lower and in that section is where the majority of the hydrogen sulfide removal is performed. The main disadvantage of this design is its complicated control and high capital cost. In addition to this, this method is not suitable for gas streams with high carbon dioxide content compared to the hydrogen sulfide one as a significant amount of caustic solution will be spent for carbon dioxide removal instead of the desired hydrogen sulfide scrubbing. The same problem is presented with the use of a sparged tank or a packed tower.

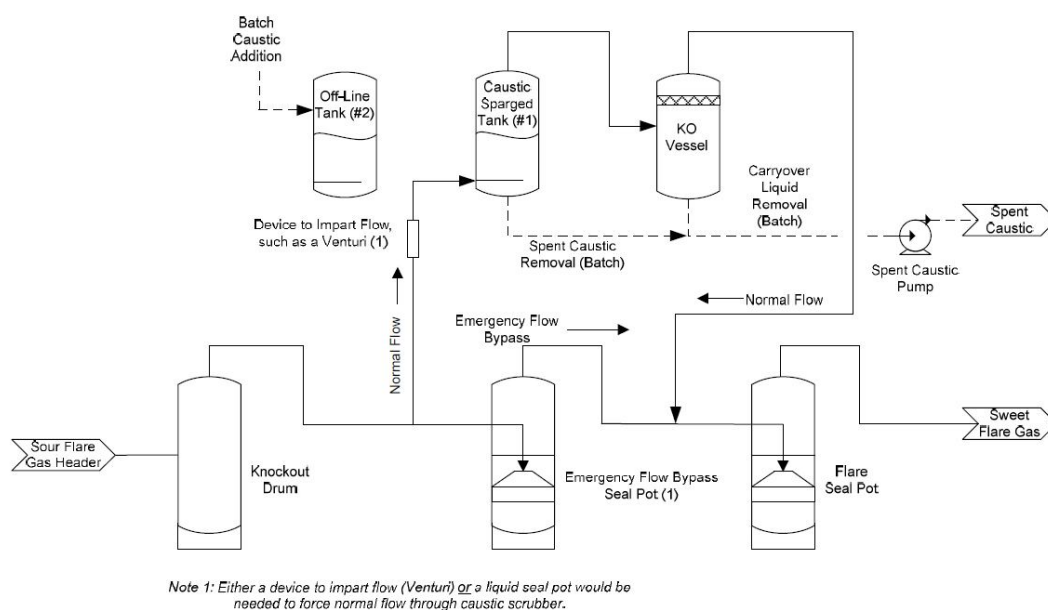


**Figure 12:** Caustic Scrubber Column with Dual Configuration (Mamrosh, Darryl, McIntush, Fisher, 2014)

If the treated gas has a high carbon dioxide content, the use of a short contact system is more appropriate as it absorbs mainly the hydrogen sulfide instead of the carbon dioxide. This is achieved due to the quicker hydrogen sulfide than carbon dioxide absorption at high pH conditions. In this case, static mixers, Venturi contactors and other specialized contacting devices are required.

Unfortunately, the continuous, short contact time systems have high operating complexity and capital cost that are not negated by the caustic solution savings making them inappropriate for low sulfur load. Therefore, a simple semi batch design, such as

a sparged tank system (Figure 13), is the optimal selection. The sparged tank can also act as a liquid seal device. In case the sparked tank causes undesired high pressure drop then it can be replaced by a packed or trayed tower. The tower must include a large sump at its bottom capable of accepting a large enough caustic solution quantity and a small to recirculate the solution over the packing. This design is applied in a number of refineries as a backup service for Claus SRU.



**Figure 13:** Semi Batch Caustic Treating (Mamrosh, Darryl, McIntush, Fisher, 2014)

This semi batch caustic treating method consists of two sparged tanks, one on line treating gas and the other off line as spare, and one knockout vessel. The two sparged tanks must be identical vertical vessels housing a gas sparger near their bottom section. The treated gas is directed from the on line tank to a large enough knockout drum equipped with a demister. The on line sparge tank will remain in use until the pH of the solution drops to a specific value that will cause the loss of sweetening gas efficiency or the solids precipitation. The point of caustic batch replacement is indicated with the aid of an on line hydrogen sulfide monitor. At this moment, the flare gas is rerouted to the second, off line tank and the first one is drained and resupplied with a fresh caustic batch.

The caustic treating system must be positioned as near as possible to the flare and flare knockout drum. In case of abnormally high sour flare gas flow rate, the bulk of the gas should be able to bypass the scrubber system with the use of the emergency



flow bypass seal pot and to be routed to the flare header. The emergency seal pot can also be replaced by other similar devices, like a buckling pin valve or a rupture disk.

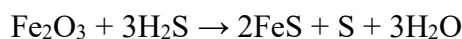
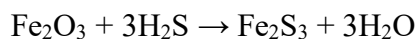
The main advantage of caustic treating systems is the low capital, due to its simple design, and chemical, due to low caustic price, costs. In addition to this, a semi batch mode, sparged tank system is simple to operate. Despite the frequent caustic replacement, the relevant process is easy. The spent caustic solution is a single phase liquid that is pumped to a waste collection system and is easily replaced by fresh caustic with the use of a truck or a local tank.

The main disadvantage of this technology is the complete carbon dioxide scrubbing that confines the sulfur removal. Furthermore, the caustic must not be fully utilized due to the undesired sodium bicarbonate salts precipitation. This precipitation is not expected under normal operating conditions but in some cases, like high carbon dioxide concentration or delayed caustic solution replacement, salt formation is possible that can cause vessel or lines plugging.

If the sodium hydrosulfide concentration of the spent caustic is high, it is valuable enough to be sold to a third party. If this is not the case, the spent caustic must be disposed cautiously due to its high pH. Using a strong acid to neutralize the high pH may not be recommended due to potential hydrogen sulfide liberation.

#### **7.4.2 Solid Scavenger Treating**

There is a great variety of solid chemicals that can be used as hydrogen sulfide scavenging agents. Ferric oxide can react with hydrogen sulfide, with water or steam present, to form iron sulfur compounds.



The iron oxide is a granular solid or a solid mixture on an inert substrate like clay and must have a sufficient contact time with the gas to ensure the hydrogen sulfide removal to ppm levels.

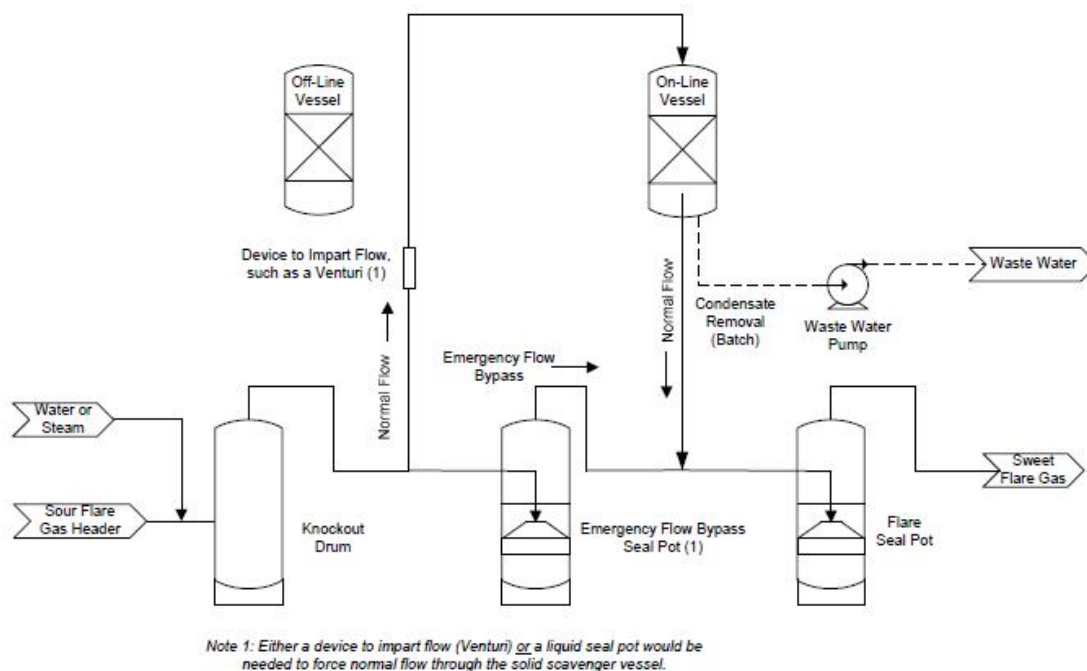
Other solid scavengers are potassium permanganate and copper or zinc oxides. Usually, they are more expensive than the iron oxide based ones. Their main advantage

is that they are used when the gas stream treatment must be realized without the addition of water as dry gas treatment with iron oxides will result in reduced capacity.

Iron sponge, which is consisted of iron oxide deposited on wood chips, is one of the oldest solid scavengers used due to its low cost. Its main disadvantage is the pyrophoric property of the spent product. As a result, it must be kept wet or else its exposure to air initiates exothermic reactions that can lead to fire. It is safer to use iron oxide based scavengers that are not pyrophoric and their substrate is not flammable. Nevertheless, they too can create raised temperatures and it is recommended to remove them wet to avoid any fire hazards.

A non-pyrophoric iron oxide scavenger system is presented in Figure 14. Two vessels are used, with only one of them being on line and treating sour gas. The other one will be available to act as spare. The sour gas stream enters the system saturated with the addition of water or steam to increase the adsorbent lifetime. A waste water pump is used to remove any condensate water from the vessels. Finally, an emergency flow bypass seal pot or other special device, like a buckling pin, rupture disk or relief valve, must be installed to bypass the flow during emergency, excess flow conditions.

This method has many advantages. The process is well tested, reliable, simple and cost efficient. The system, if properly designed, can cause almost negligible pressure drop, below 1 psi. If desired, it can also offer a long time period of months between change outs. The spent product can be safely disposed as a non-hazardous solid waste. Finally, the system can efficiently operate way below the design flow rate, preventing any turndown operating failures.

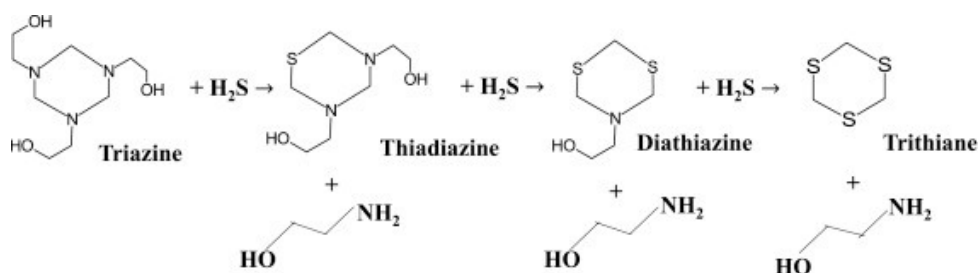


**Figure 14:** Solid Scavenger Treating (Mamrosh, Darryl. McIntush, Fisher, 2014)

The main disadvantage of this technology is that the spent material is worthless and must be disposed. Furthermore, the cleanout must be done manually, requiring more effort and time than the caustic treating case. Finally, water is needed in order to flush the spent material and keep the temperature low during cleanout and to keep the feed gas water saturated for a more efficient operation.

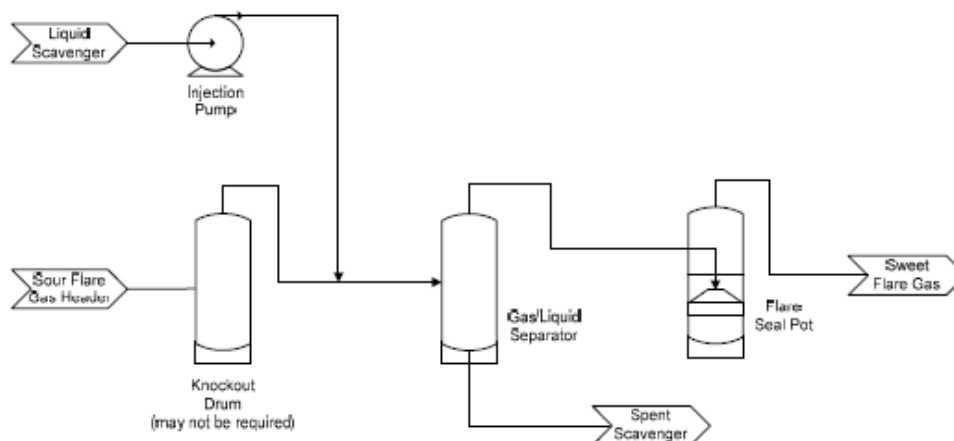
### 7.4.3 Liquid Scavenger Treating

In small scale applications, liquid scavengers are also used for sulfur removal. One type of chemicals that are used as liquid scavengers is the triazines ( $C_3H_3N_3$ ). Their molecular structure is a six-member ring in which three nitrogen atoms replace carbons. The triazines are mixed with water and react with hydrogen sulfide to create water soluble products according to the reactions indicated in figure 15. The spent solution is a single phase liquid with some, if any, solid formations.



**Figure 15:** Triazine –  $H_2S$  Reactions (Subramaniam, Yasa et al, 2018)

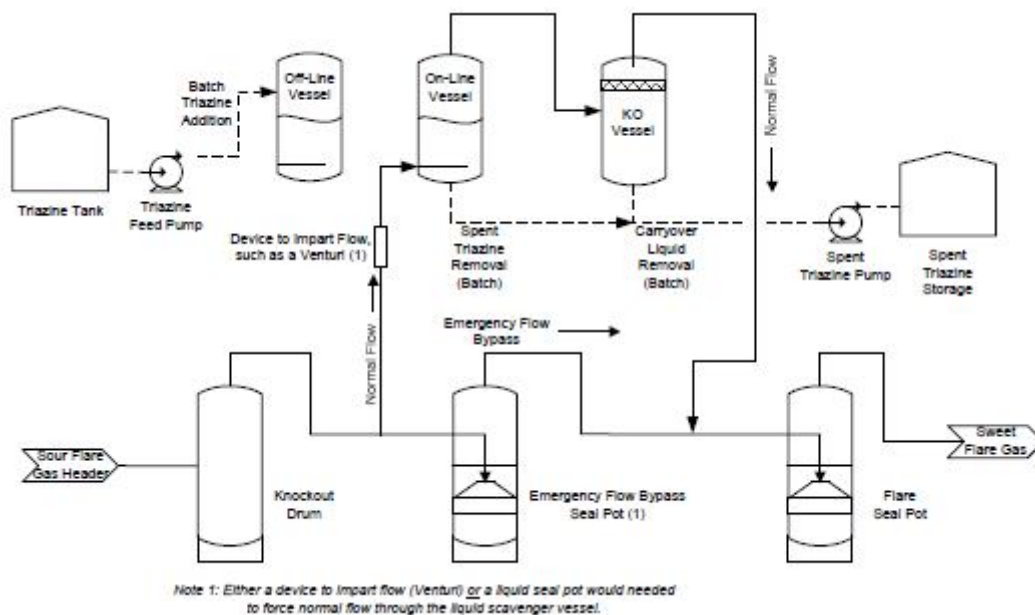
Sulfur removal with triazine liquid scavenger is rarely utilized in refineries. There are cases that refineries use a direct injection scavenging system (Figure 16) on flare gas to lower the sulfur oxides emissions from the flare. Usually, this method has low sulfur removal efficiency.



**Figure 16:** Direct Injection H<sub>2</sub>S Scavenging System (Mamrosh, Darryl, McIntush, Fisher, 2014)

The direct injection process consists of an injection pump that introduces the liquid scavenger into the sour gas pipeline, of the pipeline that provides the scavenger and sour gas mixing and of a downstream gas liquid separator that disposes the spent liquid product. This method, due to its simplicity, has a low capital cost.

As the scavenger – sour gas interaction occurs inside the pipeline, the longer the pipeline length is the more sulfur is removed. If there is a restriction in the pipeline length, then a sparged tower could be installed to enhance the sulfur removal efficiency. In addition to this, with the implementation of a proper sparger tower design significant pressure drop reduction can be achieved. The use of the sparger tower and the addition of storage for the fresh and spent liquid scavenger can transform the direct injection into a semi batch process similar to the semi batch caustic treating mentioned earlier (Figure 17).



**Figure 17:** Liquid Scavenger Treating in Semi Batch Mode (Mamrosh, Darryl, McIntush, Fisher, 2014)

Other examples of liquid scavengers that are used in industry include sodium nitrite, bleach and peroxide. Their disadvantage is that they lack the simplicity and the economic efficiency of caustic or iron oxide treating.

#### 7.4.4 Amine Solution Treating

Installing a new amine unit to treat the flare gas is not a common practice due to its high capital cost. The most efficient solution is the utilization of an existing amine system. That can be achieved by exploiting a small amine amount and by redirecting it from the main lean amine line to a dedicated column that will remove the sulfur from the flare gas. The spent amine will then end up to the main rich amine header of the amine system. Unfortunately, this method has a lot of drawbacks that need consideration. The flare gas operating temperature and pressure can affect negatively the sulfur removal efficiency, with the low pressure being the biggest issue. The amine contacting column will have to handle a wide spectrum of flare gas flow rates. Finally, the flare gas may contain oxygen and other contaminants that can significantly degrade the amine solution and cause corrosion to all the amine system network and impact its efficiency.

## CHAPTER 8: GAS-TO-LIQUID TECHNOLOGY

### 8.1 CONVERTING FLARE GAS TO LIQUEFIED PETROLEUM GAS (LPG)

This technology is an alternative way of utilizing flare gas because of its easy storage and transport to local markets. In most refineries, propane and butane constitute a significant percentage in the flare gas composition. In addition, most refineries have already LPG production plants installed. If this is not the case, the annual LPG production income does not compensate the required cost of columns and distillation towers and does not justify the installation of a new LPG plant.

The process flow diagram of LPG production is indicated in Figure 18. The flare gas is recovered before reaching the stacks and is sent to be treated for removal of carbon dioxide and hydrogen sulfide. Then the sweetened flare gas is compressed then cooled and sent to a three phase separator. The separated gas phase and liquid phase enters into the de-ethanizer and de-butanizer respectively. The de-ethanizer removes ethane and any lighter hydrocarbons and sends propane and heavier hydrocarbons to the de-butanizer. The gaseous product of the de-butanizer is directed to the de-propanizer where the main LPG unit products propane and butane are separated.

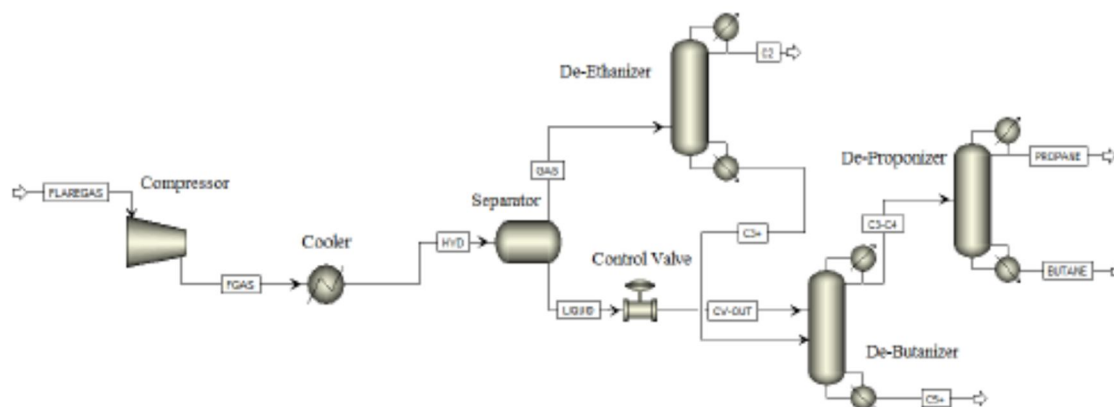


Figure 18: LPG Production Process Flow Diagram

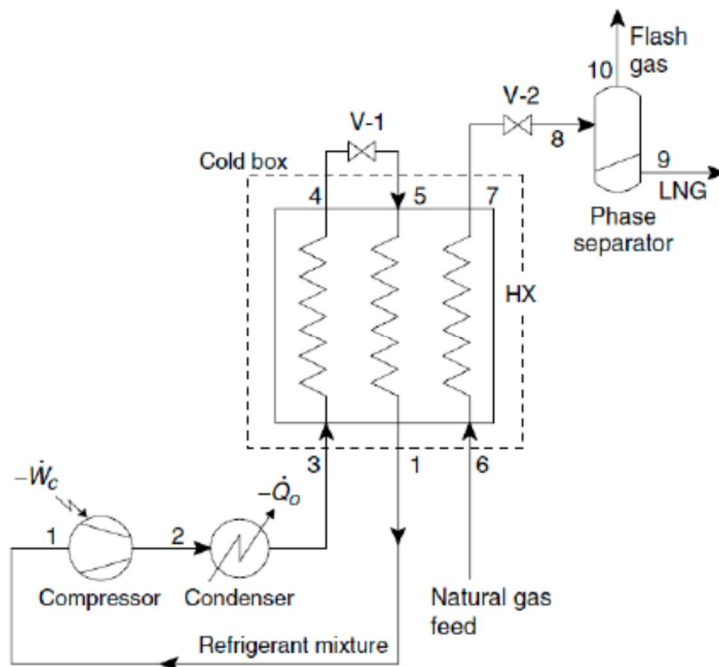
### 8.2 CONVERTING FLARE GAS TO LIQUEFIED NATURAL GAS (LNG)

LNG conversion is similar to LPG method with the exception of an additional refrigeration process. The flare gas is pre-treated for impurities like in the LPG production method, methane is extracted from the top product of the de-ethanizer and is liquefied by being cooled to  $-162^{\circ}\text{C}$ . The produced LNG, which now has a volume

of approximately 1/600 that of gas at room temperature, is stored until it is shipped onboard LNG tankers to be transferred and regasified to the desired designation.

There are many refrigeration cycles that are used for methane liquefaction. In oil refiner cases, where flare gases flow rate is low, the PRICO (Poly Refrigerant Integrated Cycle Operations) cycle is usually used (Barekat-Rezaei, Farzaneh-Gord, Arjomand, Jannatabadi, Ahmadi, Yan, 2018). This cycle is also called SMR (Single Mixed Refrigerant) process. Its main advantages, comparing with the other technologies, is its simplicity, resulting in low capital and operating cost, high flexibility and reliability and rapid startup.

The PRICO cycle flow diagram is presented in Figure 19. The refrigerant fluid is usually a mixture of methane, ethane, butane and nitrogen. This mixture passes through a compressor for pressure increase and then is sent to a condenser and a multistream heat exchanger for further cooling. From the multistream heat exchanger it is further sent to a throttling valve for pressure and consequently temperature reduction. The low pressure refrigerant is re-directed to the heat exchanger to cool and liquefy the natural gas derived from the deethanizer.



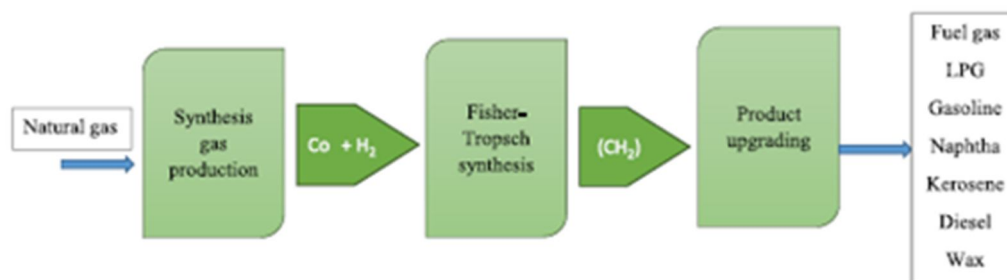
**Figure 19:** Poly Refrigerant Integrated Cycle Operations Cycle

### 8.3 CONVERTING FLARE GAS TO CHEMICALS AND FUELS

Gas-to-liquid (GTL) technology converts the recovered flare gas to longer chain hydrocarbons producing synthetic transportation fuels, zero sulfur, fully fungible products and compatible with existing liquid fuels, which can be introduced into the current infrastructure and supply system. As a result, a significant emission reduction can be achieved, benefitting the environment and simultaneously profitable synthetic fuels and chemicals can be produced. In addition to this, refineries are faced with new stringent standards. Blending zero-sulfur GTL diesels into the current crude based product mix facilitates the refineries effort. Those advantages are the reason why many countries consider GTL technology very attractive and promising.

### 8.4 FISCHER-TROPSCH PROCESS DESCRIPTION

The GTL technology is based on various chemical reactions providing a wide and flexible selection of produced chemicals. The most common GTL technology is the Fischer-Tropsch. (F-T). Its process consists of three stages (Rahimpour, Jamshidnejad, Jokar, Karimi, 2011). Synthesis gas production, Fischer Tropsch synthesis and product promotion (Fig. 20).

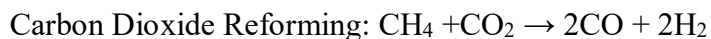


**Figure 20:** GTL Stages (Zolfaghari, Pirouzfard, Sakhaeinia, 2017)

Initially, methane is extracted from flare gas, sweetened and converted to syngas, which is a mixture of carbon monoxide and hydrogen, by partial oxidation, steam reforming or a combination called auto thermal reforming. For this method, to be economically viable, there is the prerequisite for high methane concentration in the flare gas mixture. The sweetening is required in order not to poison the F-T reactor catalysts.



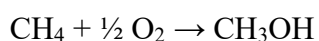
The primary reactions used to produce syngas from methane are:



#### **8.4.1 Partial Oxidation**

The partial oxidation reaction yields a hydrogen to carbon monoxide product ratio of 2:1 that is ideal for Fischer–Tropsch. Its main disadvantage is its large oxygen requirement. Air use is not feasible due to its nitrogen content and pure oxygen is expensive.

The partial oxidation route also offers the ability of direct methanol synthesis from methane in a single reaction.



#### **8.4.2 Steam Reforming**

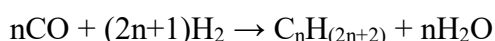
Steam reforming is the most common syngas producing method. Its high hydrogen to carbon monoxide product ratio of 3:1 is ideal for ammonia, urea and hydrogen production. Hydrogen can be used as an alternative to fossil fuels. However, this reaction is highly endothermic, requiring temperatures of at least 750°C and causing significant cost increase. The cost is also increased due to additional steam requirements in order to minimize catalyst deactivation.

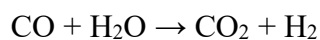
#### **8.4.3 Carbon Dioxide Reforming**

The carbon dioxide reforming reaction is the most environmentally friendly option as it uses methane and carbon dioxide, which are significant greenhouse gases, and allows the reuse of carbon dioxide produced by other processes. However, the reaction is highly endothermic, requiring high temperature of at least 800°C, and the rapid catalyst deactivation due to carbon deposition.

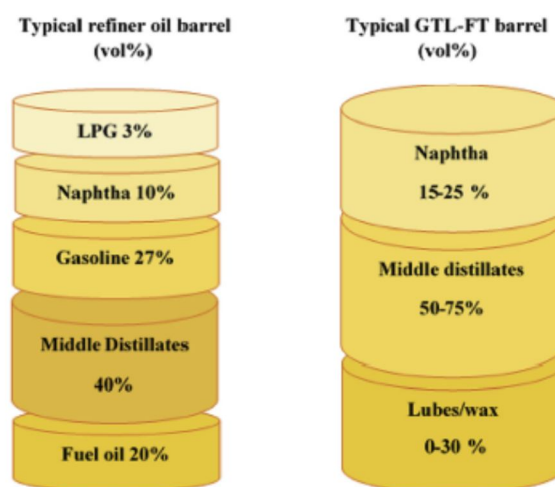
#### **8.4.4 F-T Synthesis**

The syngas is then directed to a F-T reactor to produce synthetic crude oil, containing longer and more valuable chain hydrocarbons. The main reactions that take place are:





The byproducts of this reaction are water and a higher pressure and temperature tail gas consisting of hydrogen, carbon monoxide, carbon dioxide and various light hydrocarbons. The synthetic crude oil is of higher quality due to the lack of sulfur, nitrogen, aromatics, and other contaminants typically found in ordinary crude oil. As a result, the gasoline produced from synthetic crude oil has a very high octane number and lower sulfur content. A comparison between a typical oil refiner barrel and a GTL-FT barrel is presented in Figure 21.



**Figure 21:** Typical Barrel Comparison (Zolfaghari et al, 2017)

#### 8.4.5 F-T Disadvantages

The GTL technology has some serious disadvantages. As mentioned previously, this method processes only methane. In addition, the F-T conversion facilities have a significant cost and their products are attractive compared to other alternatives such as hydrogen, methanol, dimethyl ether and conventional biofuels. The high capital and operating cost can be reduced combining the exothermic and endothermic reactions into a single chamber. As a result, the equipment size will decrease and the high thermal demands of the endothermic reaction can partially be satisfied by the produced heat of the exothermic reaction reducing energy and resources consumption.

#### 8.4.6 F-T Implementation Evolution

The F-T process was first implemented by Franz Fischer and Hans Tropsch in 1920s by using iron and iron – cobalt based catalysts. By that time, many implementations were tested including various reactor types like multi-tubular fixed

bed reactor, bubble column slurry reactor, bubbling fluidized bed reactor, three-phase fluidized bed reactor and circulating fluidized-bed reactor.

Nowadays, new practices allow us to accomplish higher conversion rates. In 2010, Tonkovich applied microchannel technology and cobalt as catalyst to F-T method to enable cost effective production at the smaller scale GTL facilities. As a result, the steady state carbon monoxide conversion was over 70 % and selectivity to methane was under 10 %. Additionally, the reactor operation and conversion rate remained steady for more than 1,100 hr of operation.

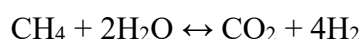
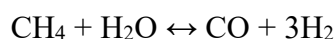
In 2011, Rahimpour studied the F-T synthesis performance difference of two cascading membrane dual-type reactors, one fluidized-bed reactor versus a fixed-bed one. The study concluded that the fluidized bed reactor achieves 5.3 % increase in the gasoline yield and 12 % decrease in carbon dioxide yield compared to fixed bed reactor offering additionally more precise temperature control and a smaller pressure drop.

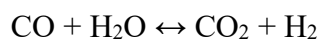
In 2013, Knutsen simulated and optimized the operational performance of a GTL plant based on autothermal reforming and using a multi tubular fixed bed reactor together with a cobalt catalyst. His method achieved a synthetic crude production with a carbon efficiency of about 77 % and thermal efficiency of about 62 %.

In 2015, Weimer developed a new catalyst using atomic layer deposition in order to convert low value gas to high value synthetic crude oil. The use of this catalyst produces 2.5 times more synthetic crude with a high conversion rate of about 90 % and low methane selectivity for about 6 wt%. In addition to this, the catalyst is robust and has a low deactivation.

#### **8.4.7 Syngas and Hydrogen Production**

One of the many F-T implementations is the hydrogen production. Hydrogen based energy systems are known for their high efficiency and for their low to no polluting emissions. The methane contained in flare gas, via methane steam reforming (MSR), is one of the most interesting hydrogen production feed. The main disadvantage of this method is the coproduction of carbon monoxide and carbon dioxide according to the following reactions.





In addition to this, this process requires high temperatures to allow an economically viable methane conversion. Unfortunately, the high temperature causes the deterioration of the catalyst condition and activity.

All these drawbacks can be resolved with the use of a hydrogen selective membrane reactor. There is already a wide utilization of palladium and palladium - silver based membrane reactors because of their high permeability and selectivity towards hydrogen and high temperature and corrosion resistance. In order to achieve more efficient hydrogen production, the reaction and separation take place simultaneously in a single unit. Due to the simultaneous hydrogen removal from the reaction zone of the membrane reactor the equilibrium limitations are less severe and the reaction is realized at lower temperatures without a process performance impact (Saidi, 2018).

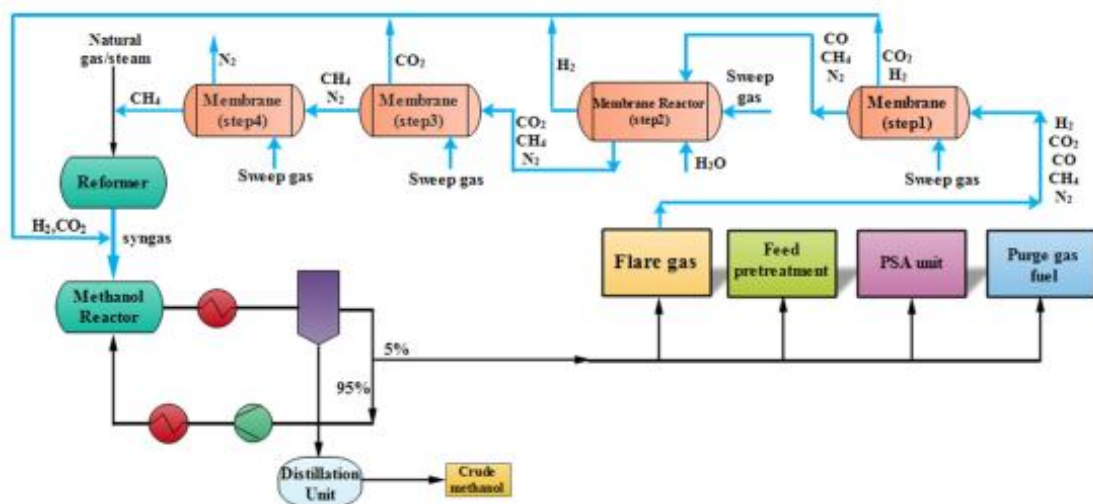
Furthermore, there are many types of catalysts capable to enhance the process efficiency. Nickel based catalysts have been extensively investigated due to their low cost and high activity. Noble metals catalysts exhibit high activity, low deactivation and enhanced coke deposition resistance, but at a higher cost. The noble metal catalysts can also be added in small amounts to nickel based catalysts providing great improvement. Also, oxides such as cerium oxide and zirconium dioxide are commonly used due to their high oxygen storage capacity and redox properties, which causes less coke formation.

#### **8.4.8 Syngas and Methanol Production**

Methanol is produced from syngas and plays an important role to many chemical and petrochemical processes in industry. Using methanol as a liquid fuel has the advantage of ease of storage and transportation, compared to compressed natural gas. It can also be used to produce dimethyl ether, methyl formate, formaldehyde, acetic acid and olefins such as ethylene and propylene (Khanipour, Mirvakili, Bakhtyari, Farniaei, Rahimpour, 2017). Unfortunately, its current production is achieved through a conventional two-step process which is expensive and energy intensive. This two-step process is based on Fischer-Tropsch method by the methane steam reforming which is followed by the high pressure catalytic conversion of the produced syngas to methanol. As already mentioned in partial oxidation, methanol can also be produced by

methane in a single reaction but its main disadvantage is the side reactions and its poor methanol selectivity (Khirsariya, Mewada,2012).

In order to enhance the performance of methanol production, unreacted synthesis gas and methane can be recycled with the use of a combination of membrane based separations. The recycled streams are located upstream the steam reformer and the methanol reactor according to the schematic diagram indicated below.



**Figure 22:** Schematic diagram of the Modified Methanol Process (Khanipour et al, 2017)

The flare gas recycling cannot be applied without the separation phase due to nitrogen presence. The continuous recycling results in nitrogen accumulation and in creation of undesired by-products such as nitrogen oxides and ammonia. Subsequently, it causes more problems like increased corrosion, lower quality and productivity and excess environmental impact. Furthermore, the separation process ensures that the recovered methane is sent to the steam reformer reactor and that the recovered syngas is directed to the methanol reactor.

The modified methanol process is composed by the following steps:

- Removal of hydrogen and carbon dioxide from the recycled stream in step 1
- Removal of hydrogen and conversion of carbon monoxide to carbon dioxide with the use of water gas shift (WGS) reaction in step 2
- Removal of carbon dioxide in step 3
- Removal of nitrogen in step 4

- Injection of the recovered methane stream to the steam reformer
- Injection of the recovered hydrogen and carbon dioxide to the methanol reactor

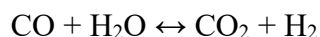
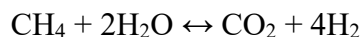
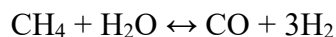
In the first step, the use of a polymeric membrane allows the simultaneous removal of hydrogen and carbon dioxide from the recycled stream due to their smaller kinetic diameters and higher permeability. Nitrogen, methane, and carbon monoxide have similar kinetic diameters and is difficult to be extracted in a single stage.

In the second stage, the recycled gas, derived from carbon dioxide and hydrogen, is directed to a catalytic membrane assisted reactor. The shell side of the WGS membrane reactor converts carbon monoxide to carbon dioxide with the use of water ( $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ ) and the aid of iron – chromium - copper catalyst particles. Water also allows the cooling of the shell side as the water gas shift reaction is exothermic. The tube walls of the reactor are a palladium and silver alloy membrane that allow the extraction of the produced hydrogen. Extracting hydrogen and heat from the reactor enables the shift of the equilibrium and the improvement of the reaction efficiency.

The third step is similar to the first one. The same membrane is used to allow for carbon dioxide separation.

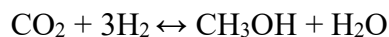
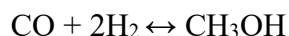
In the previous steps the membrane separation was based on size difference not allowing nitrogen and methane separation due to their similar kinetic diameters. In the fourth step, CHA zeolitic membranes, like SSZ-13 or SAPO-34, are used to extract nitrogen from the recycled stream. The recycled stream, composed mainly from methane, is directed to the steam reformer.

In the steam reformer, three simultaneous equilibrium reactions can be observed:



The recovered hydrogen and carbon dioxide recovered from the first three stages are collected and sent to the methanol reactor. In this reactor, three equilibrium

reactions take place using the syngas produced from the steam reformer and the recovered gases:



The gas recycling method applied in steam reforming can offer a 4.6% increase in the methanol production capacity (Khanipour et al, 2017).

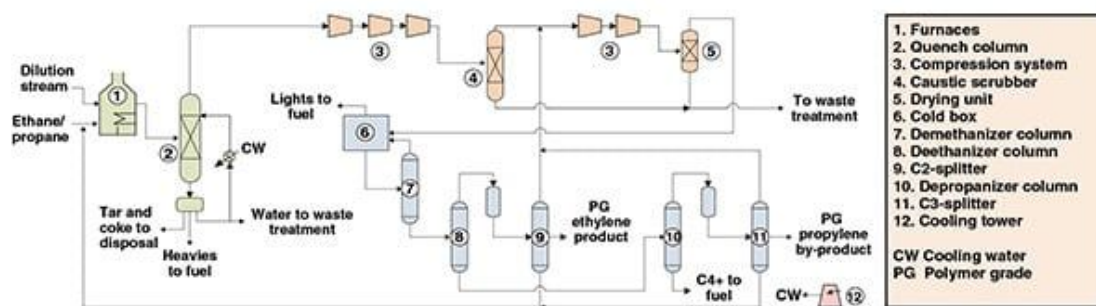
This method could also be used for other Fischer-Tropsch processes. In carbon dioxide reforming, the method can be the same with the only difference being the use of the collected carbon dioxide in the carbon dioxide reactor. In partial oxidation, this method could reduce the products of the side reactions and improve methanol selectivity.

## **8.5 GAS-TO-ETHYLENE (GTE)**

Ethylene ( $\text{C}_2\text{H}_4$ ) is a very important chemical product with a variety of commercial uses and therefore it has a large, worldwide demand and production. It does not exist in the nature and is produced industrially from methane or ethane. The importance of ethylene lies to its double molecular bond in its molecular structure, which provides a high reactivity that enables its conversion to a wide range of other desirable chemical compounds. Of all these products, the most significant is the low and high density polyethylene, which are used in many industrial sectors like construction, communication and packing (Zolfaghari, Pirouzfard, Sakhaeinia, 2017).

Ethylene can be produced by a steam cracking process from ethane – propane mixture derived from the flare gas. The process is shown in Figure 23 and can be divided into three main sections. Cracking - quenching, compression – drying and separation (Chemical Engineering, 2015).

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**Figure 23:** Ethylene Production Process via Ethane – Propane Cracking (Chemical Engineering, 2015)

The initial stage is the cracking and quenching. The ethane – propane mixture is sweetened, to remove the sulfur, and fed to a furnace in which, under high temperature and pressure, is cracked and converted in ethylene, propylene and other byproducts. The cracked mixture is then sent to a water-based quench tower to prevent further undesired cracking and byproducts formation. Downstream the quench tower, a decanter removes tar, coke, heavier components and the condensed steam. The cracked gas exits the tower and is directed to the next section.

In compression and drying section, the cracked gas is initially compressed in three stages and sent to a caustic scrubber in order to remove carbon dioxide and sulfur using caustic soda and water washes. After the scrubber, an additional two stage compression is performed and the compressed gas is cooled and dried by molecular sieves to remove most of the water.

The separation stage is initiated with the entry of the dried cracked gas into a cold box in order to remove hydrogen and light hydrocarbons and to minimize ethylene losses. The cold box condensates are routed to a series of separation columns.

The first one is the demethanizer where methane is derived from the top and send back for further use in the cold box, while the bottom stream is fed to the deethanizer.

The top stream of the deethanizer, mainly ethylene and ethane, is fed to an acetylene converter and then to the C2- splitter for fractionation. The light overhead stream of the splitter is recycled back to the compression stage. The desired polymer grade (PG) ethylene is derived from a side stream. The C2- splitter bottoms contain ethane and are sent back to the cracking furnace.



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The deethanizer bottoms are directed to the depropanizer which removes C4+ hydrocarbons from its bottoms. The overhead stream and its C3 components are catalytically hydrotreated, to remove methyl acetylene and propadiene, and then routed to the C3- splitter. In this splitter, the light top stream is sent back to the compression system, polymer grade (PG) propylene is extracted as a side stream and propane is extracted from the bottoms and recycled back to the furnace.

## CHAPTER 9: GAS-TO-SOLID TECHNOLOGY

### 9.1 CONVERTING FLARE GAS TO NATURAL GAS HYDRATES (NGH)

This technology is in the research state. NGH is crystallized, solid, natural gas and is chemically stable at  $-20^{\circ}\text{C}$ . The advantage of this method is lower capital, transportation, and storage costs due to its much higher temperature. However, NGH is far less dense than LNG containing fewer natural gas.

## CHAPTER 10: ENERGY PRODUCTION

The increased energy carriers cost has drawn the industry's attention to new, unconventional energy sources. One of these sources can be the flare gas of the refineries due to its high thermal value and no supply cost. Energy can be produced from flare with various methods for various uses (Shayan, Pirouzfard, Sakhaeinia, 2019).

### 10.1 FUEL GAS BLENDING

Refineries operation must maintain a balance between the production and the consumption of the fuel gas. Usually, most of the hydrocarbon gases which the refinery produces are used by the fuel gas unit of the refinery as a fuel source of the various combustion devices inside the plant. In case of excess fuel gas demand, the fuel gas balance is maintained with the addition of natural gas from an external source or with the adjustment of fuel gas consumption reducing the performance of combustion devices.

Recovered flare gases can be directed into the fuel gas unit helping the maintenance of fuel gas balance. They must certainly be of the appropriate quality, meaning they are mainly composed from light hydrocarbons and their content of nitrogen, steam, sulfur and other low BTU gases is low enough. This blending is a complex process as the different qualities of produced fuel gases and recovered flare gases must combine into a final fuel gas with a sufficient heating value to maintain properly the combustion and with a limited sulfur content to avoid the formation of sulfur oxides (Valero Refining Company – California, 2010).

### 10.2 HIGH PRESSURE STEAM GENERATION

Flare gas combustion can produce high pressure steam which is used at oil refineries as utility. It is utilized in four forms, very high pressure steam (VHP), high pressure steam (HP), medium-pressure steam (MP) and low pressure steam (LP).

Produced steam can be used for heat generation, pressure control, mechanical motion and water supply to various processes. As the steam heat is mainly in latent form, it can be transferred efficiently in a constant temperature, allowing heat transfer

in controllable conditions. Steam has also the ability to be converted to superheated steam and transfer large heat amounts. With this form, steam is very useful to refineries, especially in starting up steam turbines.

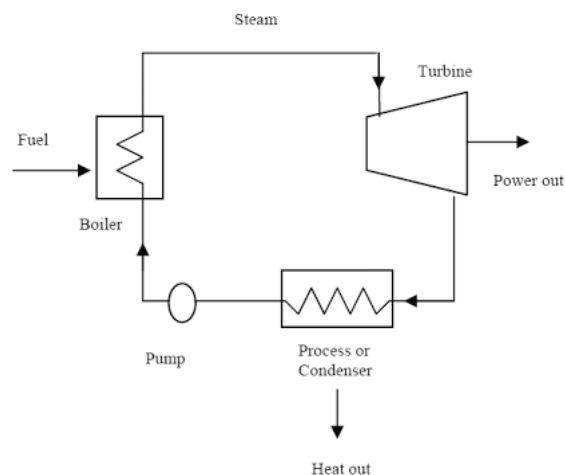
### 10.3 ELECTRICITY GENERATION

Flare gas can be used as fuel in a gas turbine, a steam turbine or an internal combustion engine to produce power which can be converted to electric power by a coupled generator. The produced electric energy can be used to cover the various power demands of the plant operations or even be sold if there is a surplus of electricity production.

### 10.4 ELECTRICITY GENERATION BY TURBINE

#### 10.4.1 Steam Turbine

The flare gas electricity generation can be achieved with various cycles. One of the most common and old technologies is the Steam Rankine Cycle (SRC). At first, the flare gas and air are mixed and compressed to enter the combustion chamber. The heat generated from the flare gas combustion evaporates water into a boiler, raises steam pressure and converts it into a high kinetic energy fluid. This fluid drives the steam turbine blades, converting the high kinetic of the steam to mechanical energy and that to electricity.

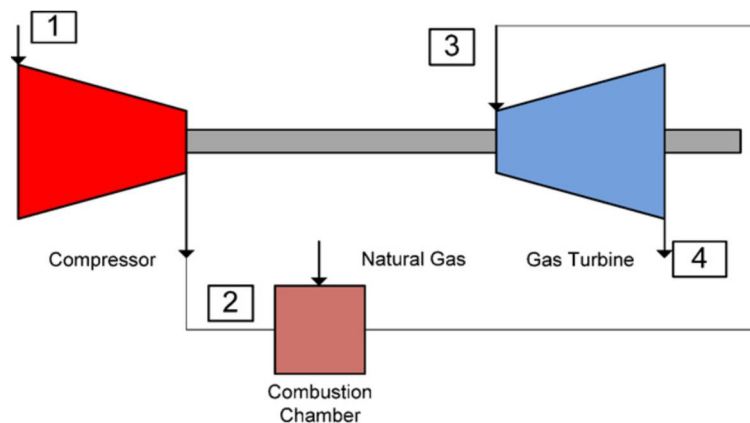


**Figure 24:** Steam Turbine Diagram

If water is replaced by organic fluids with a lower boiling point, higher vapor pressure and higher molecular weight higher mass flow can be achieved and, as a result, improved efficiency with reduced temperature and heat demand. This technology is called Organic Rankine Cycle (ORC). ORC system required heat temperature can be as low as 148 °C, whereas steam systems need a source temperature of more than 260°C.

#### 10.4.2 Gas Turbine

Gas turbine generators tend to produce high power outputs at high efficiency and low emissions. Furthermore, the maintenance cost of gas fuels is lower than liquid fuels. These are some of the most important reasons why oil and gas industries decide to install an increasing number of gas turbine generators. A single shaft gas turbine operating under Brayton cycle is indicated in Fig. 25. Ambient air is compressed at point 1 and directed to a combustion chamber at point 2. At this point the pressurized air is mixed with the flare gas collected from the flaring network and their mixture is combusted. The heated and pressurized gas is driven to the turbine at point 3 where it expands and conveys its high kinetic energy which is converted to mechanical and then to electrical. At point 4, the exhausted gas exits the gas turbine (Rahimpoura, Jokar, 2012).



**Figure 25:** The Brayton Cycle (Rahimpoura, Jokar, 2012)

The main disadvantage of this method is the variation of properties like the flare gas rate and composition, its temperature and pressure, H<sub>2</sub>S content, solid and metal particles and humidity. The size of this variation is an important factor for the selection of the generators. (Zolfaghari et al, 2017).

### **10.4.3 Examples**

On 2015, Heydari studied and compared two methods of flare gas electricity production. The first scenario uses a simple Brayton cycle turbine. In the second method, turbine inlet air cooling is added. The direct consequence of cooling the turbine inlet air are power output augmentation and energy efficiency improvement. The electricity production in the first and second method are 38.5 MW and 40.25 MW respectively and their payback periods are 3.32 and 3.48 years.

## **10.5 ELECTRICITY AND HEAT COGENERATION**

The use of heat and electricity cogeneration technology has been expanded into most of mechanical or electrical power generators due to its high energy efficiency. Nowadays, any power generation system can take advantage of the cogeneration method. Using this method, the initial energy losses that occur during the electrical or mechanical power generation can be used to produce useful heat and steam. As a result, these power generators are characterized by high power-to-heat ratios and electrical efficiency. This process can be realized with the use of a steam turbine which uses as fuel the flare gas.

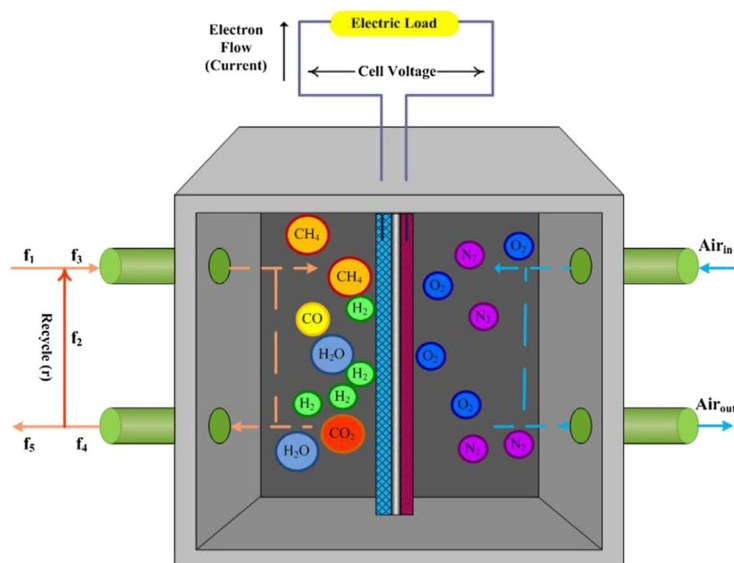
## **10.6 COMBINED CYCLE TECHNOLOGY**

Combined cycle power generators are often used in industry as the base load system. In this process, two power circles are combined, the Brayton cycle used by a gas turbine and the Rankine cycle applied by a steam turbine as auxiliary. The gas turbine uses flare gas as fuel to generate energy and the produced exhaust gases are used to create the steam required for the steam turbine which will generate additional energy.

## **10.7 FUEL CELLS FEED**

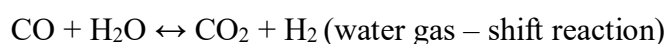
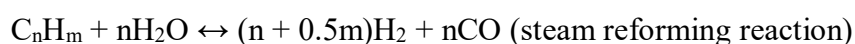
Flare gas can also be used as a feed for fuel cells, systems that produce electricity by the direct conversion of chemical energy of a fuel (usually hydrogen) and an oxidizing agent (often oxygen) through a redox reaction. Of the various fuel cell types, solid oxide

fuel cell (SOFC) is the most efficient for refinery use. Figure 26 presents schematic diagram of a typical SOFC.



**Figure 26:** Solid Oxide Fuel Cell Unit (Saidi, Siavashi & Rahimpour, 2013)

Solid oxide fuel cells are made up of very thin layer of ceramics, two porous electrodes separated by a non-porous oxide ion conducting ceramic electrolyte. The ceramics electrical and ionic activation is achieved at temperatures between 600-1000°C and that high temperature enables the SOFC to oxidize various fuels such as gasoline, diesel, natural gas, biofuels, hydrogen and even coal gas. The most interesting and researched of those fuels is methane. The hydrocarbon feed produces hydrogen, which is oxidized by oxygen, according to the following reactions.



40-70% of the produced heat in a SOFC is used by this endothermic steam reforming reaction facilitating the cell cooling. Furthermore, the rest of the generated heat can be used to provide a percentage of the required for the reforming reaction steam. In addition to this, the continuous hydrogen consumption in the SOFC shifts the steam reforming reaction to the right and improves hydrocarbon conversion efficiency. As a result, with the use of an appropriate catalyst in the anode side no external reformer is required and the cost and complexity of the system are reduced considerably. The

most suitable catalysts for this method are nickel / zirconium ceramic - metallic (cermet) anodes as they facilitate both the power generation and the steam reforming reaction.

Unfortunately, the internal steam reforming causes carbon deposition on the nickel based anode resulting in catalyst poisoning and cell performance and lifetime reduction. The high steam/carbon (S/C) ratio can mitigate this problem but also harms the electrical efficiency due to fuel dilution by steam. As a result, the S/C ratio to prevent carbon formation on anode must be as low as possible, which in the case of methane is about 1.5. The excess steam present in the anode outlet gas can be utilized in the steam reforming reaction by recycling the anode outlet gas.

One significant disadvantage of this technology is that the ceramic construction needed to provide stability and reliability makes SOFCs more expensive than other fuel cells. In addition to this, since the operating temperature is so high, SOFCs require significant time to reach operating temperature and are slow to respond to changes in electricity demand. As such, they are best suited for large applications, like refineries.

The SOFC method is considered as an environmentally friendly power generation technology. When the SOFC feed is methane, the high operating temperature and the proper catalyst presence can ensure its complete reformation, eliminating a very powerful greenhouse gas. The SOFC final products are carbon dioxide and water. Due to the water gas – shift reaction equilibrium there is also an unconverted amount of carbon monoxide. This technology application can achieve carbon dioxide reduction by about 55 %, almost no emissions of other pollutants (nitrogen oxides, sulfur oxides, carbon monoxide, particles and organic compounds) and significant noise reduction compared to a traditional power plant (Saidi et al, 2013).



## CHAPTER 11: FLARE GAS REDUCTION IN OPERATION

There are various methods that we can implement in order to reduce the flare gas production. Some examples are indicated below:

- Improvement of condensers performance, especially during hot weather periods. A more efficient condenser improves the gas stream cooling and condensates higher quantity of light hydrocarbons, like propane and butane.
- Installation of automatic trip valves on reboilers and heaters on equipment items to eliminate the flaring during operation upset.
- Over-engineering of the equipment items. They will be able to withstand higher internal pressures, confining the overpressure cause inside the equipment and preventing the activation of the safety valves and the flaring.
- Optimization of the production and consumption of fuel gas in order to maximize the recovered gases usage. This can be achieved by reducing the import of other sources of fuel, like natural gas, by lowering the capacity of the units that produce fuel gases and by using spare steam turbine drivers as main to maximize the consumption of the fuel gas fired boilers.
- Sufficient compressor capacity to increase the recovery of the flare gas to the Fuel Gas Unit.
- Sufficient storage volume to balance the flow rate to the flare gas header.
- Adequate treatment scrubber systems to prepare the flare gas for the Fuel Gas Unit, mainly by removing the sulfur (Valero Refining Company – California, 2010).

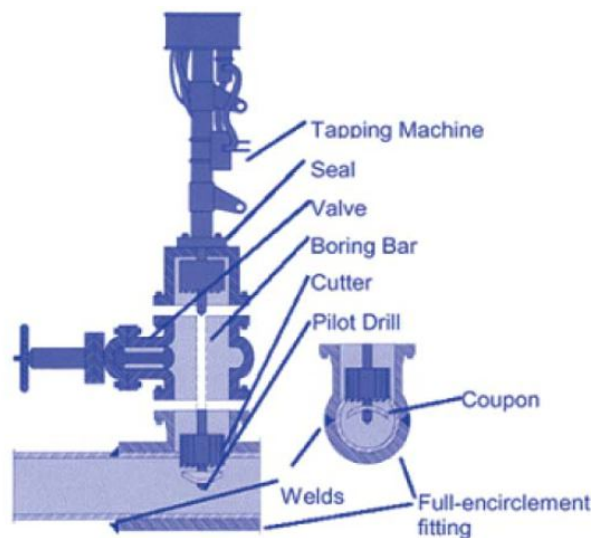
## CHAPTER 12: FLARE GAS REDUCTION IN MAINTENANCE

In order to maintain, repair, expand or modify one existing refinery system it is necessary to shut down a portion of it, dispose the included product to the environment through venting or flaring and purge this portion with inert gas to ensure a safe connection (EPA 2016).

### 12.1 HOT TAPPING

Hot tapping can be realized instead, to allow a new pipeline connection while the system remains in operation. The main steps of the procedure are (Figure 27):

1. The fitting connection on the operating pipeline and the valve installation.
2. The hot tap machine installation through the newly installed valve.
3. The opening of the valve and the cutting of the operating pipeline coupon.  
Then a special device retains the coupon, withdraws it through the valve and the valve is closed.
4. The removal of the tapping machine and the connection, purge and activation of the new branch pipeline.



**Figure 27:** Schematic of hot tapping machine with profile (EPA 2016)

The hot tapping procedure alternative offers various significant advantages:

- No product release to the environment.
- No operation interruption.

- No cutting and restoration of existing pipelines.
- Simplified operation with less planning and coordination.
- Increased safety.
- 

## **12.2 RELIABILITY IMPROVEMENT**

Improving the reliability of the equipment and the processes of the refinery not only improves the efficiency of the refinery but also reduces the amount of flaring. The reliability improvement can be achieved through the application of upgraded metallurgy, improved designs and equipment replacements. The flare gas reduction is gained through the reduction of the unexpected shutdowns due to equipment failure and through the extension of the average process unit run (Valero Refining Company – California, 2010).

## **12.3 CHEMICAL CLEANING**

Liquid phase and vapor phase chemical cleaning during shutdown and prior any maintenance activity can replace the purge with gases that will end up being flared. When liquid phase chemical cleaning is used, the washing agent as an aqueous solution is circulated in the equipment and then recovered and treated. Vapor phase chemical cleaning consists of steam in combination with the chemical washing agent to remove heavier materials by increasing their volatility. These two methods can also be combined (Valero Refining Company – California, 2010).

## **12.4 SUB-COOLED LIQUID NITROGEN COOLING OF EQUIPMENT**

The use of a cooler gas stream demands less time to cool down any equipment item. This can be achieved by injecting sub-cooled liquid nitrogen into a gas stream, such as nitrogen or hydrogen. The liquid nitrogen vaporization results in the cooling of the gas stream and reduces the required cooling time. As a result, the purge gas consumption and flaring will be reduced (Valero Refining Company – California, 2010).

## CHAPTER 13: CONCLUSION

The gas flaring in oil refineries causes various significant health and environmental problems. The flaring also causes an economic impact due to the wasted resources. Furthermore, the international agreements regarding the environment protection make the flare gas reduction even more critical and more important than the economic results. In order to deal with all these problems, we collected and presented various methods and technologies. There are simple solutions, like implementing changes in operation and maintenance as well as common and affordable ones, like the flare gas collection, compression and transfer to the fuel gas unit. There are also more complicated and expensive methods, like creating new units to produce profitable chemicals. The final selection of technology depends on many factors, like the flare gas quantity and composition, the refinery complexity and the market demands.

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