

Evaluation of the Exact Production Quantity of Nitrogen Fertilizer in Real-Time from any Particular Associated Gas Flare Volume in Nigeria

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Abstract

Fertilizers acts in two ways to enhance the growth of plants i.e. either by providing the essential nutrients such as nitrogen, phosphorous potassium et cetera .or improving the effectiveness by modifying its water retention and aerations. Nitrogen can be fixed into chemical compounds such as ammonia (NH₃) for plants use either by bacteria in the root nodules or synthetically fixed using Haber-Bosch process. Pure ammonia is gaseous and is sometime injected into the ground directly, but most often, it is used as a feedstock to produce all the other nitrogen fertilizers in either liquid or solid forms. Presently, over 80% of the fertilizer consumed in Nigeria is imported, while usage is 20kg per hectare on the average, against the expected usage rate of over 200kg per hectare for developed countries. This investigation on the real-time monetization of the flared gas in Nigeria through production of nitrogenous synthetic fertilizer ammonia/urea, applied the stoichiometric balanced equation of ammonia production with the Haber-Bosch process. The available 16.090 MM scfd, methane produced 655,399, 762. 4 grams of ammonia which produce 1, 156,587.816 kg of urea, equivalent of about 23,132 bags of 50kg fertilizer per day.

Keywords: Ammonia production; Flare natural gas; Nitrogen fertilizer; Stranded monetization; synthetic Urea. Gas

1.Introduction

Fertilizer is any organic or inorganic material of natural or synthetic origin that is added to the soil (foraminifera market research; fertilizer wikipedia), to supply one or more plant nutrients (nitrogen, phosphorous, potassium etc) essential to the growth of plants, either as nitrogen fertilizer (ammonia/urea), phosphate fertilizer, potassium fertilizer or compound fertilizer etc. Every living thing (plants and animal) needs nitrogen because it is a chemical component of proteins and nucleic acids (Ebbing et al., 1995). Our bodies are mostly made out of proteins, a biological polymer that is made up of 16 percent nitrogen by weight, and also contain carbon, hydrogen, oxygen and sometimes other elements (Myers et al., 2007) such as phosphorus, sulfur, iron and copper (Levorsen, 1967). Proteins heated in acidic solutions hydrolyze into amino acids which are carboxyl acids in which one hydrogen atom has been replaced by an amino group (-NH₂). Thus, the building blocks of proteins are amino acids, a combination of amino group of atoms (-NH₂) and the carboxylic acid group (-COOH).The simplest of amino acids is glycine, CH₂(NH₂) COOH. While all the hereditary characteristics resulting from division and re-division of the single cell that started human formation from both parents are stored chemically in a compound called nucleic acid, an organic compound either deoxyribonucleic acid DNA or ribonucleic acid RNA (Brown et al., 2005). The greatest percentage of the gases in air is nitrogen (a full 78%), oxygen 20% (Hess, 1980). Nitrogen in the air is very un-reactive, thus it must be incorporated into chemical compounds before plants can use it, and subsequently, human beings get their nitrogen by eating plants and by eating other animals that have eaten plants (Ebbing et al., 1995). For many years, farmers supplemented the natural sources of fix nitrogen by using manure i.e. organic fertilizers, which are typically made from plants and animal wastes, such as farm animals and guano (bird dropping).

Naturally therefore, the nitrogen cycle provides the essential nitrogen compound for plant life (Hess, 1980), that is, bacteria in the roots leguminous plants oxidize nitrogen into proteins, which in turn decompose to form nitrates in the soil, and other bacteria cause the decay of plant and animal tissue, producing ammonia and free nitrogen, which returns to the atmosphere. Subsequently, the ammonia is oxidized to nitrates by other bacteria (a process known as 'Nitrogen Fix' by Bacteria), while the much of the free nitrogen combines directly with oxygen in the atmosphere during electrical discharges in the storms, forming oxides e.g. Nitrogen Monoxide (NO) which are washed to the ground by rain and converted to nitrates by bacteria (a process known as 'Nitrogen Fix' by Lightning). With increased demand for crops as the world population grows, chemists then started, to investigate on the possibility of using the rich pool of nitrogen in the air with hydrogen to produce ammonia synthetic fertilizer.

1.1. Literature Review

Successfully, a German Chemist Fritz Haber (1868-1934), by 1905, found that the catalyst, (iron mixed with metal oxide) as well as other conditions are required to change nitrogen's slow reactivity at ordinary conditions (Alkusaier, 2015). Commercial ammonia production, using this process started in 1910 due to further development of the process by Carl Bosch, while working for the German Chemical Company BASF (creative commons Attribution, 2017), thus the industrial process based on this reaction is either called the Haber process or Haber-Bosch process for the synthesis of ammonia: to synthesize means to combine the parts into the whole (Sherman and Sherman, 1999). Pure ammonia is a gas under ordinary conditions, which can either be injected into the ground directly as a nitrogen-based straight fertilizer or used as a feedstock for the production of all the other nitrogen fertilizers in either liquid or solid forms. Liquid fertilizers comprise anhydrous (water-free) ammonia, aqueous solutions of ammonia, aqueous solutions of ammonium nitrate, (that is, when the concentrated products are diluted with water). Predominantly, a large portion of ammonia is allowed to react with either nitric acid, HNO_3 or sulfuric acid, H_2SO_4 to form ammonium nitrate NH_4NO_3 , and ammonia sulfate, $(\text{NH}_4)\text{SO}_4$, common components of solid fertilizers. Typically solid fertilizers are available in prills, solid globules, granulated or powdered, which makes it stable and easier for storage or transportation at room temperature. Almost 90% of fertilizers application on farms worldwide are in solid forms, mostly (80%) urea $\text{CO}(\text{NH}_2)_2$, a dense nitrate, which is non-explosive, unlike ammonia and ammonium nitrate. These synthetic fertilizers, with consistent composition of nutrients, enables the yields from modern agriculture to be uniform every season, from any particular farm, as well as satisfy the increasing demand for crops as the world's population grows.

1.2. Significance of the Research

In Nigeria, agriculture has remained the largest sector of the economy. About 70% of the 190.3 million estimated population of Nigeria (that is about 133.21 million people) are engaged in small, medium or large-scale farming or other agro related business (foraminifera market research). Nigeria has a total land area of 98.3 million hectares, with about 34 million hectares or 48% being used for cultivation. Fertilizer consumption in kilograms per hectare of arable land was 2.12 in 2009, 9.98 in 2006 and presently, it is between 20-30 kg on the average, against the expected usage rate of over 200kg per hectare for developed countries (Odum, 2015). Currently, on the average Nigeria imports over 80% of all fertilizer consumed although there is abundant raw materials for fertilizer production in the country, such as: (1) natural gas (methane) for ammonia gas (available in the whole Niger Delta States: Abia, Akwa-Ibom, Bayelsa, Cross River, Delta, Edo, Imo, Ondo and Rivers); (2) Phosphate rock for phosphonic acid and phosphate powder (available in Ogun and Sokoto States); (3) Potash Ore (available in Borno and Jigawa State); (4) Clay is available in the following 24 States Abia, Adamawa, Akwa-Ibom, Anambra, Bauchi, Borno, Delta, Edo, Enugu, Kaduna, Katsina, Kebbi, Kogi, Kwara, Lagos, Nassarawa, Niger, Ogun, Oyo, Plateau, Rivers, Yobe, Zamfara and Abuja (Ehiaghe, 2005; Akinjiyan, n.d); (5) Plus, Calcium carbonate and fillers. The first effort to improve on fertilizer production in Nigeria, was in 1973, when the first fertilizer manufacturing company was established; Federal Superphosphate fertilizer Company (FSFC) at Kaduna, which became operational in 1976. And in 1981, the National Fertilizer Company (NAFCON) was established, for the manufacture of nitrogenous compound for both domestic use and exports (Bello, n.d) Actual production started in 1987 at Onne, near Port Harcourt, in River State. Subsequently, about eleven (11) local blending plants were established across the country starting with Kaduna, Minna and Kano (Ewepu, 2017). Later, both FSFC and NAFCON were privatized and Notore Chemical Industries PLC, the new owner of the NAFCON started production in January 2010, with a capacity of 300,000 Metric Tons (MT) per annum ammonia and 500,000 MT per annum granular urea (Odum, 2015).

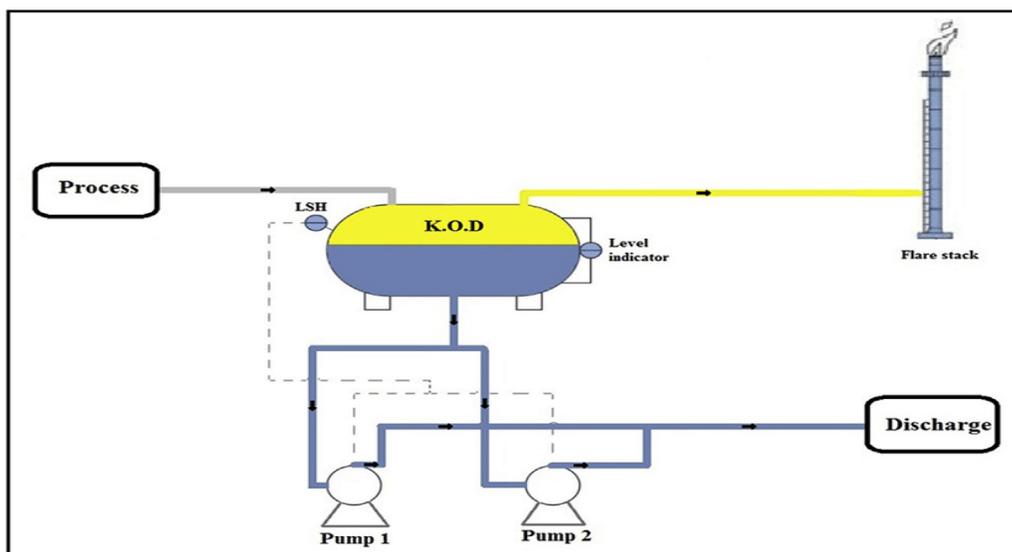
Fertilizer producers and suppliers association of Nigeria FEPSAN, the national trade association of fertilizer manufacturers, importers, blending plants and major distributors and dealers is currently responsible for all matters in the nations fertilizer business (Nigeria Exchange, n.d) FEPSAN, through the assistance of the Federal Government, in an effort to alleviate the perennial unavailability and un-affordability of fertilizer in the country, initiated the importation of phosphate and potash, the major components for the fertilizer blending companies (plants), from Morocco (Ewepu, 2017).

It is expected to yield one million metric tons of NPK (Nitrogen, phosphorous, and potassium) fertilizers, equivalent of 20 million 50kg bags of fertilizer for 2017 wet season farming and 500,000 metric tons for 2017 dry season farming, from the eleven (11) fertilizer blending plants in the country. A bag of NPK fertilizer is currently being sold between N7,500 and N9,000 in the open market, while FEPSAN is distributing at N5,500. In another development, the pan-African conglomerate Dangot is investing on a fertilizer plant with capacity of 2,200 tons per day of ammonia in each of two trains and 3,850 tons per day of granulated urea in each of another two trains (Stephan, 2013).

1.3. Objectives of the Research

This investigation will focus on the real-time evaluation of the probable quantity of ammonia/urea hence synthetic nitrogen fertilizer that can be produced from any identified associated natural gas flare stream (line) in Nigeria (figure 1).

Figure 1: Natural Gas Flare from a Separator



Source: Adapted from the images of the complete flare line from the wellhead to the flare stack.

2. Materials and Methods

Table 1 shows the typical representative composition of the flared associated stranded natural gas stream in Nigeria, obtained from statistical analysis of 36 flare streams, selected from 150 flare line data samples. And Table 2 contains the average operational parameters of the Nigeria flare gas stream.

TABLE 1: A Typical Representative Composition of Flare Associated Stranded Natural Gas in Nigeria

Component	Mole %
Methane	78.5375
Ethane	78.5375
Propane	5.9625
i-butane	1.4842
n-butane	1.8882
i-pentane	0.6964
n-pentane	0.4982
Hexane plus	0.7550
Nitrogen	0.1729
Carbon dioxide	2.0105
Other undesirables	0.2066
	100.0000

Source: Adapted From Ekejiuba, 2017

TABLE 2: Flare Conditions of the Associated Stranded Natural Gas in Nigeria (Source: Adapted From Ekejiuba, 2017)

Parameter	Range	Value for the Study
Gas Gravity (air)	0.607 to 0.996	0.755
Flow rate MMscfd	5 to 63	20
Pressure Psig	7 to 75	10
Pressure	21.7 to 89.7	25
Temperature °F	60 to 115	80
Base Temperature During Analysis	-	60°F
Base Pressure During Analysis	-	14.7psia

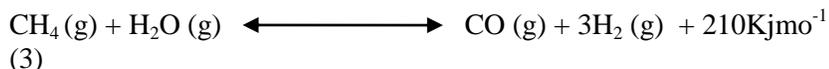
Production of ammonia before World War 1 (28 July 1914- 11 Nov. 1918) was by dry distillation of nitrogenous vegetable and animal products; the reduction of nitrous acid and nitrites with hydrogen; and the decomposition of ammonium salt (s) by alkaline hydroxides or by quick lime e.g. ammonium chloride. Also known as salammoniac (creative commons attribution, 2017; ammonia production wikipedia, n.d). The manufacture of ammonia commercially by Haber-Bosch process (1910), hence synthetic nitrogen fertilizer, at the early stage, depended solely on Nitrogen derived from the air and a hydrocarbon, coal (coke) reaction with steam as the raw materials for its supply of hydrogen (Engineers guide, 2007).



Subsequently, the hydrogen for ammonia producing (processing) plants was reformed from other hydrocarbon sources, such as natural gas “methane” (Capplestone and Kirk, n.d.) liquefied petroleum gas (LPG i.e. propane and butane), petroleum naphtha streams; partial oxidation of high-molecular weight refinery residual materials (residua, asphalt), and from hydrocarbon- rich off-gases (Czuppon and Lee, 1987), such as methanol purge gas, ethylene plant H₂ gas, CO plant H₂ gas, caustic soda plant H₂, Coke- oven gas, cyclar and BTX plants H₂. The production of ammonia via hydrogen rich off gasses e.g. exhaust gas which contains mostly CO with variable concentration of sulfides SO₂ and H₂S, involves separating CO from the mix, converting it in a water-gas shift reaction to carbon dioxide and hydrogen molecule; thus providing suitable feedstock for ammonia and urea productions.

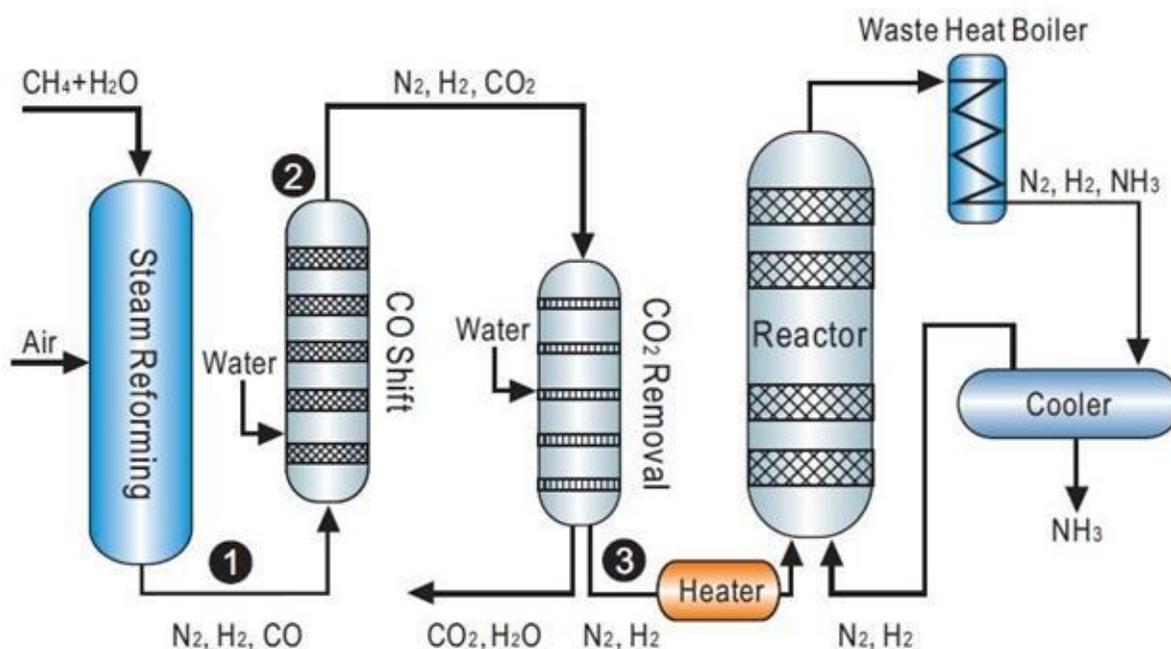
Water-Gas Shift

A more recent patent (Alkusayer, 2016) is another method for synthesizing agricultural fertilizers (ammonia), employs water (H₂O) as the source of hydrogen. Currently, the bulk hydrogen (about 95%) for ammonia production is generated from catalytic steam reforming of natural gas (methane), otherwise known as steam methane reforming (SMR).



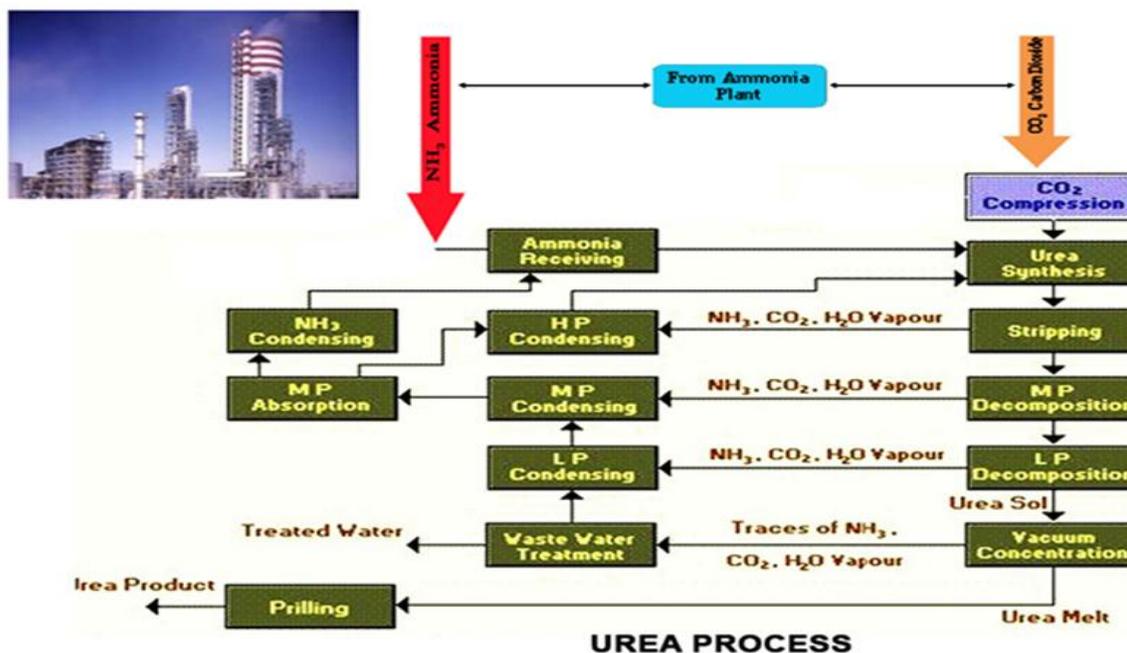
The conventional Haber- Bosch process for industrial ammonia production since 1910 have undergone countless modifications, but the general reaction stoichiometric remain largely consistent, that is one mole of nitrogen with three moles of hydrogen produces two moles of ammonia in an exothermic process (Sherman and Sherman, 1999). Six basic steps are involved in plants that use catalytic steam reforming for synthetic ammonia production: Figure 2, natural gas desulfurization, catalytic steam methane reforming, carbon monoxide (water-gas) shift, carbon dioxide removal (capture from SMR), methanation and ammonia/urea synthesis (figure 3). Thus, most plants now are designed to incorporate water –gas shift reaction such that, while the produced hydrogen is used for ammonia synthesis, the carbon monoxide by-product is used for carbon dioxide production. And most often, both products ammonia and carbon dioxide are synthesized to urea. There by preventing carbon monoxide, potential green house gas from entering the atmosphere. Approximately, 80% of ammonia synthesized today worldwide is eventually converted into urea fertilizer. The synthesis of ammonia from elemental nitrogen and elemental hydrogen is a reversible process (reaction proceeds in both directions) resulting to homogeneous equilibrium.

Figure 2: Ammonia production from Natural Gas (methane).



Source: Adapted from images of ammonia process units.

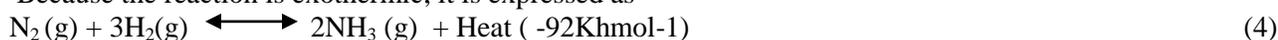
Figure 3: Urea Production from the synthesis of Ammonia and Carbon Dioxide



Source: Adapted from images of ammonia process units.

Ammonia Synthesis

Because the reaction is exothermic, it is expressed as



Water -Shift:

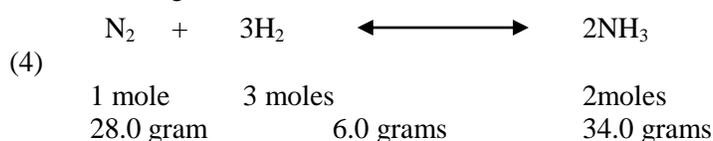


Urea Synthesis:



3. Theoretical Model

Stoichiometry is defined as the calculation of the quantities of substances involved in chemical reactions (Sherman and Sherman, 1999). A balanced equation shows how many moles of the various substances, that are involved in the reactions as well as the ratio of the molecules or atoms involved. With the number of moles of each substance in a reaction, we can find out how many grams (or kilograms or pounds) of each substance using their respective atomic masses. In the Haber-Bosch process balanced equation, 1 mole of nitrogen and 3 moles of hydrogen react to produce 2 moles of ammonia (ratio: 1 N₂ :3H₂: 2NH₃). The atomic mass of nitrogen is 14.0, while the atomic mass of hydrogen is 1.0. Thus, 1 mole of nitrogen has a mass of 28.0 grams; 1 mole of hydrogen a mass of 2.0 grams, and 1 mole of ammonia a mass of 17.0 grams.

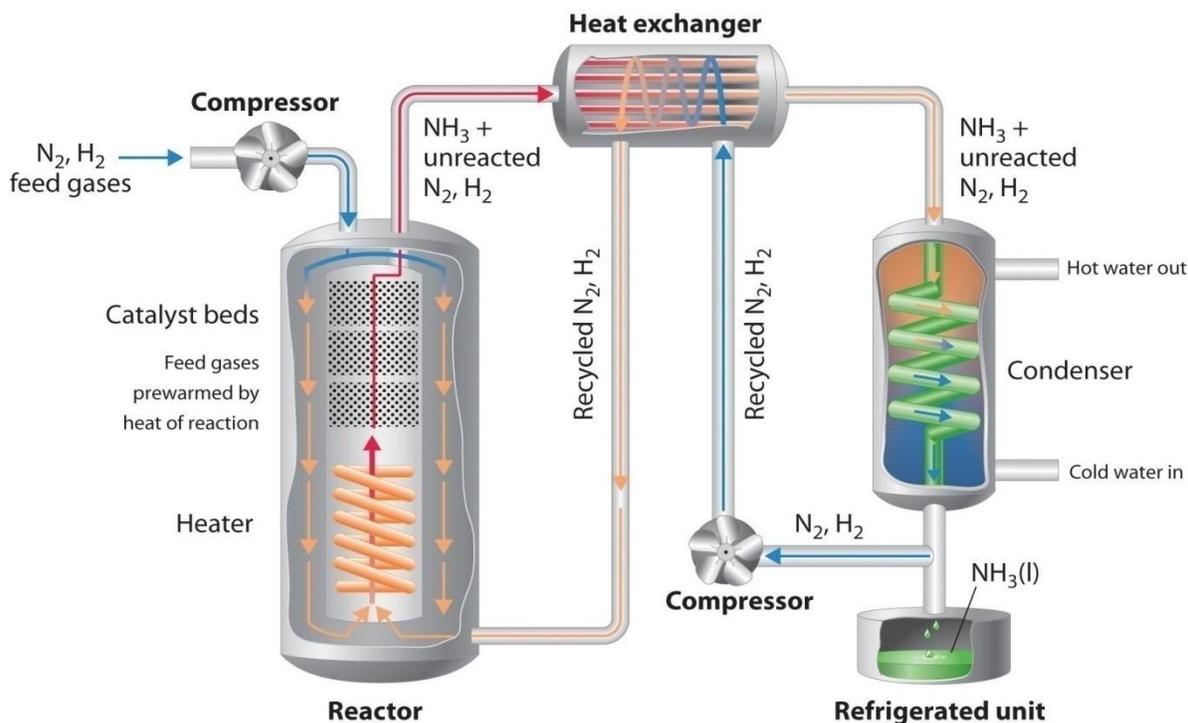


Notably, the above balanced equation satisfied the law of conservation of mass, (or indestructibility of matter), which states that in any chemical reaction, the total mass of the primary substances is equal to the total mass of the products of the reaction (Heys, 1980), hence the mass of the product (ammonia 34.0 grams) is equal to the sum of the masses of the reactants (28.0 grams + 6.0 grams). In terms of the reaction rates, the length of time required for the completion of a reaction depends on at least the following four factors (Ebbing et al., 1995) viz:

- i. The identity of the reactants.
- ii. The concentration of the reactants.
- iii. The temperature of the reaction mixture.
- iv. The presence of a catalyst.

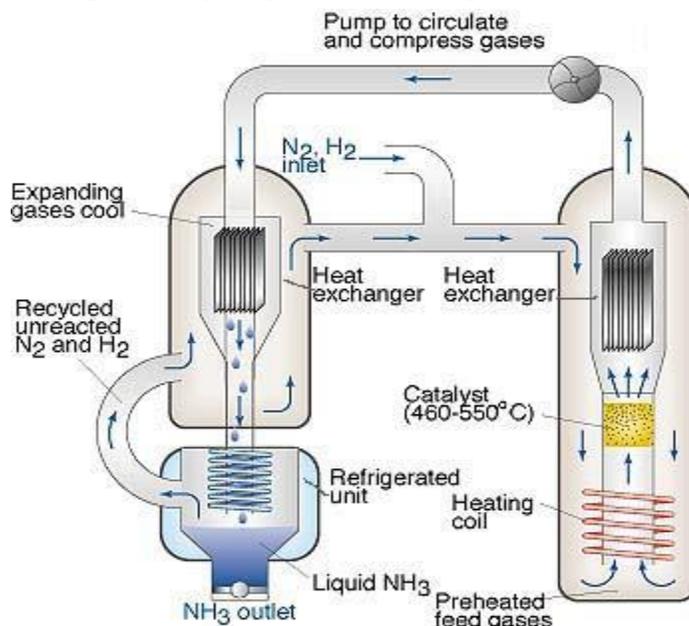
The above factors are accounted for by the ‘Collision Theory’. The Le Chatelier’s principle is used to improve the yield of ammonia by decreasing the temperature (removing heat) i.e. keeping the reaction mixture at a temperature that is as low as practical. Using a cyclic process, the gases are forced to leave the reaction vessel and cooled. Ammonia liquefies because its boiling point is much higher than the boiling points of hydrogen and nitrogen. Liquid ammonia is removed from the reaction mixture before the hydrogen and nitrogen are recycled to the reaction vessel, where they can begin to react once again (figures 4, 5 and 6) showing different configurations.

Figure 4: Cyclic production of liquid Ammonia



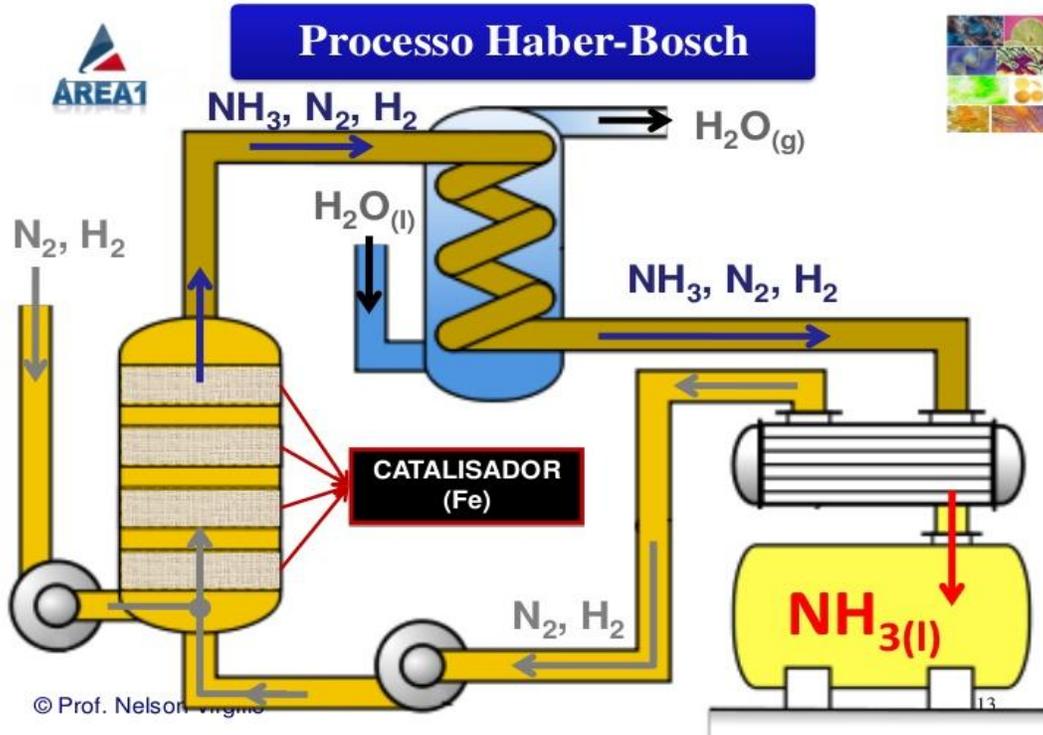
Source: Adapted from images of ammonia process units.

Figure 5: Cyclic production of liquid Ammonia



Source: Adapted from images of ammonia process units

Figure 6: Cyclic production of liquid Ammonia



Source: Adapted from images of ammonia process units

4 Model Applications

Conventionally, processing the flared associated stranded natural gas to remove undesirable components such as, carbon dioxide, hydrogen sulfide and other sulfur components, and nitrogen is termed sweetening (Campbell, 1976). Figure 7, is the proposed model block design process layout for the overall sweetening of the associated flared natural gas and the detailed possible Real-Time Production of Synthetic Nitrogen Fertilizer from the Flare Line.

Figure 7: Process Layout for Real-Time Monetization of Flare Stream via Synthetic Nitrogen Fertilizer Production.

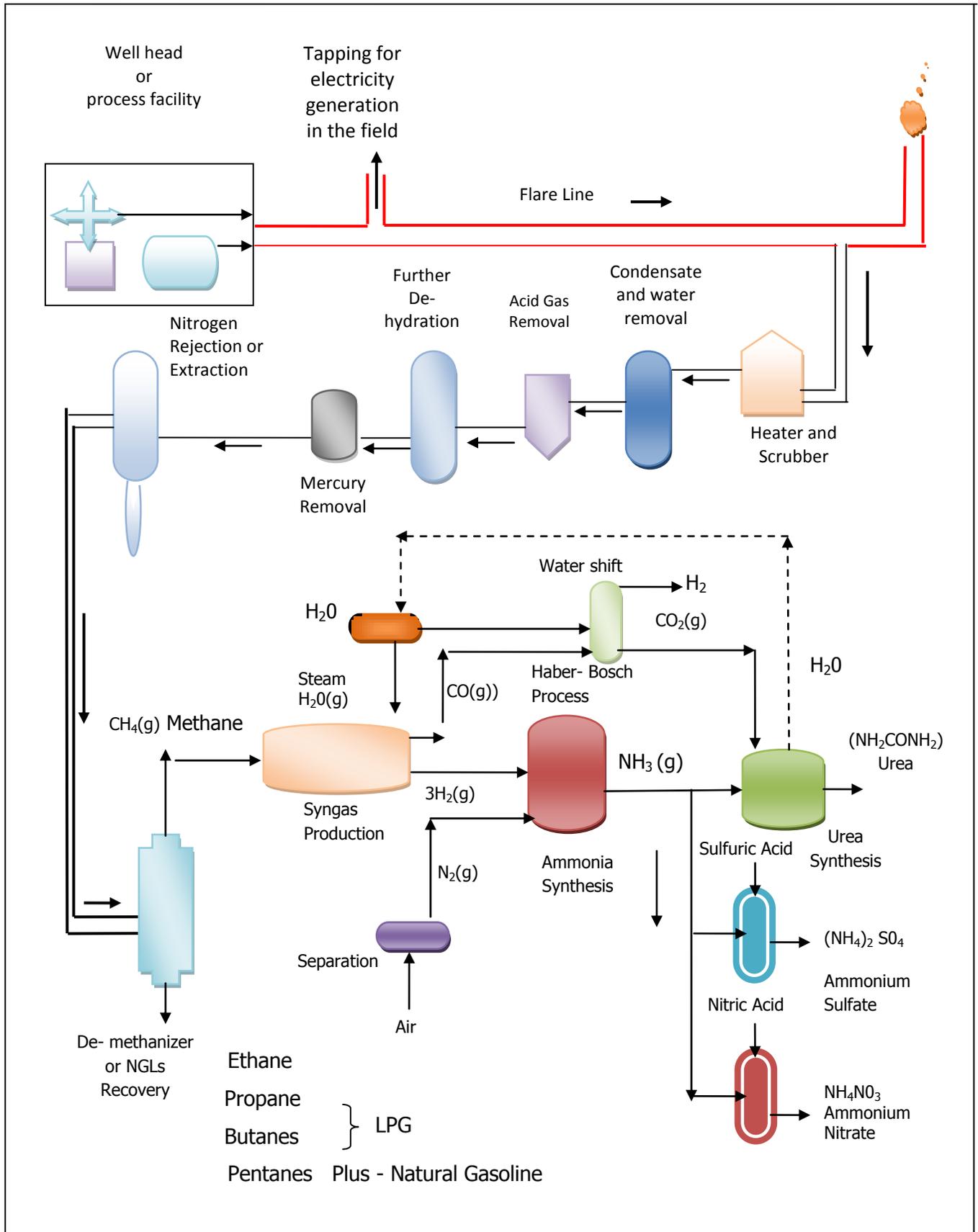
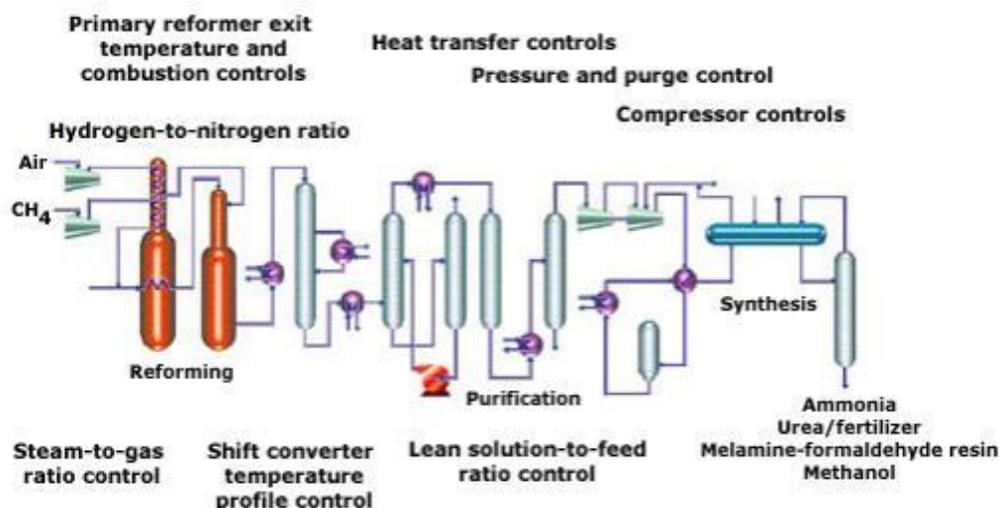


Figure 8, illustrates the various reaction ratio and operational conditions control, from the Air and Methane reforming unit to the Ammonia/Urea end products.

Figure 8: Ammonia/Urea synthesis Controls



Source: Adapted from images of ammonia process units

5. Results and Discussion:

Sweetening the typical representative flared associated stranded natural gas table (1) for Ammonia production entails removing the undesirable components, which in this case, constitutes 2.39% of the flare gas stream. Assuming that each molecular component release exactly, equal amount (moles) of the undesirable in sweetening the stream, that is $(2.39/97.61 = 0.0244)$ per mole. It implies that the sweetened compositional (mole %) for methane becomes $78.5375 + (78.5375 \times 0.0244) = 80.4538$. And the overall compositional (mole %) for the entire flare stream on component by component basis is as shown in table (3), while Table 4 shows the estimated real-time component by component quantities, based on the sweetened typical natural gas composition Table 3 and 20MM scfd flow rate.

Table 3: Sweetened Composition of the Typical Flared Associated Stranded Natural Gas (Source: Adapted From Ekejiuba, 2017)

Component	Mole %
Methane	80.4538
Ethane	7.9780
Propane	6.1079
i-butane	1.5204
n-butane	1.9343
i-pentane	0.7134
n-pentane	0.5104
Permissible undesirable	0.7734
	0.0084
	100.0000

Table 7: Water-Gas Shift {CO (g) + H₂O (g) \longleftrightarrow CO₂(g) + H₂(g)}

Molecular formula	Number of moles	Atomic mass per mole (grams)	Overall mass (grams)
CO {carbon monoxide}	19,276,463.6	28.0	539,740,980.8
H ₂ O {water}	19,276,463.6	18.0	346,976,344.8
CO ₂ {carbon dioxide}	19,276,463.6	44.0	848,164,398.4
H ₂ {hydrogen}	19,276,463.6	2.0	38,552,927.2

Table 8: Urea Synthesis {2 NH₃ (g) + CO₂(g) \longleftrightarrow (NH₂)₂CO (s) + H₂O(l)}

Molecular formula	Number of moles	Atomic mass per mole (grams)	Overall mass (grams)
NH ₃ {ammonia}	2(19,276,463.6)	17.0	655,399,762.4
CO ₂ {carbon dioxide}	19,276,463.6	44.0	848,164,398.4
(NH ₂) ₂ CO {Urea}	19,276,463.6	60.0	1,156,587,816
H ₂ O {water}	19,276,463.6	18.0	346,976,344.8

The expected final end products are:

- Urea (1,156,587,816 grams), from the urea synthesis reaction-table 8.
- Water, H₂O (346,976,344.8 grams), from the urea synthesis reaction-table 8 and
- Hydrogen (38,552,927.2 grams), from the water-gas-shift reaction-table 7.

Both H₂O and H₂ are recycled while urea 1,156,587.816 kg is bagged in 50kg per bag.

This implies, that 1,156,587.816 kg/50kg

= **23, 131.75632 bags**, Thus, approximately 23,132 bags per day (synthetic nitrogen fertilizer), can be obtainable from a flare line with 20 MM scfd flow rate and composition Table 3.

6. Conclusion

The basic nutrients required by plants for growth such as nitrogen phosphorous, potassium etc, can also be added to the soil through various synthetic fertilizers e.g. nitrogen fertilizer (ammonia), phosphate fertilizers, potassium fertilizers and compound fertilizers. Nitrogen fertilizer is the most important because it is a component of proteins and deoxyribonucleic acid DNA. Commercial production of synthetic nitrogen fertilizer (ammonia) started in 1910 with the Haber-Bosch process, which presently have undergone countless modifications. The largest sector of the Nigerian economy is agriculture with 70% of the population, 190.3 million (about 133.21 million people) engaged in small, medium or large scale farming or other agro related business. Although the raw material for fertilizer production are abundant in various states of the country, imported fertilizer accounts for over 80% consumed by the farmers. The first fertilizer production company in Nigeria, the Federal Superphosphate Fertilizer Company (FSFC) started operation in 1976 at Kaduna while the second, the National Fertilizer Company (NAFCON) at One in Rivers State (now own by Notore Chemical Industries Plc) started 1987 for the manufacture of nitrogenous fertilizer.

And since then about 11(eleven) Local blending plants have been established across the country. For this 2017 wet and dry season farming, the fertilizer producers and suppliers association of Nigeria (FEPSAN) through the assistance of the Federal Government imported phosphate and potash from Morocco, expected to yield one million metric tones of NPK (nitrogen, phosphorous, and potassium) fertilizers, equivalent of 20 million 50kg bags of fertilizer after blending at the eleven (11) fertilizer blending plants. Initially the Haber-Bosch process depended on hydrogen from coal (coke), but currently the bulk of its hydrogen supply is from various hydrocarbons sources such as methane and most plants include water-gas - shift, for the conversion of produced carbon monoxide to carbon dioxide which combines with ammonia to produce urea. For a flare stream with the sweetened composition table 3 and 20 MMscfd flow rate, the daily quantity of methane yield is 16.090 MMscfd. In the Haber-Bosch process balanced equation, 1 mole (28.0 grams) of nitrogen and 3 moles (6.0 grams) of hydrogen reacts to produce 2 moles (34.0grams) of ammonia. Usually, 1 mole (16,0 grams) of methane reacts with steam to produce exactly the required 3 moles of hydrogen in the process. This implies that 16.090 MMscfd of methane which is equivalent to 19,276,463.6 moles (308, 423,427.6 grams) of methane on conversion will yield 3(19, 276,463) moles, that is 57, 829, 390.8 moles (115,658,781.6 grams) of hydrogen.

The reaction of this quantity of hydrogen with nitrogen produced 655, 399,762.4 grams of ammonia which subsequently reacted with carbon dioxide to produce 1,156,587.826 kg of urea, equivalent of about 23, and 132 bags of 50kg per day.

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