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ABSTRACT

This project investigates the causes and mitigations of black soot in the oil and gas process plant, so as to develop possible solutions for improvement and protection of the ecosystem. Particle pollution commonly referred to as “soot,” is one of the deadliest forms of air pollution, which results from the incomplete combustion of hydrocarbon during gas flaring. The first part of this thesis explains the causes and mitigation of soot with special reference to the effect of temperature and pressure on methane, in the oil and gas processing plant. This project focuses on methane, a constituent of hydrocarbon which is present in high quantities and a major cause of soot formation, if its emission is not properly managed. Methane is also one of the gases implicated in global warming, thus the need to curb its emission. The methodology involves the use of Aspen HYSYS to design and simulate the hydrocarbon (methane) break down into its components and Aspen Plus, (Aspen Plus is a design tool based on the Gibbs reactor model), both tools are used to simulate oxygen, nitrogen, water, carbon monoxide, carbon and carbon dioxide based on different temperature and pressure sensitivities. The intake of hydrocarbon (methane component) while varying parameters like temperature and pressure determines the level of soot production. The result of varying these parameters shows that higher carbon formation happens at low pressures and high temperatures. The second aspect of this thesis is for research which involves the theoretical evaluation of some of the causes of soot as well as sampled opinions from the industrial experts. In conclusion, Aspen HYSYS and Aspen Plus are used at low temperatures and high pressures to mitigate soot formation. It is also recommended to have adequate control in place so as to prevent liquid carryover, which is another source of soot generation in the
process plant. The economic benefit of saving hydrocarbon by automation does not only save the company cost, but also creates a cleaner air hence providing better health benefits for the inhabitants.
ACKNOWLEDGMENTS

My profound gratitude goes to Dr Srinivas Shastri for his tireless guidance, advice and supervision. I would like to acknowledge the generous support for this project by my wife, Uwaila, my children, friends and the entire Industrial Automation Engineering department at EIT. Above all, I acknowledge the all-knowing and invulnerable God for His guidance throughout the course of this study.
CHAPTER 1. INTRODUCTION

Soot is a major environmental problem, especially in the Southern part of Nigeria, where oil exploration takes place on a large scale. My interaction with various oil and gas process plant personnel yielded that, waste gases are vented in an uncontrolled manner, thereby polluting the atmosphere with harmful gases which have a detrimental effect on the earth’s biosystem.

The constituent of the smoke from combustion depends on the gas being flared, quantity and distribution of combustible air around which results in black carbon from flares.

Natural gas is the gaseous form of petroleum comprising, hydrocarbon gases or saturated light paraffin(s), examples of which are methane and ethane. Both methane and ethane are gaseous under atmospheric conditions and other mixture may also contain other hydrocarbon constituents, such as propane, butane, pentane, and hexane, but for the purpose of this project, the interest is on methane. Pentane and hexane are usually limited and drop out by the time it reaches flare. The composition of the gas being flared will depend upon the source of the gas going to the flare system. Associated gases released during oil-gas production mainly contain natural gas which is more than 90% methane ($\text{CH}_4$) together with ethane and a few other hydrocarbons.

Aspen HYSYS [13] is used to model and simulate the effect of pressure and temperature on the carbon composition in soot produced during methane breakdown. Aspen plus on the other hand is used to validate the simulation.
The complete combustion of methane in stoichiometric oxygen will give rise to carbon dioxide and water. While, the incomplete combustion of methane in the presence of oxygen will give rise to carbon monoxide and water or just carbon and water, which are sources of dangerous gaseous pollutant and very sooty flares.

1.1 Gas Flaring

Flare is a combustion process that uses the naked flame from the pilot line to ignite the gases in the presence of atmospheric air around the flame, and gases then burn independently.

Flaring is mostly of hydrocarbon waste gases from industrial operations. The following hydrocarbon gases like; propane, ethylene, propylene, butadiene and butane are limited in quantity and may not even get to flare. Meanwhile, The natural gas methane form over 95 % of the unwanted gases which are flared. Gaseous hydrocarbons react with atmospheric oxygen to form carbon dioxide (CO₂) and water during combustion. The product includes some unwanted/waste gases, such as carbon monoxide (CO) as the main combustible component. The reaction below is an example of methane combusting with atmospheric air:

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \quad \text{...............(1)}
\]

Numerous transitional products are produced during the reaction, but the majority is converted to carbon dioxide (CO₂), water (H₂O) and nitrogen oxide, though, nitrogen oxide is not covered extensively in this thesis since our focus is on soot formation. Most of the stable intermediate products such as carbon monoxide, hydrogen, or even hydrocarbons will escape as emissions.
Flares are mostly used to dispose of:

- Purged and wasted products from refineries,
- Vented gases from relief valves,
- Unrecoverable gases emerging with oil from oil wells,
- Uncontrolled gases from blowdown, and
- Gaseous wastes from chemical industries.

Gases flared from refineries, petroleum production, chemical industries, and to some extent, from coke ovens, are mainly hydrocarbon of low molecular weight with a very high value of heating. Flares may also be used to burn waste gases produced by sewage digesters, furnace blast gases, coal gasification, heavy water plants, rocket engine testing, nuclear power plants with sodium/water heat exchangers, and ammonia fertilizer plants.

Gas flaring often refers to the process of burning off surplus hydrocarbon gases. This has become a common practice at oil and gas processing facilities as well as refineries. The gas produced in developing or developed nations without gas buyers and gas handling facilities is either released into the atmosphere or ignited, also known as flared [12].

The associated gases from the reservoir are considered here for the purpose of the Thesis. The associated gases are gas that occurs with oil in the same reservoir, sometimes known as “wet Gas”. Associated gas is either re-injected into the oil wells to enhance oil recovery where the situation of the reservoir permits it or gathered and liquefied to provide energy source for domestic use or electricity generation. Other
than the law from our various leaders in place to control the vented gas, flaring is considered as a safety intermediate solution.

Flaring is considered as a panacea to the vented gas, so as to safely de-pressurize gas handling facilities in an emergency situation, or plant maintenance purposes or under normal plant control mode. In controlling the process, if flaring is not monitored, can lead to a thick clouded black smoke, known as “soot”. Various conditions that can lead to soot are; high process pressure, low temperature and any other situation which can make gas vented in an uncontrolled manner. From my technical experience and also from my interaction with field operators, many still believe the soot control law in place, especially in the developing world are still not strong enough to mitigate or totally eradicate it.

Gas flaring is a menace that has brought complex multiple negative effects. Flaring natural gas is wastage of valuable natural resources which could have been channelled for economic development. Several attempts to bring the menace to an end have been futile.

1.1.1 Gas flaring systems

Gas flaring systems are installed on onshore and offshore platforms production fields, on transport ships and in Port facilities, at storage tank facilities and along distribution pipelines. A complete flare system consists of the flare stack or boom and pipes which collect the gases to be flared, as shown in Figure 1.1 [19].

The flare tip at the end of the stack or boom is designed to assist entrapment of air into the flare to improve burn efficiency. Seals installed in the stack prevent flashback of the flame, and a vessel at the base of the stack removes and conserves
any liquids from the gas passing to the flare. Depending on the design, one or more flares may be required at a process location.

Figure 1.1 Overall flare stack system in a gas plant [32].

A flare is typically visible and produces both heat and noise. The burned gas generates mainly water vapour and CO2 in a ‘well-controlled flare’. Efficient combustion in the flame depends on achieving good mixing between the fuel gas and air (or steam) [20], and in the absence of fluids, in order to totally avoid liquid into the flare system.

1.1.2 Types of flares

- Elevated flares
- Ground flares.
1.1.2 **Elevated flares** are the most popular type with even greater capacities than ground flares. In elevated flares, a waste gas stream is fed through a stack anywhere from 10 to over 100 meters tall and is combusted at the tip of the stack [33]. The flame is exposed to atmospheric as disturbance to the wind and precipitation [33].

![Figure 1.2 Elevated flare design [10].](image)

1.1.2 **Ground flares**, combustion takes place at ground level. Ground flares vary in complexity, and they may consist either of conventional flare burners discharging horizontally with no enclosures or of multiple burners in refractory-lined steel enclosures.
An example of a typical flare system comprises of:

- a gas collection header and piping for collecting gases from processing units,
- a knockout drum to remove and store condensable and entrained liquids,
- a proprietary seal, water seal, or purge gas supply to prevent flash-back,
- a single- or multiple-burner unit and a flare stack,
- gas pilots and an igniter to ignite the mixture of waste gas and air, and, if required,
- Steam injection or forced air for smokeless flaring.

Smoking or soot are results from combustion, though depending upon waste gas components and the quantity and distribution of combustion atmospheric air.

Waste gases containing methane, hydrogen, CO, and limited ammonia usually burn without smoke. Waste gases comprising heavy hydrocarbons such as paraffin, olefins, and aromatics may also cause smoke. An external momentum force, such as steam
injection or blowing air, is used for efficient air/waste gas mixing and turbulence, which promotes smokeless flare.

1.2. Other forms of flares are stated below

1.2.1 Flares with steam injection

In order to ensure sufficient air and a good mix for the flame, steam is injected into the combustion zone in this type of flare. Flares with steam injection have a single burner and are, for safety reasons, still tower flares. This type of flare is the most common type of flare in the chemical and petrochemical industry. To limit noise problems from the steam lance, it is recommended to keep the steam pressure below 7 bar [17].

1.2.2 Flares with air injection

In flares with air injection, air is injected into the combustion zone to produce sufficient air and turbulence for smoke-free burning. These flares are constructed with a star-shaped burner head with many small holes and are found at the top of a tube with a diameter of at least 0.6 m. This results in effective dispersion of gases. At the bottom of the tube, one finds a ventilator with variable speeds, which supplies air for combustion. The speed of the ventilator determines how much air is provided. The advantage of air injection is that steam is not needed around the flare. This type of flare is less commonly used for large flares [17].

1.2.3 Flares with pressure mixing

Flares with pressure mixing use the pressure from flare gases to create a good mix at the burner head. If enough pressure is available from flare gas, this type of
flare can be used for smoke-free burning, instead of flares with steam or air injection. Flares with pressure mixing are normally found at ground level and must thus be in a remote location with sufficient space. These flares have multiple burner heads, which become operational depending on the volume of to-be-treated gas [17].

The figure below shows, peak carbon conversion as a function of pressure for flames of methane, ethane, and propane. Curves for different fuels that seem unrelated to each other at first sight conceal a universal pressure dependence. It is explained in [18] that there is a universal behaviour, a single empirical equation that might be extended towards other gaseous hydrocarbon fuels not included in [18]. The analysis is based on three premises: (i) Roper’s correlation [18] which applies to hydrocarbon flames at high pressure. As the inverse pressure dependence of flame cross-sectional area implies, flame height is linearly proportional to the mass flow rate of the fuel. Fig.1.3, carbon conversion into soot, Maximum soot yield (Y) scale with the residence time for non-smoking flames. As a result, soot yield scales with the square root of the mass flow rate of fuel. (ii) For relatively simple aliphatic fuels, soot yield is related to the complexity of the fuel according to Ys of M, where M is the molecular mass of the fuel and Y Maximum soot yield [18]. They found a P2 dependent on the final soot volume fraction formed for constant flame temperatures above 1376.85OC and C/O ratios from 0.65–0.75 molar and pressures from 1–5 barg. The conclusion from these studies is that an increase in pressure decreases soot formation at a rate, which could be very high, although, the mechanism is uncertain [18].
Figure 1.4 Maximum carbon conversion into soot of co-flow laminar diffusion flames of Methane, ethane, and propane as a function of pressure at different fuel carbon flow rates. Measurements were performed using the spectral soot emission technique [18].

1.2.4 Flares without additional mixing

These flares have a burning-tip without auxiliary materials to improve mixing with air. Their use is limited to gases with low combustion values, and gases with a low carbon/hydrogen ratio, that burn easily without forming soot. These gas streams require limited air for complete burning, give lower combustion temperatures (whereby cracking reactions are reduced) and are more resistant to cracking [17].

In order to save time and make it possible to compare the results of the various reactions, the reactors come into use.
1.3 Reactors

Reactions are the heart of the chemical processes most time, in which moderately low price raw materials are transformed into more economically favourable products. In other cases, reactions play essential safety and environmental protection roles [21].

![Simple reactor block](image)

**Figure 1.5 Simple reactor block [21].**

1.3.1 Reaction Classifications

Chemical reactions can occur in several ways. These are:

- **Reversible reactions:**

  In these type of reaction, the reactants are converted to products, while the products react to form the reactants at a different rate, though at equilibrium, the two rates become equal.

  An example of the reversible reaction is the formation of ammonia from hydrogen and nitrogen.

- **Irreversible reactions**

  In irreversible reactions, the reactants react to form the products, which cannot revert back into reactants that is the rate of conversion of products to reactants is zero.
For example, the hydration of calcium oxide to form calcium hydroxide is an irreversible reaction.

- **Homogeneous reactions**

  Homogeneous reactions are chemical reactions which occur in one phase or reactions in which the reactants and products are in similar phases. For example, the burning of methane, since it only occurs in the gaseous phase.

- **Heterogeneous reactions**

  Heterogeneous reactions have reactants of two or more phases in the presence of a catalyst. It can also be considered as chemical reactions which occur in more than two phases. An example is the burning of coal (solid), in the presence of oxygen (gas).

### 1.4 What Necessitates Gas Flaring?

From time immemorial, flaring has been the order of the day because, it seems to be the only way for unwanted gases to be excreted from the hydrocarbon processing plant. It is no longer news that associated gases are produced in huge volumes and most of the time, only very tiny quantity is consumed by the production process as fuel for the day-to-day running of turbines/gas engines [12], generators and compressors. Some also make use of small amount of fuel from the scrubber after plant start-up for operating the instruments supply to instrument operated field devices. Greater volumes of the associated gas produced are left unused, so with production platform not equipped with gas infrastructures, they are faced with the challenge of storage of higher quantities. The fact that they are highly flammable means therefore that these gases need to be carefully discharged before it ends up in a
fire. Any slight source of ignition could result in fire which could lead to the destruction of lives (both human, wildlife) and property, becoming a serious and urgent issue with the safety concern.

Consequently, flaring is seen by oil exploration companies as a cheap and convenient means of carefully disposing of waste or unwanted gases through the use of combustion. This is why associated gases are most times flared in the course of crude oil production and processing [12]. This on the contrary, results in the production of greenhouse gases by the so-called messiah procedure by the operators. Some flares may or may not lead to soot production as depicted in Figure 1.5 below.

![Flaring without or minimum soot seen visually at Oredo gas plant](14.

1.5 Soot

Soot is a black powdery or flaky substance consisting largely of amorphous carbon, produced by the incomplete burning of organic matter according to Oxford
dictionary definition. Combustion is complete if all volatile organic compounds are converted to carbon dioxide and water, see eqn.2 below.

1.5.1 *Burns with a blue flame*

\[
\text{CH}_4+2\text{O}_2 \rightarrow \text{CO}_2+2\text{H}_2\text{O} \]

Incomplete combustion results in some of the volatile organic compounds being unaltered or converted to other organic compounds.

1.5.2 *Incomplete combustion of methane-producing carbon monoxide*

\[
\text{CH}_4+1.5\text{O}_2 \rightarrow \text{CO}+2\text{H}_2\text{O} \]

1.5.3 *Incomplete combustion of methane-producing soot*

\[
\text{CH}_4+\text{O}_2 \rightarrow \text{C}+2\text{H}_2\text{O} \]

Flares that run outside the optimum design envelope may produce undesirable by-products, such as Sulphur dioxide, (SO2), Nitrogen oxides (NOx), in addition to Carbon monoxide (CO) which are released into the air as extremely small particles, smoke or liquid droplets. Some solid particles (example Carbon) are emitted directly into the air while other sources of air pollution could be formed from gas particles ensuing from thousands of miles away.

The incomplete combustion can be caused by a deficiency of oxygen. The following are some parameters that may contribute to incomplete combustion [2].

- Available reverse wind
- Amount of liquid carry over to flare stack (from knock-out drum)
- Fuel exit velocity
• Temperature
• Pressure
• Pipeline sabotage

These parameters cause some of the waste gases to remain unconverted or transformed into other organic compounds such as soot, and etc. The nonlinear control system designed based on operator’s experiments can, to some extent, minimize SO2, NOx and CO pollution to acceptable levels during the burning of waste gases, while minimizing heat radiation and smoke with reasonable temperature [11].

Figure 1.7 Soot from Pipeline sabotage in Niger-Delta region of Nigeria [15].

In Oil and Gas industry, all the tail gases containing H2, CO, CO2 and C2 to C5, vary in its composition. As smoke cannot be seen, sometimes un-burnt
hydrocarbon escapes from scrubber and knock-out as this may not be effective enough to constrain the escape of hydrocarbons. Sophisticated vessel design can bring about proper control.

Emissions from flaring include carbon particles (soot), unburned hydrocarbons, CO, and other partially burned and altered hydrocarbons. Also discharged are NOx and, if a sulphur-containing material such as hydrogen sulphide is flared, sulphur dioxide (SO2) is produced. The quantities of hydrocarbon emissions generated relate to the degree of combustion [2].

The degree of combustion depends largely on the rate and extent of fuel-air mixing and on the flame temperatures achieved and maintained. Properly operated flares achieve at least 98 percent combustion efficiency in the flare plume, meaning that hydrocarbon and CO emissions amount to less than 2 percent of hydrocarbons in the gas stream. The tendency of a burning fuel to smoke or make soot is influenced by fuel characteristics and by the amount and distribution of oxygen in the combustion zone. For complete combustion, at least the stoichiometric quantity of oxygen must be provided in the combustion region. The hypothetical volume of oxygen requires some increases with the molecular weight of the gas burned. The supplied oxygen as the air ranges from 9.6 units of air per unit of methane to 38.3 units of air per unit of pentane, by volume [9].

Air is supplied to the flame as primary air and secondary air. Primary air is mixed with the gas before

Combustion, whereas secondary air is drawn into the flame.

26
CHAPTER 2. LITERATURE REVIEW

At present, very limited work has been published in this area. The following are some of the closest work done by various authors/writers;

2.1 Srinivasa and Krishna (2012)

Srinivasa and Krishna in [8] developed a technique used broadly in the oil and gas industry to burn undesirable flammable gases. According to this study, oxidation of the gas can preclude emissions of methane (a potent greenhouse gas), however, flaring creates other pollutants of particulate matter (PM10) in the form of soot or black carbon (BC) [8]. As at the end of 2011, 150 × 109 cubic meters (5.3 × 1012 cubic feet) of associated gas was flared annually [8]. That is equivalent to about 25 percent of the annual natural gas consumption in the United States or about 30 percent of the annual gas consumption in the European Union [8]. That amount of flaring and burning of associated gas from oil drilling sites is a significant source of carbon dioxide (CO2) emission. Some 400 × 106 tons of carbon dioxide is emitted annually in this way and this amounts to about 1.2 percent of the worldwide emissions of carbon dioxide [7].

2.2 Study by Jalama (2012)

A study by [26] showed the steam reforming process of vegetable oil which was simulated using ChemCad 6.4. This was to study the effect of temperature, pressure and steam-to-carbon (S/C) ratios on the process [26]. Pressures from 1 to 20 barg and temperatures from 100 to above 500oC were considered with S/C ratios of 3, 6 and 9. The vegetable oil was modelled by triolein and the data shows that the main reforming products under the operating conditions used are H2, CO2, CO, CH4 and
C. Higher H2 production happens at low pressure, high temperatures and high S/C ratios. Lower operating temperatures and pressures must be avoided to prevent significant carbon formation. Higher S/C ratio reduces carbon formation [26].

2.3 Srinivasan and Krishna (2014)

Another study reported that about ten countries accounted for 70% of the flaring, and twenty for 85% [3]. The top ten leading contributors to world gas flaring in 2010, were (in declining order): Russia (26%), Nigeria (11%), Iran (8%), Iraq (7%), Algeria (4%), Angola (3%), Kazakhstan (3%), Libya (3%), Saudi Arabia (3%) and Venezuela (2%) [4].

In recent times, most of the oil and gas process plants flare their excess gas [8]. The flare is manually observed by the utility operator for any abnormality, with a higher emphasis on the production output. Manual observation of the flare is not a dependable means to detect irregularities [3]. In case of a plant shutdown, emergency or pressure relief valves pop up. Sudden flaring causes a smoky flare.

2.4 World Health Organization (WHO) also reported as follows

- In 2015, 94 percent of Nigerians were exposed to air pollution levels that exceeded particulate matter (PM10) World Health Organization (WHO) level [30].
- In 25th March 2014 in Geneva, WHO reported that in 2012, 7 million people died from air pollution and that, one in eight of total global deaths is as result of air pollution exposure [31].
The direct result of pollution (soot) are air quality decline, the risk of stroke, heart disease, lung cancer, chronic and/or acute respiratory diseases, including asthma and etc.

2.5 Motivation

Following up on the recent findings and work done by various researchers, it is conspicuous that no one has looked into the Separators and Knock-out drum vessel control with the use of modelling and simulation, using HYSYS and Aspen plus [13]. The majority have not considered combining the causes, effects and mitigations of soot.

The sensitivity of the project topic which has to do with the safety implications of the vessels (separators and knock-out drums) in the process plant, during which slight changes in the control system and its processes (variable Temperature, Pressure, etc.) can easily create an upset, that may lead to an unwanted shutdown. This can consequently cause a blowdown, which can result in uncontrollable colossal soot production.

Lastly, haven worked in various fields as an Electrical & Instrument Engineer, as a plant operator as well as an Instrument Control and safety System Engineer, addressing this problem will be a plus to the oil and gas Industry as it concerns the hydrocarbon or oil and gas process plant.

There are different simulation programs used in this industry depends on the field of application and desired simulation product. When HYSYS and Aspen Plus are used in full capacity, they are very powerful tools for an engineer to gain effective and profitable designs aimed at improving plant control, operability, eliminating
process bottlenecks and minimizing process network. It also reduces human error and
time requirement [13].

2.6 Expected result

Flare is an inevitable process in Plants for numerous reasons, but the most
paramount, is for safety reasons. Flares are used extensively to dispose of purged and
waste products from refineries and also to safely degas the vessel so as to avoid
rupturing of the vessel. Also flared are non-associated gas, unrecoverable and or,
unusable gases emerging with oil from oil wells. In Burner management system, to
avoid excessive residual gas in the vessel, gases are vented to the atmosphere from
blast furnaces but often to flare for the safety of the equipment as well as personnel.
Unused gases from coke ovens also are flared. Gaseous wastes from chemical
industries must be flared in a stoichiometric amount of oxygen to provide good
combustion zone devoid of chemical pollution to the atmospheric habitats’ in
particular and both the terrestrial and aquatic habitats in general.

Flaring is an important safety means, particularly at gas processing plants. In
an emergency situation where vessels and piping become too over-pressurized, the
safety relief valves on the equipment automatically discharge the gas through piping
to flare stacks. In the absence of good flare system, plants would be subjected to
higher risk of fire or explosion. Flares are also used as an outlet for gas during
maintenance and equipment repairs. In these circumstances, all the gases are flared
temporarily until the upset condition is resolved for the smooth running of the process
again. For maintenance purpose, gases are also flared to avoid similar consequences
as above, until plant maintenance activities have been completed. In the developing
world of today, flaring has been the order of the day. Often times, the associated gases
are not completely used in commercial quantities, thereby forcing the operator to flare.

The purpose of this thesis is to proffer solutions aimed at reducing the amount of gas being flared under normal operation, as well as to limit or totally eradicate the soot to air emission in an eco-friendly manner. The Aspen HYSYS is used to model and simulate the effects of temperature, pressure and carbon in relationship to soot generation and ways to mitigate it.
3.1 Aspen HYSYS

Aspen HYSYS is the industry’s leading simulation software for oil & gas refining, power reactor and engineering processes [13]. With an extensive collection of component operations, specialized work environments, and a robust solver, modelling in Aspen HYSYS v9 enables the user to:

- Improve the design of equipment and the performance
- Monitor plant safety and operational issues in the plant
- Optimize processing ability and operating situations
- Recognise energy saving prospects and reduce greenhouse gas (GHG) emissions
- Perform commercial evaluation to gather savings in the process design

Aspen HYSYS v9 builds upon the legacy modelling environment, adding increased value with integrated products and an improved user experience. The ease of use and flexibility of model calculations have been preserved, while new capabilities have been added.

If the high pressure is required and low pressure is used instead, thereby raising the mole vapour fraction to one, that brings about soot formation in the surrounding atmosphere.
3.2 Dynamic Simulation in Chemical Engineering

Dynamic simulation is an extension of steady-state process simulation whereby time-dependence is built into the models via derivative terms [13], that is, accumulation of mass and energy. The advent of dynamic simulation means that the time-dependent description and control of real processes in real or simulated time are possible. This includes the description of starting up and shutting down a plant, changes of conditions during a reaction, holdups, thermal changes and more. Dynamic simulations (see Figure 3.2 below) require an increased in the calculation time and are mathematically more complex than steady-state simulations. They can be seen as repeatedly calculated steady-state simulations (based on a fixed time step) with constantly changing parameters. Dynamic simulation can be used in either an online and offline fashion.
- The online case being model predictive control, where the real-time simulation results are used to predict the changes that would occur for a control input change, and the control parameters are optimized based on the results.

- Offline process simulation can be used in the design, troubleshooting and optimization of process plant as well as the conduction of case studies to assess the impacts of process modifications.

![Figure 3.2 Dynamic Simulation sample [13].](image)

Aspen HYSYS is used to design new plants or model existing ones at what is considered to be the nominal process operating conditions at steady-state. However, real processes operate at steady-states which may be very different from the nominal one assumed by the static simulator. In particular, HYSYS Dynamics which allows
users to observe how the system switches from one steady-state condition to another, or how the process responds to all sort of disturbances—reactant stream flow rate or purity changes, pressure or temperature variations at different locations—and finally, the prediction of worst-case scenarios in case of power loss, fires, deactivated catalyst bed in reactors or reactors in runaway conditions.

Aspen HYSYS used to minimize or better “reject” the effect of severe disturbances on the plant performance and, as you may expect, process dynamics and process control can hardly be conceived without one another. Process parameters/variables are dynamic, hence, there is need to adequately control the process to avoid liquid carry over from the vessels (knock-out drum and scrubber), resulting in huge liquid carry over to flare, which produces soot. HYSYS will automatically perform the appropriate flash calculation when it recognizes that sufficient stream information is known. This information may have been either specified by the user or calculated by an operation. Depending on the known stream information, HYSYS will perform one of the following flashes: Temperature-Pressure, Temperature-Vapor Fraction, Temperature - Heat of reaction, Temperature-Saturated vapour, Pressure- Vapor Fraction, Pressure-Heat of reaction, or Pressure - Saturated vapour.

3.3 Temperature to Pressure (T-P) Flash Calculation

The independent variables for this type of flash calculation are the temperature and pressure of the system, while the dependent variable is the vapour fraction, enthalpy and entropy.
With the equations of state and activity models, rigorous calculations are performed to determine the coexistence of immiscible liquid phases and the resulting component distributions, by minimization of the Gibbs free energy term.

If the mixture is single-phase at the specified conditions, the property package calculates the isothermal compressibility \((\frac{dv}{dp})\) to determine if the fluid behaves as a liquid or vapour. Fluids in the dense-phase are assigned the properties of the phase that best represents their current state. Note that material which is solids will appear in the liquid phase of two-phase mixtures, and in the heavy (aqueous/slurry) phase of three-phase systems. Therefore, when a separator is solved using a T-P flash, the vapour phase will be identical regardless of whether or not solids are present in the feed to the flash drum.

3.4 Vapour Fraction Flash

Vapour fraction and either temperature or pressure are the independent variables for this type of calculation. This class of calculation embodies all fixed quality points including bubble points (vapour pressure) and dew points. To perform bubble point calculation on a stream of known composition, simply specify the vapour fraction of the stream as 0.0 and define the temperature or pressure at which the calculation is desired. If the simulated value of Vapor Fraction = 0, an ideal without soot, meanwhile at V.F=1 soot is inevitable, Like the other types of flash calculations, no initial estimates are required. Note that the vapour fraction is always shown in terms of the total number of moles.
3.5 Dew Points

Given a vapour fraction specification of 1.0 and either temperature or pressure, the property package will calculate the other dependent variable (P or T). If the temperature is the second independent variable, HYSYS will calculate the dew point pressure. Likewise, if pressure is the independent variable, then the dew point temperature will be calculated. Retrograde dew points may be calculated by specifying a vapour fraction of -1.0. It is important to note that a dew point that is retrograde with respect to temperature can be normal with respect to pressure and vice versa.

3.6 Bubble Points/Vapour Pressure

A vapour fraction specification of 0.0 defines a bubble point calculation. Given this specification and either temperature or pressure, the property package will calculate the unknown T or P variable. As with the dew point calculation, if the temperature is known, HYSYS will calculate the bubble point pressure and conversely, given the pressure, HYSYS will calculate the bubble point temperature. For example, by fixing the temperature at 100°F, the resulting bubble point pressure is the true vapour pressure at 100°F.

3.7 Quality Points

Bubble and dew points are special cases of quality point calculations. Temperatures or pressures can be calculated for any vapour quality between 0.0 and 1.0 by specifying the desired vapour fraction and the corresponding independent variable. If HYSYS displays an error when calculating vapour fraction, then this means that the specified vapour fraction doesn't exist under the given conditions, that
is, the specified pressure is above the cricondenbar, or the given temperature lies to the right of the cricondentherm on a standard P-T envelope.

3.8 Handling of Water

Water is handled differently depending on the correlation being used. The PR and PRSV equations have been enhanced to handle H2O rigorously whereas the semi-empirical and vapour pressure models treat H2O as a separate phase using steam table correlations. In these correlations, H2O is assumed to form an ideal, partially miscible mixture with the hydrocarbons and its K value is computed from the relationship:

3.9 Heat of reaction

The heat of reaction is the amount of heat that must be added or removed during a chemical reaction in order to retain all of the constituents present at the same temperature. If the pressure in the vessel containing the reacting system is kept at a constant value, the measured heat of reaction also represents the change in the thermodynamic quantity called enthalpy, or heat content, accompanying the process—i.e., the difference between the enthalpy of the substances present at the end of the reaction and the enthalpy of the substances present at the start of the reaction. Thus, the heat of reaction determined at constant pressure is also designated the enthalpy of reaction, represented by the symbol ΔH. If the heat of reaction is positive, the reaction is said to be endothermic; if negative, exothermic [16].

3.10 Oxidation

Oxidation is a continuous process wherever oxidizing species are present, from the time of particle inception until late soot burnout. Smaller particles oxidize more easily than larger ones but are possibly a greater health threat if they escape.
The soot particle occurs during oxidation when the temperature is higher than 1300 K and the equivalent ratio is less than one. Once there is less oxygen in the flaring system, there is bound to the release of the polluted substance, either as a carbon (II) oxide or just carbon. Refer to equation 5 and 6 below, shows the various equation associated to the modelling process of HYSYS

- Burns with a blue flame. Complete combustion of Methane.

  \[ \text{CH}_4 + 1.5\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]  

- Incomplete combustion of Methane-producing Carbon Monoxide.

  \[ \text{CH}_4 + 1.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O} \]  

- Incomplete combustion of methane-producing soot

  \[ \text{CH}_4 + \text{O}_2 \rightarrow \text{C} + 2\text{H}_2\text{O} \]

3.11 Gas Scrubber System

Scrubber systems are various groups of air pollution control devices that can be used to remove some unwanted component liquid or gases from industrial exhaust header [9]. The exhaust gases of combustion may contain substances considered harmful to the environment, and the scrubber are used to remove or neutralize the effects. A wet scrubber is used for cleaning air, fuel gas or other gases of various pollutants and dust particles [9].

The first air scrubber was designed to remove carbon dioxide from the air of an early submarine, conventionally; the term "scrubber" has referred to pollution
control devices that use liquid to wash unwanted pollutants from a gas stream [35]. The gas scrubber will be equipped with various instruments to check temperature, inlet and an outlet flow, vessel instrumentation with reference to API 14C, see Figure 3.3 below [35].

![Figure 3.3 Safety System design for pressure vessel [10].](image)

3.11.1 Gas Scrubber Design Considerations

Important design considerations for a chemical/gas scrubber include:

- Pollutant Targeted
- Removal Efficiency
- Process Conditions (i.e. flow rate, temperature, concentration)

As part of the research on causes and mitigations of Soot, it was discovered that, an effective Gas Scrubber removal efficiency is achieved by ensuring the appropriate contact time between the gas and the scrubbing liquid. These systems
incorporate a scrubbing vessel with a system fan, recycle pump, instrumentation and controls, mist eliminator, and exhaust stack. Packed Bed Scrubbers include random packing to facilitate gas to liquid contact. Exhaust gas enters the scrubber where it contacts the scrubbing fluid. The fluid captures the pollutant and is collected for discharge or is treated for reuse.

3.12 Knock-out Drum

Knock-out Drums are used to slow down gasses and allow liquids to drop out of the gas stream. Knockout Drums are installed in the waste gas header or in the flare stack base, see Figure 3.4 for an example. Knock-out Drum is vapour (gas)–liquid separator, a device used in several industrial applications to separate a vapour (gas)–liquid mixture. A vapour-liquid separator may also be referred to as a Knock-out pot, Flash Drum, Break pot, Knock-out drum, Compressor suction drum or Compressor Inlet Drum. It is also called a demister when it is involved in the removal suspended water droplets from streams of air. If the level is not properly monitored, it can overfill thereby carrying the liquid to the flare stack popularly called liquid carry-over, which is a major cause of soot. When Mesh pads of the knock-out drum suffer from excessive liquid flooding and the mesh becomes soaked with liquid, there is loss in efficiency by carryover. Mesh pads are also prone to solids fouling by particle deposition at the mesh structure surface, further reducing their efficiency and causing considerable maintenance costs and failures.

They are configured either to be horizontal or vertical or are sized according to each requirement. Construction could be of carbon steel, or of corrosive service stainless steel. Automatic drain (open or closed) controls are also included to thwart the buildup of process fluids in the seal. Two-inch piping and flanged are connected
to draining line as well as use for vessel cleaning. All vessels are manufactured in accordance with ASME code bent in the form of a U, called U-tubes.

3.12.1 Features

- Automatic liquid controls
- Specially designed separation internals
- Used in combination with liquid sea
- No water carryover to the compressor
- Differential output can be used to effectively monitor the liquid of the process

![Figure 3.4 Knock-out Drum [36].](image)
3.13 Soot and slag generation from stabilization unit

In any combustion process of a fuel, there will always be some unburned carbon (soot) generated and some ash carried with the stack gas stream. Soot, ash, and molten ash (slag) will accumulate at the tube banks of the heat exchangers. Some ash will even meltdown at the tube surface. The final result is a layer insulating the tubes against the hot combustion gases. Soot generation has various causes such as;

3.13.1 Freezing the chemical reaction

This occurs when the flame comes too close to the boiler walls, “freezing” the kinetic reaction. This effect is best demonstrated with a knife one passes through a candle flame. The flame will blacken the knife. Major causes are over the firing of the boiler, too much excess air and worn out burner nozzles.

3.13.2 Insufficient atomization of fuel oil

Three T’s which are for; Temperature, Turbulence and Time are involved in this process. Low oil line pressure and lack of turbulence will result in poor atomization of fuel oil, resulting in larger droplets leaving the flame envelope partially unburned. Major causes are low oil line pressure, lack of primary combustion air, or low fuel oil preheating temperature.

3.13.3 High moisture content in the fuel

Too much water in a fuel leads to a “cold” fire causing excessive smoke generation because there is not enough fuel energy available to generate a sufficiently high flame temperature. However some water helps to speed up the kinetic reaction, it
also shortens the flame length. A major cause of this type of soot generation is a combination of high moisture content and excessive air.

3.13.4 Erratic feeding of solid fuels

Solid fuel firing is not as “smooth” as a liquid or gaseous fuel firing. Excess air is changing constantly, causing cold pockets in the furnace, where too much fuel and not enough “fire” and air are present. The result is a smoke generation. Major causes are bad combustion air distribution and malfunctioning, or badly designed feeding mechanism.

3.14 Reactors

Reactions are the heart of the chemical processes most time, in which moderately low price raw materials are transformed into more economically favourable products. In other cases, reactions play essential safety and environmental protection roles [21].

Such design is usually based on thermodynamics, chemical kinetics, and transport studies coupled with experience and economic considerations to provide good design and operation of the reactor for desired outcome [21]. The products are paramount in the study of chemicals. Other considerations should be how fast and the extent to which the reaction should go.

The study of such factors in addition to the detailed design of the reactor consists of the chemical reaction engineering field in which process simulation can be of great help [21]. Aspen Plus provides several libraries to model reactive processes. The selection of the model depends on the amount of information available and the type of simulation [21].
3.15 Gibbs reactor

Gibbs free energy is also known as free enthalpy and is a thermodynamic capability that can be used to calculate the maximum of reversible reactions that may be accomplished by a thermodynamic system at a fixed temperature and pressure [22].

The Gibbs energy is also the thermodynamic potential that is minimized when a system reaches chemical equilibrium under isothermal and isobaric conditions. Its derivative with respect to the reaction coordinate of the system vanishes at the equilibrium point. As such, a reduction in Gibbs free energy is a necessary condition for the spontaneity of processes at constant pressure and temperature. The SI unit is in joules [22].
CHAPTER 4. SIMULATION OF GAS PROCESSING PLANT USING HYSYS AND OTHER PARAMETERS FOR SOOT CONTROL AND RESULT

The simulation model is developed on AspenTech HYSYS 9.0. The type of fluid package selected is methane. Knock-out drum is also used as an aqueous absorbent to absorb water or moisture or vapour from gas streams. Before entering the flaring system, the gas is passed through an inlet separator where entrained droplets of liquid are removed from the gas stream. The aim is to see the causes of soot with respect to pressure, temperature, carbon constituents and the effect of heat of reaction.

Aspen HYSYS was used to model the Gas Processing Unit. The first step in creating the model was the selection of a standard set of components and a thermodynamic basis to model the physical properties of these components. The selected components required for the simulation are shown in Figure 4.1.

![Figure 4.1 Addition of the hydrocarbon component.](image)
Specification of feed gas is shown in Figure 4.1 XHP parameter and 4.2 for that of LP knockout drum

![Figure 4.2 XHP parameter.](image)

The simulation model is developed on Aspentech HYSYS 9. The type of fluid package selected is Pengrobinson package. Specification of the feed gas is shown in Figure 4.2 above.

![Figure 4.3 Flow sheet of the Gas Processing Plant [14].](image)
In simulating the processing plant in Fig 4.3, natural gas with condensate and water is drawn from one well. The gas composition of this field is used. The industrial data are obtained from the simulation. Then the gas pressure is reduced and control valve equipped with inlet header to heat the gas so as to prevent hydrate formation. Then the outlet streams of the headers are passed through pressure reduction manifold though not included in the PFD to the inlet two-phase separators. The two-phase Separators have a level control loop to control the flow, and the other going to a three-phase separator (V-1300). Separator (V-1800) separates to a closed drain. Separator (V-2600) has two outlets with one outlet passing through the LP/HP Knock-out drum to HP/LP-FLARE

![Figure 4.4 LP knockout drum parameters][13].

---

[13]: #figure4_4.png
Figure 4.5 HYSYS Input parameters for HP knockout drum [13].

Figure 4.4 and 4.5 above shows the effect of pressure and temperature, together with the resulting vapour/phase fraction of the LP and HP knockout drum.

4.1 Pressure Effect

This is the influence of pressure on soot formation during flaring and the behaviour of the Aspen HYSYS model with respect to hydrocarbon breakdown (methane) to carbon (II) oxide and carbon. It is found that the pressure and the temperature can be well predicted by the Aspen HYSYS and virtual inspection flame during a burning flare.

The designed soot yield is mostly complex to the soot surface growth rate and increase of the pressure. The increase of pressure leads to the decrease of soot surface growth rate and hence increase in the soot volume fraction. Smoke-point fuel mass flow rate decreases with increasing pressure. For tractable measurements to assess the effect of pressure, the fuel mass flow rate at all pressures should be kept constant, and this mass flow rate should be equal or less than the smoke-point fuel mass flow rate at the highest pressure considered. Soot particle size measurements above 100psi are not
as reliable as those at lower pressures. Available high-pressure soot yield data from gaseous diffusion flames seem to display a unified dependence on pressure when the soot yield is properly normalized. In summary, the results (Fig 4.7) showed that soot concentration increased significantly as pressure decreased.

To illustrate the effect of pressure on the generation of carbon/soot, CO, and CO2, case studies were created.

<table>
<thead>
<tr>
<th>Case Study Name</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure Effect on Methane (Mole Frac)</td>
<td>Success</td>
</tr>
<tr>
<td>Temperature Effect on Methane (Mole Frac)</td>
<td>Success</td>
</tr>
<tr>
<td>Pressure Effect on CO2 (LP&amp;HP)</td>
<td>Success</td>
</tr>
<tr>
<td>Temperature Effect on CO2 (LP&amp;HP)</td>
<td>Success</td>
</tr>
<tr>
<td>LP-Pressure Effect on Carbon, CO, &amp; CO2</td>
<td>Success</td>
</tr>
<tr>
<td>LP-Temperature Effect on Carbon, CO, &amp; CO2</td>
<td>Success</td>
</tr>
<tr>
<td>HP-Pressure Effect on Carbon, CO, &amp; CO2</td>
<td>Success</td>
</tr>
<tr>
<td>HP-Temperature Effect on Carbon, CO, &amp; CO2</td>
<td>Success</td>
</tr>
</tbody>
</table>

**Figure 4.6 Case study to show the effect of pressure and temperature on soot generation [13].**

For the effect of pressure, a range was taken between 100 and 1300 Psia to see how it will affect the mass flow of carbon/soot. Figure 4.7 shows that as pressure is reducing, the carbon/soot is increasing. Other factors also considered are the burning temperature and the hydrocarbon content.
4.2 Temperature Effect

Soot formation depends upon fuel type, oxidizer, concentrations, temperature and pressure. When fuel is heated without substantial atmospheric air, substances that are steadier at high temperatures (carbon-rich soot) which is the end product is formed. Eventually, the soot will either be oxidized through surface reactions or persist as insignificant black spheres or a lot of agglomerated particles. The temperature in the flare was varied between 60, and 240 K to confirm the effect of temperature on soot formation. It is assumed the air is constant at that point as shown in Figure 4.8 below. The increase in temperature entails an increase in the carbon monoxide, carbon dioxide and carbon, hence, increases the soot formation.

Normally it would be expected that the higher temperature would produce more soot, but there are other factors to be considered in real life scenarios, ranging from the velocity, constituents, thickness of the hydrocarbon, quantity of air supplied, other environmental and independent variables. It is not possible to say whether one temperature produces more soot than the other without the other conditions in a live plant.

Figure 4.7 Effect of pressure on soot generation [13].
The temperature graph Figure 4.8, below shows that the amount of soot generally increases as the master composition mass flow CO and CO2 also increase. To determine the effect of temperature, a range was taken between 50 and 230 °C to see how it will affect the mass flow of Carbon/Soot.

Figure 4.8 The effect of the Temperature range to the mass flow of Carbon/Soot formation [13].

4.3 Heat of reaction

This is the amount of heat that must be added or removed during a chemical reaction in order to keep all of the substances present at the same temperature. If the pressure in the vessel containing the reacting system is kept at a constant value, the measured heat of reaction also represents the change in the thermodynamic quantity called enthalpy, or heat content, accompanying the process—that is, the difference between the enthalpy of the substances present at the end of the reaction and the enthalpy of the substances present at the start of the reaction. Thus, the heat of reaction determined at constant pressure is also designated the enthalpy of reaction,
represented by the symbol ΔH. If the heat of reaction is positive, the reaction is said to be endothermic; if negative, exothermic [16].

To account for the reaction that will be taking place in the Flaring Unit, the reactions shown below was added to the process simulation. When the component list was created, HYSYS created a new component list called “Component List-1”. The next step was the selection of a ‘Fluid Package’. The ‘Fluid Package’ is the thermodynamic system associated with the chosen list of components. We use the Peng Robinson Equation of State (PR) property package (see Figure 4.9) and the equation of state was chosen for this process because it is mostly hypothetical and light hydrocarbons.

![Figure 4.9 Selected thermodynamics for fluid package [13].](image-url)
Figure 4.10 HYSYS Equation of reaction for complete combustion in the Flaring Unit [13].

Figure 4.11 HYSYS Equation of reaction for Partial Combustion in the Flaring Unit [13].
The prediction and quantity of the heat effects that follow chemical changes are imperative to the acceptance and use of chemical reactions. If the vessel comprising the reacting system is in an adiabatic condition, that is, no heat movement in or out of the system, the heat effect that escorts the transformation may be demonstrated by either an increase or a decrease in temperature, with respect to the substances present. For accuracy purposes, the right amounts of heat of reaction are needed for the proper design of equipment for use in processes [16]. To measure the heat of reaction for every reaction that occurs and because for some reactions such a measurement may not even be feasible, it is expected to guesstimate heats of reactions from suitable combinations of compiled standard thermal data [16]. These data usually take the form of standard heats of formation and heats of combustion. The standard heat of formation is in this project defined as the amount of heat absorbed or evolved at 25°C (77° F) and at one atmosphere pressure when one mole of a hydrocarbon compound produce a mole of CO2 and water as the constituent elements, each substance being in its normal physical state (liquid or gas). The heat of formation
of an element is arbitrarily assigned a value of zero. The standard heat of combustion is similarly defined as the amount of heat evolved at 25°C and at one-atmosphere pressure when one mole of a substance is burned in excess oxygen [16].

4.4 Gibbs reactions

An equilibrium reactor is simulated by using the GIBBS reactor modules in Aspen plus version 9. The flow diagram is demonstrated as a simulation to all parameters. This method involves the direct minimization of Gibbs free energy and it is used when reactions are not known or are high in number due to many components participating in reactions. GIBBS reactor modules are the block in Aspen Plus that can be used for solid, liquid and gas phase equilibrium. The following equations were used to confirm the soot generation;

- Burns with a blue flame

  Methane + oxygen $\rightarrow$ carbon dioxide and water (exothermic reaction)

  \[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \] \[ \text{[9]} \]

  Incomplete combustion results in some of the volatile organic compounds being unaltered or converted to other organic compounds.

- Incomplete combustion of methane-producing carbon monoxide and partly soot

  Methane + oxygen $\rightarrow$ carbon monoxide and water

  \[ CH_4 + 1.5O_2 \rightarrow CO + 2H_2O \] \[ \text{[10]} \]
• Incomplete combustion of methane-producing soot

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{C} + 2\text{H}_2\text{O} \] \[11\]

The following species are considered using the following compounds at equilibrium at assumed temperature ranging from \((T = 100 - 500^\circ\text{C})\), pressure \((P = 100\text{ to } 1500\text{psi})\) and steam to carbon ratio \((S/C = 3.5)\); \text{CH}_4, \text{O}_2, \text{CO}_2, \text{H}_2\text{O}, \text{CO}, \text{C}.

Figure 4.13 ASPEN PLUS scream conversion result summary [13].
CHAPTER 5. MITIGATIONS OF SOOT GENERATION AND RECOMMENDATIONS MITIGATION

5.1 Mitigations of Soot Generation and Recommendations Mitigation

These are the actions and measures taken intending to reduce (or eliminate) negative impacts and promote positive bio-physical environmental, social and health impacts of soot generation as a result of flaring.

5.2 Modelling Optimization

The type of hydrocarbon fluid selected is a methane and plant/model optimization which will be having both independent and dependent variables in adequate proportions, in order to prevent soot generation. If we were to go by plotting the output of temperature and pressure, the point of interception of the various parameters would be an optimization point. The following are results of the modeling.

5.1.1 Temperature control

Temperature can be a source of soot generation if not appropriately controlled. When fuel is heated without substantial atmospheric air, the end product is carbon-rich soot. The soot produced may eventually either be oxidized through surface reactions, or persist as insignificant black spheres or a lot of sooty particles. The temperature in the flare was varied between 60K, and 240 K to confirm the effect of temperature on soot formation. It is assumed that the air is constant at this point, and the temperature increased. This brings about an increase in carbon monoxide and carbon (IV) oxide production, which in turn increases soot formation.
The temperature chart shows that the amount of soot generally increases as the master composition mass flow CO and CO2 also increase. The mitigation will therefore be to apply adequate control measures in the plant and actual plans to relate process temperature with an acceptable limit or setup parameters.

![Temperature Chart]

**Figure 5.1 The effect of the Temperature range to the mass flow of Carbon/Soot formation [13].**

5.1.2 *Pressure control*

It was found that the soot production increases with a decrease in pressure, as predicted by the Aspen HYSYS and virtual inspection flame during a burning flare. The designed soot yield is mostly complex to the soot surface growth rate and the increase of pressure. The increase of pressure leads to the decrease of soot surface growth rate and therefore, increase the soot volume fraction.

Smoke point fuel mass flow rate decreases with increasing pressure. For tractable measurements in most modern plant, choke valve and inlet heater is used to control pressure output. High-pressure soot yield data from gaseous diffusion flames
seem to display a unified dependence on pressure when the soot yield is properly normalized. In summary, the results from Figure 5.1 showed that soot concentration increased significantly as pressure decreased.

For the effect of Pressure, a range was taken between 100 and 1500 Psia to see how it will affect the mass flow of Carbon/Soot, as pressure is reducing, the carbon/soot is increasing. Other factors to also consider will be the burning temperature and the hydrocarbon contents. The mitigation will, therefore, be to apply adequate control measures in a process plant or actual plant to control process pressure to an acceptable limit or set point.

![Graph showing the effect of pressure on carbon generation](image)

**Figure 5.2 Effect of pressure on soot generation [13].**

5.2 **Reduction of formation of the CO, unburned hydrocarbons and soot**

If oxygen deficiency occurs and if the carbon particles are cooled to below their ignition temperature, carbon monoxide, unburned hydrocarbon and smoking occurs. Therefore it is important to keep the right temperature in the combustion zone.
If there is no enough air to burn the gas completely, combustion will still occur but it will leave some of the gas unburned. Smoking may also result from combustion depending on the distribution of air. So injection rate of air has a great effect on the efficiency of combustion in a flare. For plant optimization, therefore, the CO should be monitored using the product, regulating flow rate of the hydrocarbon end product with an appropriate air supply other than the atmospheric air, if need be.

5.3 Flare Efficiency

One of the mitigations of soot control is flare efficiency. In characterizing the performance of a flare, it is convenient to define the term “Efficiency” of the flare. Several similar but different definitions of efficiency have been proposed and used in the past. The most rigorous and useful definition of these is properly termed a “conversion efficiency” which quantifies the effectiveness of a flare to fully oxidize the fuel. For a flare burning a mixture of hydrocarbon fuels, the relevant parameter is the “carbon conversion efficiency” which is defined in terms of a rate as follows [11]:

$$\eta = \frac{[CO_2]}{[CO_2] + [CO] + [THC] + [soot]}$$

Where:

CO2: the CO2 concentration produced by the flare,

CO: the CO concentration exiting the flare,

THC: the concentration of total hydrocarbons exiting the flare, and

[soot]: the concentration of any soot present exiting the flare.
This mass-based definition is indicative of the mass conservation equations. Though properly called the “carbon conversion efficiency”, this term is often referred to as the “combustion efficiency”,

“efficiency” or “flare efficiency”. Sometimes the performance of a flare is presented by means of

“inefficiency” that is defined by $1 - \eta$ [11].

5.4 Government regulations

The government needs to be fully committed to putting an end to gas flaring especially in the developing world like Nigeria and the other world. This is as a result of the negative consequences of gas flaring that result in soot production, which impacts negatively on both lives and the ecosystem of the region. This is especially so in the Niger Delta in the southern part of Nigeria, that government in its knowledge propagated "The Petroleum Act, 1969" and "The Petroleum (Drilling and Production) regulations 1969". In 1979, the associated gas re-injection act was publicized [12] but the short of the bill then was that there were no provisions for gas utilization. The petroleum drilling and production regulation were explicit on designing programs that will end gas flaring [12]. It states in section 42 that not more than five years after the commencement of production, the prospective company must submit to the minister any feasibility study, program or proposal for the utilization of natural gas produced [12], whether associated or not, discovered in the relevant area. There were no provisions in the regulation for sanctions to erring multinationals. Although it was an interesting provision, there was no information indicating that the above regulation was ever implemented by the government or complied with by the multinationals.
The associated gas re-injection act of 1979 specified, in section 14 a, and b, that gas flaring should stop on 1st January 1984. Instead of enforcing this regulation, the government chickened out by amending this regulation to provide for continuous flaring to protect its interest because of the Government-owned major shares in the multinational oil business in Nigeria. In some cases, as much as 60% worth of shares and yet will not want to pay its own share of project funding. It is not just enough to promulgate the law on paper, stringent actions need to be taken to implement these laws.

Under the provisions of the petroleum act [12], the minister of petroleum may revoke a lease or license or order the suspension of operations under a lease or license granted [12]. This suspension could remain until he is satisfied that necessary arrangements have been made to prevent a threat to life and ecosystem.

5.4.1 Gas Utilization Law

The financial cost of gas infrastructural development is huge and the prospect of recovering the money within a short time after the investment is very slim. The situation has led to the preference for flaring rather than investing to harness the non-renewable, gas energy resources [12]. If the government is serious about flare out, the penalty for flaring must be increased in line with current reality and inflationary trend applicable in the country. From my interaction with the industrial personnel, the current penalty for flaring in the country is just too small and shameful to serve as a deterrent.

A fine or penalty should not always be money. It could come in a way of sanctions including shutting down any platform that can’t meet up with the provisions of the regulation to end gas flaring [12].
Recently, there have been major ongoing infrastructural developmental projects for gas production undertaken by the multinationals. The rate of development of gas infrastructure in Nigeria is slow when compared to what Shell did in Malaysia. It took Shell less than six years to complete and start-up the project. The proposed liquefied natural gas plant (LNG) in Brass submitted by Shell since the early 90s has remained a proposal till date.

The integrated power project (IPP) is for the purpose of using gas to run gas turbine generators for generating electricity in order to increase total national grid power supply. The situation has increased the call on the government to give investors free hands to bring in turbines, buy gas to run it from the multinational oil companies and sell power to interesting members of the public and pay tax to the government. In recent years, there have been international directions to reduce gas flaring and venting through the World Bank Global Gas Flaring Reduction (GGFR) in partnership with the global methane initiative (GMI) [29]. Several countries are now signatories on the GGFR partnership’s voluntary standard for flare and vent reduction [45], and both the GGFR partnership and GMI actively promote demonstration projects to reduce flaring and venting [29]. Other regulations that can be used to reduce flaring such as direct regulation can be found in Norway, where there is an enforced policy of zero flaring [28] and North Dakota in the U.S., where oil producers will be required to meet gas capture targets or face having their oil production rates capped [47]. Additionally, the United Nations’ Development Mechanism, by offering ‘Certified Emissions Reductions’ provides flaring and venting reduction projects [27].
5.5 Proper control to avoid liquid carry-over

When any solid, liquid or vaporous waste product leaves the process separators or vessels (examples; scrubber, knock-out drum or even seal pot) to flare uncontrolled, the phenomenon is called ‘carryover’ or ‘liquid carry over’. Carryover though does not sound like a serious issue but can affect the smooth burning of the flare system which can result in serious cloudy soot. Carryover results from a stoichiometric imbalance of heavy methane passing to flare uncontrolled, resulting in the incomplete separation of liquid from the gas. The following are causes of carryover that must be avoided;

5.5.1 Load characteristics

Fluctuating Gas handling facility load intakes decreases the chances of carryover to flare. When gas demand suddenly decreases, the separator pressure builds-up. As a result, the hydrocarbon will suddenly increase resulting in a phenomenon called ‘carry-over’. On the other hand, as the gas handling facility loads and takes in more loads, there will be a drop in pressure and also level drop. When gas demand suddenly increases, the separator pressure loses its level. As a result, the hydrocarbon content will suddenly decrease, or increase if the level decreases below the low level. This will result in a phenomenon known as ‘gas blow bye’.

5.5.2 Vessel drum size and design

Design specification should cover minimum requirements for the vessel design, fabrication, and shop testing of oil-field type oil and gas separators which is used in oil and gas process plant. These are usually located but not limited to some point on the production flow line between the wellhead and pipeline. Separators
covered by this specification may be vertical, spherical, and single or double barrel horizontal [23]. This factor is by design three-element drum level control and makes it possible to design smaller diameter drums. The drum internals includes baffle plates, cyclone type separators, chevron separators or screen driers, perforated boxes. The drum diameter should be selected so that the distance from the water-steam interface to driers is quite adequate. Failure to address this would result in carryover [24].

5.5.3 High drum level operation

The operating level, alarm levels & trip levels such as low and high operating pressure and operating level, as well as high and low of vessel parameter and conditions should be clearly marked and set by competent persons. The carryover is more with high liquid level. The set point of the level should be reduced to ensuring that liquid doesn’t go beyond 85 % of the vessel separator by tuning the control valve action [24].

5.6 Proper flare recovering system (Gas flaring reducing and recovery)

Environmental and economic considerations have amplified the use of Flare Gas Recovery Systems (FGRS) to minimize the amount of gas being flared. The recovery of flared gas reduces noise and thermal radiation, operating and maintenance costs, air pollution and gas emissions and also reduces fuel gas and steam consumption.

A complete flare system consists of the flare stack or boom and pipes which collect the gases to be flared. The flare tip at the end of the stack or boom is designed to assist entrainment of air into the flare to improve burn efficiency. Seals installed in the stack prevent flashback of the flame, and a vessel at the base of the stack removes
and conserves any liquids from the gas passing to the flare. Depending on the design, one or more flares may be required at a process location. The efficient use of fuel gases required for proper operation of the flare and better control of steam to achieve smokeless burning which contribute to flare reduction [29]. These recovery methods optimally require minimizing environmental and economic disadvantages of burning flare gas.

![Flare Stack System](image)

**Figure 5.3 Overall flare stack system in a gas plant process plant [25].**

5.7 Gibbs reactor

An equilibrium reactor is simulated by using the RGIBBS reactor modules in Aspen plus version 9. The flow diagram is demonstrated in simulation to all
parameters. This method involves the direct minimization of Gibbs free energy. See Figure 5.4 Gibbs free energy reactor;

![Figure 5.4 Gibbs Reactor.](image)

Table 1 Aspen Plus Mole Flow of Various Parameters Used.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Vary 1, B1 parameter temp K</th>
<th>CH4 KMOL/SEC</th>
<th>O2 KMOL/SEC</th>
<th>CO2 KMOL/SEC</th>
<th>H2O KMOL/SEC</th>
<th>CO KMOL/SEC</th>
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### 5.8 Temperature effect results and recommendation

It was observed that at equilibrium with operating pressure at zero, under the following assumptions, that there was a pressure drop and temperature equilibrium at 300oC (574K). As temperature increased there was an increase in the outlet mole
flow of carbon monoxide (CO) and carbon dioxide (CO2) with constant methane (CH4), water (H2O) and relatively constant oxygen O2. The mole flow of carbon was observed to be constant throughout the process. As seen in Figure 5.5 below, CO and CO2 dropped to the very minimum at various points even with the increase in temperature. The fall of CO and CO2 started at a temperature of 578K but CO2 dropped to minimal before CO. The CO2 mole flow completely dropped to a minimum at operating temperature of 610 K and the mole of CO decreased to the barest minimum at 638K later.

The interpretation can, therefore, be connoted that soot (CO and CO2) increases with an increase in temperature.

![Figure 5.5 Sensitivity Results Curve of Gibbs reactor aspen plus for Temperature effect.](image)

5.8.1 Recommendation

In the process plant, as noticed from Aspen plus simulation, soot is generated with increase in temperature to a point of the law of diminishing returns, soot is
totally eliminated. The recommendation will therefore be to set aside adequate control system in place to monitor and control the operating system temperature to that optimum point of minimal or no soot production. Figure 5.5 shows that the optimal temperature range is 610 – 640K.

5.9 Pressure effect result and recommendation

It was observed that at equilibrium with operating temperature at 0 °C or 273K, under the following assumption, that is, a temperature drop and pressure equilibrium at 6.8Atm or 100Psi (689476NqM), as pressures increased there was a decrease in the outlet mole flow of carbon monoxide (CO) and carbon dioxide (CO2) with constant mole flow of methane (CH4), water (H2O) constant oxygen O2. Finally, the mole flow of carbon was observed to be constant throughout the process see Figure 5.6 below. CO and CO2 dropped sharply to the very minimum at various points and rises immediately as pressure keeps increasing. The fall of CO and CO2 started as the pressure rises, however CO2 and CO attained the minimal mole flow at 200Psia before it rises and falls again.

![Figure 5.6 Sensitivity Results Curve of Gibbs reactor aspen plus for Pressure effect.](image-url)
5.9.1 Recommendation

It will almost be difficult to give a recommendation in the process plant, haven observed the rise and fall of CO and CO2 (soot) from aspen plus simulation, though, further study will be required as regards these modelling. Soot is generated by increase and decrease of CO and CO2. As pressure keeps increasing, soot is totally eliminated at the process optimization point. The recommendation, therefore, will be to get good control systems in place to monitor and control the operating system’s pressure to that optimal point where soot is minimal. The Figure 5.6 above shows the windfall point of pressure within 200 Psia.
CHAPTER 6. CONCLUSIONS

Gas flaring is one of the most common environmental problems producing greenhouse gases and other emissions. These emissions have high global warming potential and contribute to climate change. Flares and reports from the health effects of soot, shows that soot particles can go into the lungs, from which has been linked to a wide range of serious health conditions, including; cancer, heart attacks, stroke, acute bronchitis, aggravated asthma among children and premature death. It is therefore evident from these reports that flaring has to be checked.

Higher Carbon formation happens in the simulation with Aspen HYSYS at low pressures and high temperatures. Hence, lower operating temperatures and high pressures must be maintained to prevent soot formation which results from an increase in carbon content.

With the aid of adequate control measures in place, there is minimal liquid carry-over; hence soot generation from carry-over will be a thing of the past. The operating conditions which used H₂O, CO₂, CO, CH₄, O₂, N₂ and C (carbon) as its parameters discovered that higher soot formation happened at low pressure and high temperatures. It is therefore imperative that lower operating temperatures and pressures be maintained at safe zone to prevent significant carbon formation, however, there is an encouragement for further work on the area not covered extensively due to time constraints.

Finally, an adequate level of control should be considered in order to manage the aspect of liquid carry-over, which most times is considered by field operators as the number one source of soot formation.
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