National Petrochemical CO.

Tabriz Petrochemical CO.

"The feasibility study of flare gas recovery within Tabriz Petrochemical Company under the CDM Project"

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Abstract

Nowadays vast amount of greenhouse gas (mainly carbon dioxide) are being spread into the atmosphere via burning of organic compounds within flare gas where some of these compounds are very valuable economically such as ethylene and propylene.
In this project, by applying a Flare Gas Recovery System including a membrane process unit, it provides segregation feasibility of these valuable compounds from flare gas within olefin plant. By conducting this project under CDM (Clean Development Mechanism) Project methodology # 0037, besides economical benefits and CER (Certified Emission Reduction) issued via UN, flare gas burning and greenhouse gas emission into environment is being prevented.

The project Main benefits, in short, are as follows:

- Reduction of combustion emissions including NO_X ,CO_X ,SO_X
- Decrease of FUEL GAS consumption
- Reduction of flaring light , noise , and odor
- Decrease of steam consumption
- Extend flare tip life
- No impact on existing safety system concerning relief gas en route to flare
- Feasibility of valuable compounds recovery, i.e. ethylene and propylene, in olefin unit
- Improved public relations & company image

چکیده:

روزانه مقادیر قابل توجهی از گازهای گلخانه‌ای (به طور عمده دی‌اکسید کربن) از سوختن ترکیبات آلی موجود در گاز فلر در محیط منتشر می‌شود که برخی از این ترکیبات از جمله اتیلن و پروپیلن از لحاظ اقتصادی بسیار با ارزش هستند.
در این پروژه با استفاده از فرآیندهای ممبران، جداسازی ترکیبات با ارزش فوق از گاز فلر در داخل واحد الفین امکان‌پذیر می‌باشد. با انجام این پروژه تحت متدولوژی شماره 0037 پروژه مکانیسم توسعه پاک (CDM) و گواهی کاهش انتشار (CER)، ضمن سودآوری اقتصادی، از سوختن گاز فلر و انتشار گازهای گلخانه‌ای به محیطزیست جلوگیری بعمل می‌آید.
به طور خلاصه، مزایای اصلی پروژه عبارتند از

1. کاهش انتشارات حاصل از احتراق شامل NOxها، COxها و SOxها
2. کاهش مصرف سوخت گازی
3. کاهش نور، صدا و بوی فلر

4. کاهش مصرف بخار
5. عمر افزوده نوک فلر
6. بدون تاثیر برروی سیستم ایمنی موجود در خصوص گازهای رها شده به سمت فلر
7. امکان بازیافت ترکیبات باارزش، به عبارت دیگر اتیلن و پروپیلن، در واحد الفین
8. بهبود روابط عمومی و شهرت شرکت

Keywords: Combustion, Environment, FGR, Flare, Membrane

1. Introduction

The flare is the most visible sign of pollution and energy waste from an oil, gas and petrochemical plant. However, it is also the ultimate safety system on the installations. The key to a successful flare gas recovery system is by this reason designing a flare system only operating in emergencies.

If technologies are available for reducing flaring, why are they not being implemented? The answer is simple, economy. To enhance the implementation of environmental friendly technologies, governments have introduced various initiatives such as, emissions limits, taxes on emissions, part funding of environmental projects, CO_2 quota trading and more.

Some of these initiatives will of course help the business case of a flare gas recovery projects. However, it is also important to bear in mind that flare gas recovery projects, in addition to saving the environment, also generate income in terms of sales gas value, reduced diesel consumption, less maintenance of the flare system and even a more stable process operation. Some of the “zero flaring” projects have actually demonstrated payback times within 2 years or less.

The current study is been undertaken to investigate and to examine the concept of “zero flaring” under the CDM project activities and to evaluate the means of such a project in Tabriz Petrochemical Company (hereinafter, referred to as TPC).

2. What is flare?

A gas flare or flare stack is an elevated vertical stack or chimney found on oil wells or oil rings, and in refineries, chemical plants, refineries, chemical plants and landfills used for burning off unwanted gas or flammable gas and liquids released by pressure relief valves during unplanned over-pressuring of plant equipment.

On oil production rigs, in refineries and chemical plants, its primary purpose is to act as a safety device to protect vessels or pipes from over-pressuring due to unplanned upsets. This acts just like the spout on a teakettle when it starts whistling as the water in it starts boiling. Whenever plant equipment items are over-pressured, the pressure relief valves on the equipment automatically release gas (and sometimes liquids as well) which are routed through large piping runs called flare headers to the flare stacks.

The released gas and/or liquids are burned as they exit the flare stacks. The size and brightness of the resulting flame depends upon how much flammable material was released. Steam can be injected into the flame to reduce the formation of black smoke. The injected steam does however make the burning of gas sound louder, which can cause complaints from nearby residents.

Compared to the emission of black smoke, it can be seen as a valid trade off. In more advanced flare tip designs, if the steam used is too wet it can freeze just below the tip, disrupting operations and causing the formation of large icicles. In order to keep the flare system functional, a small amount of gas is continuously burned, like a pilot light, so that the system is always ready for its primary purpose as an over-pressure safety system. The continuous gas source also helps diluted mixtures achieve complete combustion.

Some flares have been used to burn flammable "waste" gas or by-products that are not economical to retain. Over time, the industry is moving to flare-gas recovery systems to decrease waste and reduce emissions. The flaring system is one of the vital units of both petroleum industries and any chemical plant and has a crucial rule in ensuring in having a reliable process. Flares can prevent risks, fires, explosions to happen and they can ensure the personnel safety.

Discussing flare subject is an important issue since:

- The transferred gas to the flare, economic wise, are extremely valuable and
- The combustion of this gas has a blunt effect on the environment.

Therefore flare gas management is a suitable field for scientific, research and application activities not only within the country, but also around the world. For instance most of the valuable gas combustion, within Asalouyeh region (since there are many flares within this location), have a damaging effect on the environment, which requires extensive actions in order to: a) minimize the loss of this national capital and b) prevent destruction of the environment.

The flaring system within a plant, overall, burns the transferred gas in three different operational phases:

1. Normal conditions: In these kinds of conditions, the released gas form some of the units along with purged gas are burnt in Flare.
2. Chaotic conditions: happen during the start up or complete shut down of a unit where the volume of the transferred gas to flare is more than normal conditions.
3. Emergency conditions: In these kinds of conditions, some of the unwanted gas is being transferred to the flare because of an equipment malfunction, human errors, change in entering feed and loss of electricity.

3. Flare types

Flare classification based on height:

- Elevated flare
- Ground flare

Flare classification based on mixing agent:

- Flare with steam mixing agent
- Flare with air mixing agent
- Flare with pressure mixing agent
- Flare without mixing agent

A flaring system which includes: collecting and transferring of released gas system, a liquid seal, a collecting container for liquefaction and segregation of liquids within the gas, stack and support system, gaseous seal, burner tip, burner pilot, gas supplying system to the flare and sparking system, steam or air injection system and gas discharging system

4. Flaring effects and problems

- Many unburned gas from flare, due to lack of enough time in combustion process, enter into the environment. One of the main problems is the unspecified flare efficiency. The volume of the emitted potential toxic compounds, generated via poor combustion, is beyond expectations,
- Active flares directly generate greenhouse gas, which overtime, causes global warming,
- The transferred gas to the flare, during its various operational phases, results in various gas emissions such as soot, unburned organic compounds, NO_x, SO_x, and …, which is dangerous to the human health,
- The rate of energy loss, economic wise, is considerable and very important,
- The emitted gas from flare, such as sulfur and nitrogen oxides, in the proximity of water within the atmosphere results in considerable acid rain,
- In flaring operation, there are undesirable effects like noise, soot thermal radiations.

The necessary tools for flaring operation management:

- Flare gas measuring equipment
- Monitoring of flare system
- Transferred gas reduction and recovery system to the flare

5. Flare gas measurement

Knowledge of variables quantitative amounts is the essential factor in monitoring and control of any system. To achieve to these amounts, it requires modern and reliable measuring equipment. Flare system control, as a system which guarantees a plant safety, is not exceptional and requires reliable measuring equipment. Flow rate and gas flow analysis are the two main quantities that have the utmost importance.

6. No flaring

Although any chemical process such as petrochemical plants and refineries, due to various reasons for personnel safety purposes and equipment, are obliged to use flaring system, but guidelines could be presented in order to minimize transferred flow rate to the flare. Currently a new subject termed “No Flaring” has been purposed and is being followed.

<u>Procedures to achieve “NO Flaring”</u>

Flare process involves three main parts:

1. The process itself as the source of flare gas generation
2. Collection network as the source of transferring gas to the flare
3. Flare system as the final user of the gas

Flare gas reduction and recovery procedures are applicable in all three of main parts as follows:

- Processing part: the reduction of flare gas generation via process conditions improvement and prevention of equipment and joints’ lick,
- Collection network: recovery and reuse of generated flare gas according to its specifications,
- Flare system: improvement of flare system including equipment, their functions and control and monitoring systems.

The basic benefits of initiation of NO Flaring systems:

- Reduction of environmental polluting gas generation (including greenhouse gas) resulting from combustion in flares such as CO, CO_2, NO_x and SO_x,
- Reduction of fuel gas usage
- Reduction of light, sound and odor resulting from flaring operation
- Steam usage reduction
- Purge gas usage reduction
- Increase in flare’s burner tip service life
- No change in existing flaring system to maintain its safety role within the process
- Maintaining and restoring enormous energy and capital sources and also possibility of gaining assets

The different methods of flare gas recovery

1. Physical: in this method flare gas is being purified by particular equipment, and if required, is being compressed to be used as feed or fuel in processing units,
2. Chemical: involves application of reaction in a catalyst environment in order to convert flare gas to usable industry materials,
3. Biological: is one of the newest methods of recovery which involves use of bacteria and application of decomposition reactions in towers, which in the process, gas is converted to its forming elements

7. Flare gas recovery system

Environmental and economic considerations have increased the use of flare gas recovery systems (hereinafter, referred to as FGR) to reclaim gas from vent header systems for other uses. Typically, the gas is recovered from a vent header feeding a flare. Depending on vent gas composition, the recovered gas may be recycled back into the process for its material value or used as fuel gas.

8. FGR's Design

The object of FGR unit installation, within this project is valuable compounds recovery existing in flare gas. Thus, first flare gas pressure, which is low, should be increased to the considered pressure and then condensed liquid, should be separated from it. In the next phase by membrane technology usage, nitrogen compound is being removed from this gas and is being transferred to olefin unit for valuable compounds segregation. All the remaining gaseous and liquid hydrocarbons, in this project, not being transferred to olefin unit, will be used as fuel oil.

Overview: A conventional flare system is used both for normal process releases and emergency releases. Emergency streams, such as those from pressure relief valves, depressurising systems, and so on must always have flow paths to the flare available at all times. API RP 521 states that the design of flare gas recovery systems shall not compromise this path. The flare closing arrangement should always consist of a primary and a secondary path to the flare in order to maximize the safety aspect.

FGR Equipment scope

Skid packaged process and equipment design:

- Gas compressor unit
- Gas / Liquid separator

- Heat exchanger (Gas and Liquid Coolers)
- Hydrocarbon Membrane unit
- System control logic (for fully automated unattended operation)
- Flow meter installation to measure gas flow
- Existing KO drum , flare header , liquid seal and flare remain
- Existing liquid seal may be too shallow to provide hydrostatic head and cause operating problems, thus, special internal designs are required to allow for a deeper FGR liquid seal

9. Membrane description

Membrane technology has proven itself to be commercially successful. Membranes operate at ambient temperature and can achieve product recovery competitive or better than cryogenic technology and mechanical expansion turbines without the complexity and cost inherent in them.

When applying a pressure gradient across a selective membrane the feed gas mixture is separated by the membrane into two outlet streams of different composition. With the hydrocarbon separation membrane the more easily liquefied components like propane, butane, pentane etc. or organic solvents are separated preferentially and are concentrated on the low-pressure side of the membrane. The lighter gas such as methane, hydrogen, and nitrogen remain at high pressure with only a minimal pressure drop while being processed.

The membrane technology for hydrocarbon separation uses a membrane of a polymeric composite type. A very thin non-porous high selective separating layer of a specially synthesized polymer is coated onto a porous polymeric substructure, which provides the necessary mechanical support while allowing the minimum resistance to the passage of the permeating flow of heavy components.

The membrane separation process system is based on a module concept with flat sheet membranes in an envelope type configuration. The required membrane area is provided by an appropriate number of modules. The modular structure allows a flexible design in skid-mounted or container based units and easiest installation at site.

10. Liquid ring compressor

The liquid ring compressor is of the positive displacement type where a "liquid piston" achieves the compression. The compressor performance is therefore not affected by gas composition changes. In the compressor the outlet pressure and volumetric capacity remains constant.

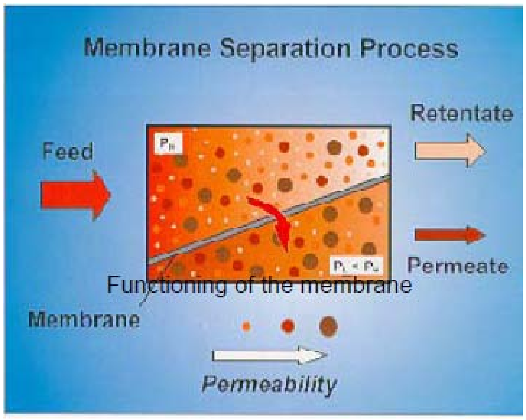

Fig 1. A schematic view of Functioning of the membrane

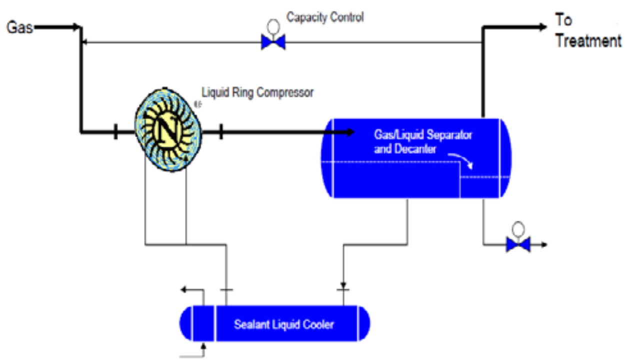

Fig2. schematic sketch of flare gas recovery using liquid ring compressor

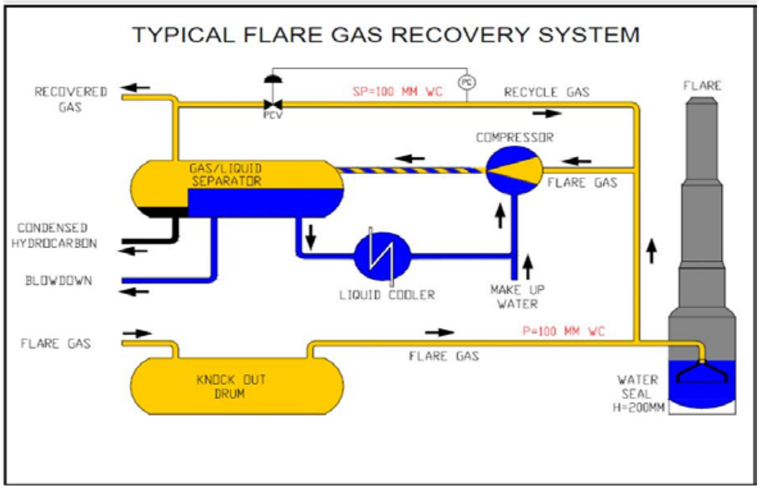

Figure 3. A schematic view of a typical flare gas recovery system

11. Safety and control

The principal potential safety risk involved in integrating a flare gas recovery system is from ingression of air into the flare header, which can be induced by the compressor suction. This could result in a flammable gas mixture being flashed off inside the system from flare pilots. It should be noted that the FGR unit does not interrupt the flare system and should be able to handle sudden increases in load. Therefore, no modification to the existing flare system will be attempted, but with two exceptions.

The connections through which the compressors will take suction on the system, and additional seal drums which will provide extra safety against air leakage into the flare system and allow the buildup of flare header pressure, during compressor shutdown or flare gas overload. Also, the compressor control system does not affect the flare system pressure and thus its design will be able to avoid low pressure suction in the flare system during normal operation. When the compressors are not functioning properly, automatic or manual shutdown should result. The flare system will operate as it does now with no compressors.

Meanwhile, if the volume of flare gas relieved into the flare system exceeds the capacity of the FGR unit, the excess gas will flow to the flare stack. If this volume is less than the full capacity of the FGR unit, a spillback valve will divert the discharged gas back to the suction zone to keep the capacity of the flare gas recovery unit constant.
Other safeguards to the flare system against air leakage are:

- The fail-safe shutdown of the FGR unit compressors on low pressure in the flare system.
- The shutdown of the FGR unit compressors upon high inlet and/or outlet temperatures.
- Adequate purge connections in the downstream of the seal drum.
- Low flow switches in the purge line to the main flare header downstream of the seal drum, to cut in fuel gas as purge gas.

12. High pressures flare in TPC:

High pressures flare is TPC's main flare, which by, almost, all of the operational units' released gas is sent to the aforesaid flare and therefore FGR project is defined based on this flare. Table 1. represents the flare's specifications.
Flare Header Size 52 " Flare gas @ 20 ^{o}C & 0.03 bar →HP flare

Based on collected data from TPC's operating plants and calculations:
Estimated flare gas flow rate = 850 kg/hr
Flare gas composition after several testing are as follows:

Table 1. Flare gas analysis results

flare gas composition	%mole fractions	flare gas composition	%mole fractions
Methane	3.62	i-Butene	0.308
Ethane	1.185	Trans 2-butene	0.077
Ethylene	16.96	1,3 Butadiene	2.83
Acetylene	0.075	1,2 Butadiene	0.002
Propane	0.12	Vinyl acetylene	0.004
Propylene	1.91	Ethyl acetylene	0.001
Propadiene	0.035	n-pentane	0.345
Methyl acetylene	1.134	i-pentane	0.55
n-Butane	0.61	Hydrogen	30.3
i-butane	0.165	Nitrogen	39.034
1-butene	0.735	Others	Balance

13. Emission control

The economic gain of installing a flare gas recovery system will vary significantly from installation to installation, depending on gas flow, type of gas and utilization of the gas. Typically continuous flaring will contribute to about 50% of the annual flaring on any oil, gas or petrochemical plant.

Gas value:

The obvious economic benefit is the value of the gas recovered, but also this could vary significantly depending on the amount of gas recovered and the sales gas contracts. For petrochemical plants product gas can be recovered, this gas often is more valuable than export gas, if gas is recovered for power generation the value will be reduced diesel consumption or reduced consumption of sales gas.

Following the Kyoto Agreement, a CO_2 Quota Trading Scheme has been identified as an economic incentive for countries and companies to implement technology-reducing emissions of hydrocarbon gas and CO_2. The quota-trading scheme is planned implemented in EU countries within 2005. The 38 countries signing the Kyoto agreement should have a common trading system in place within 2008-2012. It is expected that the value of a CO_2 ton will be between 10-20 USD per ton CO_2.

From social viewpoint including impacts and benefits, concerning conducting the project, it will include greenhouse gas emission reduction and will help in clean air production within region/country and world which is highly regarded. And also it will create a positive perspective of TPC within public. Therefore based on these facts and according to the given guidelines within CDM project methodology 0037, followings are the estimations which are being presented:

<u>Assumed baseline emissions in TPC's HP</u>
Considering the flare gas combustion temperature of about 1390 ^{o}C within the peak of the flare and enough excess oxygen availability for complete combustion, the following sample reactions with an estimated 100% conversion rate are being considered:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\qquad$ $C_3H_6 + 9/2\, O_2 \rightarrow 3CO_2 + 3H_2O$

$C_2H_6 + 7/2O_2 \rightarrow 2CO_2 + 3H_2O$ $\qquad$ $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

Considering foregoing reactions and their mass balance using flare gas composition and flow rate, the total generated CO_2-eq shall be as follows: 850 kg/hr flare gas → 755 kg/hr CO_2-eq
In order to atomize flare gas during combustion and burning without smoke, 1300 kg/hr of MPS within TPC's flare gas is being consumed. This amount is accessible via existing routes.

Up on project execution, the consumed steam can be saved. By saving this amount of steam, which is being supplied through Power & steam generation unit, the generated steam of this unit will also decrease. In other words, consumed gas combustion rate required for steam generation will decrease where by consumed gas combustion rate reduction, within Power & steam generation unit, CO2-eq emission rate resulting from combustion will also decrease as being calculated as follows:

- Power & steam generation unit
  consumed gas combustion rate per each generated steam = 70 kg fuel gas/ ton of steam
- Saved consumed gas combustion rate
  in lieu of project execution = (70 *1000)(kg fuel gas/ ton of steam)/ (1300)(kg/hr) = 90 kg/hr
  By assumption of enough excess oxygen availability and flare gas complete combustion, the following reaction takes place: Fuel gas + O_2 → CO2 + H2O

Considering the above reaction and its mass balance using the fuel gas composition and flow rate, the total generated CO_2-eq shall be as follows: 90 kg/hr→ 250 kg/hr CO_2-eq

Table 2. Fuel gas analysis results:

Fuel gas composition	%mole fractions	Fuel gas composition	%mole fractions
Methane	85.3	n-Butane	1.5
Ethane	8.2	Nitrogen	0.52
Propane	4.4	Others	Balance

Hence, considering flare gas burning within TPC's HP flare, the CO_2-eq emission rate into atmosphere is:(755 +250) 1005 kg/hr which its annual equivalency will be in the amount of (1005 kg/hr * 8000 hr) 8040 ton/yr and by conducting this project the CO_2-eq emission rate can be removed.
From economic viewpoint, despite the project investment expenditure, profits return and also generating revenues resulting from CER sales

In brief, the performed steps up to the completion of this paper are presented as follows:

- Identifying the existing flares with the complex
- Identifying the transferred gas into flare
- PIN preparation by applied comprehensive study and forwarding to the designated national authority (hereinafter, referred to as DNA)
- CDM Project registration and verification via DNA, Iran Department of Environment
- Project registration in HSEQ-NPC Affairs (permanent member of Iranian Association for Environmental Assessment Committee)
- Project registration in Canada's Energy Globe under the United Nations cover with the identification number # 2007-00529
- Inquiry from 15 Reputable International Firms considering purchase of technical know-how, equipment and receipt of technical know-how including:

IGS Anlagentechnik Gmbh & Co. Kg - IPI Canada - Huachgfeng Equipment Inc. (HAF) - Garo -Envirocomb Ltd - Sterling - Ziemens - Borsig - Shell - Nippon - Statoil – PetroTechna - Aibel - Akee Kvaerner - Sulzer

- Dispatch of a representative to Germany for direct negotiation with Borsig Co.
- Holding a mutual meeting with Borsig Co. to evaluate the project technical issues with the Complex
- Purchase of an Ultrasonic Flow Meter en route of transferred gas into the flare
- Mutual consent with Energy Changes Co. (Austria) for preparation and development of Project Design Document (PDD) Contract

14. TPC's flare gas recovery system

Considering the offers received by known foreign companies and based on the technical reviews of the offers regarding the TPC's FGR project, the latest offered system's specifications are depicted in figures 4 & 5.

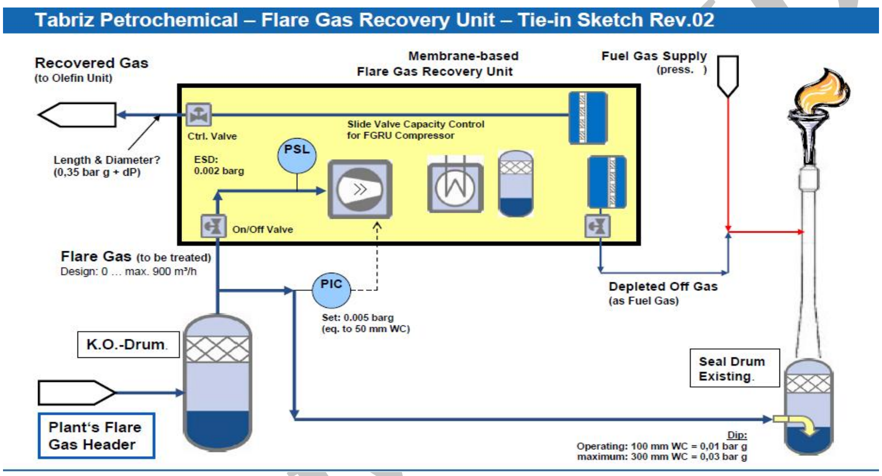

Figure 4. **A schematic view of a proposed TPC's flare gas recovery system**

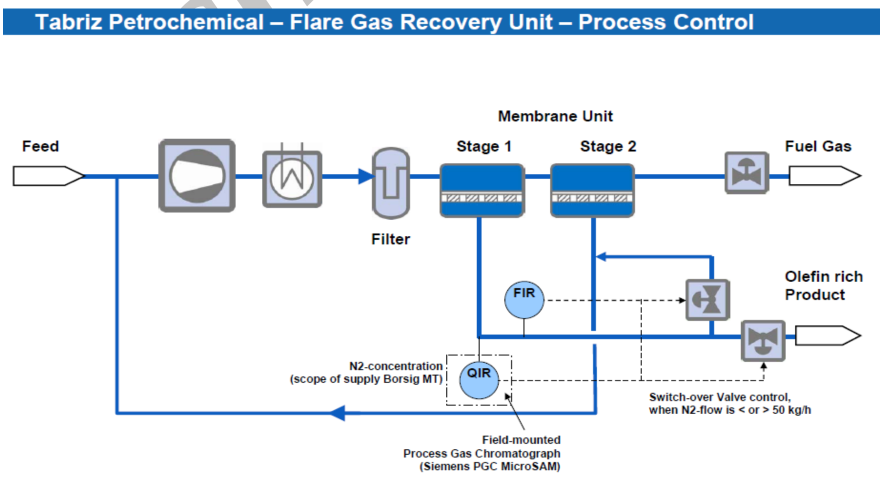

Figure 5. **A schematic view of process Control of TPC's flare gas recovery unit**

As it is apparent from the figures, the transferred gas to flare, initially, is compressed and after segregation of nitrogen by a two-staged membrane, the gas containing no nitrogen shall be transferred to TPC's Olefin unit. Table 3. represents the aforesaid system's function and transferred gas recovery rate.

Table 3. TPC's FGR's function and transferred gas recovery rate

composition	%mass fractions	Flow Kg/hr	% memebrane unit recovery	Gas flow composition to Olefin unit Kg/hr
Methane	2.658	22.6	70	15.82
Ethane	1.63	13.85	88	12.188
Ethylene	21.77	185.04	80	148.03
Propylene	3.68	31.28	90	28.15
C4,s	11.97	101.74	100	101.74
Hydrogen	2.8	23.8	22	5.23
Nitrogen	50.06	425.51	3	12.76
Others	Balance	balance	-	balance
TOTAL	100	850	-	365.5

15. Economics

The project economic evaluation is important because:

1. The rate of the gas recovery value, which will include ethylene, propylene and C4,s will be greater than prime cost of these compounds within TPC as it is illustrated in Table 4.

Products:

Table 4. The rate of the TPC's gas recovery

composition	Annual amount T/Y	Prime cost by the weight value $/T	Annual total value M$/Y
Ethylene	1184.24	998	1.18
Propylene	225.2	893	0.2
C4,s	813.92	302	0.246

By assuming 8000 hours of production for unit's operation
Products total annual profits = $ 1.62 million

2. Another important aspect, economic wise, is the gained value because of the reduction in greenhouse gas and since the project shall be implemented under CDM PROJECT (which results in issuance of CERs). The estimated rate based on 10 USD per CER is presented as follows:

- TPC'S HP flare CO_2-eq Emission rate = 1005 kg/hr or 8040 ton/yr
- Crediting Period proposed: 7 yr
- Average completed cost for the project: "CER (certified emission reduction)"
- Proposed total CER amount for the crediting period :
  $ 562800 = (CO_2 eq.: 8040 T/Y)*(crediting period proposed: 7 year) * (10 USD/CER)

16. Conclusion

In this project, by valuable compounds recovery existing within flare gas, huge profit will be shared by the TPC. In addition, by prevention of greenhouse gas emission, including toxic gas, into atmosphere, produced clean air will be effective in the region.

By conducting the project, greenhouse gas emission rate will be decreased on the national level. Also, by selling of the resulted CER, will enter this market and TPC and all the country will be benefited remarkably. In addition, a new technology, in particular in membrane field, will enter the country which can be the starting point for other industries

From social viewpoint including impacts and benefits, concerning conducting the project, it will include greenhouse gas emission reduction and will help in clean air production within region/country and world which is highly regarded. And also it will create a positive perspective of TPC within public.

From economic viewpoint, despite the project investment expenditure, profits return and also generating revenues resulting from CFR sales, this project is completely justified and above all, the project is absolved national wise and will be supported by all means.

The project conduct in TPC will involve investment expenses and certainly considering rate of return and resulting generated revenue, the project, from an economic viewpoint, within TPC is completely justified. Also, project execution, shall result in contact and co-operation with foreign firms concerning purchase of required technology and project generated CER sale, which ultimately access to up-to-date technology and profit generated by CER sale will be the indication of the positive effect of collaboration with these firms.

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