MINIMIZING CARBON DIOXIDE EMISSION BY ROUTING TO BE FERTILIZER

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Abstract

The acceleration in carbon dioxide emissions since 2000 is more than a 3% increase per year (more than 2 ppm per year) from 1.1% per year during the 1990s. Carbon dioxide is one of greenhouse gas which contribute 9–26% to global warming\(^1\).

Every ammonia plant with hydrocarbon (fossil fuel) as feedstock must produce carbon dioxide as by-product. The minimum quantity of Carbon dioxide produced is equal to ammonia production if the raw material used is light natural gas, and that will increase when it use heavier natural gas, liquid fuel oil or coal.

PT Petrokimia Gresik as one of ammonia producer also produces carbon dioxide as by-product. And to reduce emission to the environment, the carbon dioxide from ammonia process is routed to be two kinds of fertilizers. About 60% of carbon dioxide is converted to be urea fertilizer, 22% to be ammonium sulfate, and 7% is liquefied and some of that is pressed to be dry ice. Only a few of carbon dioxide is vented to atmospheric environment as purge gas to control the operating pressure.

In urea production route, carbon dioxide is directly reacted with ammonia to produce urea. Whereas routing to ammonium sulfate production consist of two main reaction steps: firstly carbon dioxide is reacted with ammonia to be ammonium carbonate and then ammonium carbonate is reacted with gypsum to produce ammonium sulfate. With this route, we can minimize carbon dioxide emission become only less than 10% of carbon dioxide produced, and maximize the fertilizer production.

\(^1\) Wikipedia encyclopedia.

1. Introduction

PT Petrokimia Gresik is a state owned company, and the most complete fertilizer producer in Indonesia which produces various kinds of fertilizers, such as: Urea, ZA, SP-36, NPK Phonska, DAP, NPK Kebomas, ZK and organic fertilizer namely Petroganik. PT Petrokimia Gresik has also been producing chemicals and non fertilizer products, such as: Sulphuric Acid, Phosphoric Acid, Ammonia, Liquid CO2, Dry Ice, Aluminum Fluoride, Cement Retarder, etc. The plant in PT Petrokimia Gresik which produces carbon dioxide is Ammonia Plant.

For producing ammonia synthesis gas, there are three principal process routes i.e:
- Steam reforming of natural gas (or other light hydrocarbon)
- Partial oxidation of heavy hydrocarbon.
- Partial oxidation (or other gasification process) of coal.

All three process routes release carbon dioxide as by-product.

The basic reactions involved in the steam reforming of methane, which is the main constituent of the natural gas, are represented by equation:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + 3 \text{H}_2 \quad \text{………………… (1)} \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \text{………………… (2)} \\
\text{CH}_4 + 2 \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + 4 \text{H}_2 \quad \text{……………… (3)}
\end{align*}
\]
The required stoichiometric 3:1 hydrogen/nitrogen ratio is attained by introducing air into the process. It is done by splitting reforming into two (or three) sections. In the first (primary) reformer reaction takes place in the furnace tubes packed with nickel catalyst. The intense heat needed for the endothermic reaction is supplied by natural gas burners in the furnace radiant box. The reaction is controlled to achieve only a partial conversion about 65-70% (methane slip about 12% dry basis) at the temperatures around 800°C. The gas then introduce to secondary reformer, where it is mixed with a controlled amount of air introduced through a burner. It introduces the right amount of Nitrogen to give the correct stoichiometric H2:N2 ratio for the eventually ammonia synthesis. The gas usually leaves the secondary reformer at 950° – 1000°C, with methane content of 0.25 to 0.3% dry basis.

The carbon monoxide is then reduced by the shift reaction of equation (2) using an iron – chromium catalyst to about 3%. After further cooling, it is subjected to a second stage of shift conversion at 200C on cupper catalyst, which cuts down the carbon monoxide content to 0.15 – 0.3%.

The carbon dioxide is next removed by scrubbing with highly efficient solvents, which is regenerated and reused. From this section, carbon dioxide is released from Ammonia Plant.

The quantity of CO2 gas is about 120% - 130% of ammonia production. In the case of Petrokimia Gresik ammonia plant, CO2 produced is between 67 to 72 ton/hour for ammonia production about 56 ton/hour.

Steam reforming of LPG or naphta which is heavier hydrocarbon than natural gas will produce higher amount of carbon dioxide gas, with the simplified equation :

\[
C_nH_m + (4n-m)/4 \text{H}_2\text{O} \rightarrow (4n+m)/8 \text{CH}_4 + (4n-m)/8 \text{CO}_2 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4)
\]

By comparing with steam reforming of natural gas (CH4), there is additional quantity of CO2 proportional to the length of carbon chain. It means the quantity of CO2 produced will increase when it use heavier natural gas, liquid fuel oil or coal.

This paper will present how PT Petrokimia Gresik minimize carbon dioxide emission in selecting raw material as feedstock to get lower quantity of CO2 product, and utilize CO2 by routing to be fertilizer and Liquified CO2.

2. Theory

First theory : In Ammonia production, for the same production rate, the lighter Hydrocarbon as feedstock, the lesser the quantity of CO2 produced and the lower energy for steam reforming.

Second theory : Carbon dioxide can be converted to be Fertilizer, Urea.

Third theory : Carbon dioxide can be used as intermediate reactant to convert gypsum CaSO4 become Ammonium sulfate in two step reaction. First reaction is between CO2 and Ammonia to form Ammonium carbonate, and second reaction : reacting ammonium carbonate with gypsum to yield ammonium sulfate.

3. Splitting different gas to get lesser quantity of CO2 Product.

Gas to PT Petrokimia is supplied from three sources : Pertagas (mix gas from Kangean and from Santos), Kodeco, and from Petrochina. Gas from Pertagas is the lightest gas with CH4 content = 97 – 98%, then from Petrochina with CH4 is about 91%, and gas from Kodeco is the heaviest gas with CH4 content = 85%.

Originally, gas from all sources are mixed at Metering station and then distributed for feedstock (process gas) and for fuel in Radiant section to supply heat for steam reforming reaction. With this scheme, energy consumption was 32.04 MMBtu/ton ammonia product.

Considering the first theory, we did evaluation to split different gas to different purpose. The lighter gas i.e gas from Pertagas and Petrochina are mixed and is used as feedstock to produce ammonia, and the heavier gas from Kodeco is used as fuel. With this scheme, energy consumption is 30.575 MMBtu/ton Ammonia. The schematic can be seen in fig.1.
By this modification we get benefit = \((32.04 - 30.575)\ MMBtu/ton \times 445,000\ ton/year = 651,925\ MMBtu/year\). With gas price = 4 USD/MMBtu = 36,800 Rp/MMBtu, the benefit is about 24 billion rupiah / year.

Fig 1: Splitting the different gas

Beside the lower energy consumption, the quantity of CO2 product decrease from 72 ton/hr become 67 ton/hr.

Carbon dioxide product from ammonia plant is distributed to three consumer, i.e Urea Plant, Ammonium sulfate Plant, and Liquified Carbon Dioxide Plant. The route can be seen schematically in fig.2 as follows:

Fig 2: Routing Carbon dioxide product in PT Petrokimia Gresik.
5. Converting CO2 to Urea

Together with Ammonia, carbon dioxide that is obtained from ammonia production, is reacted in a high pressure reactor. The reaction proceeds in two steps: (1) formation of ammonium carbamate, (2) dehydration of ammonium carbamate.

\[
2 \text{NH}_3 + \text{CO}_2 \rightleftharpoons \text{NH}_2\text{COONH}_4 + 38.000 \text{ Kcal} \quad \ldots \ldots \ldots \ldots (5)
\]

\[
\text{NH}_2\text{COONH}_4 \rightleftharpoons \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} - 5.000 \text{ Kcal} \quad \ldots \ldots \ldots \ldots (6)
\]

The first reaction is highly exothermic, while the second reaction is moderately endothermic. The first reaction is slow at atmospheric pressure, but at the elevated pressures used in practically instantaneous. The second reaction does not go to completion. It approaches equilibrium at a rate which depends on temperature and pressure. The schematic process is as follows:

6. Carbon dioxide to produce Ammonium sulfate

There are several production methods used for ammonium sulfate manufacture, in accordance with available raw materials. One of them is reacting ammonium carbonate with gypsum. It is based on combining carbon dioxide and ammonia to produce ammonium carbonate, which is then reacted with gypsum to yield ammonium sulfate and calcium carbonate with reaction as follows:

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} - 8,320 \text{ cal/mol}
\]

\[
2 \text{NH}_4\text{OH} + \text{CO}_2 \rightarrow (\text{NH}_4)_2 \text{CO}_3 + \text{H}_2\text{O} - 22080 \text{ cal/mol}
\]

\[
(\text{NH}_4)_2 \text{CO}_3 + \text{CaSO}_4 2 \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{CaCO}_3 + 2\text{H}_2\text{O} - 3,900 \text{ cal/mol}
\]

Consumption rate of CO2 to ammonium sulfate is about 0.36 ton CO2/ton ammonium sulfate (stoichiometric = 0.33 ton/ton). For ammonium sulfate plant with capacity 960 ton/day needs 345
ton/day (14.5 ton/hour). CO2 released to atmosphere together with preservation air is about 29 ton/day (1.2 ton/hour).

7. CO2 gas to Liquid CO2 and Dry Ice

By utilizing CO2 gas about 55 tons/hour as raw material to produce urea and ammonium sulfate, the remaining quantity of CO2 is 12 tons/hour. It is processed in three steps: purifying, compressing, and liquifying. Purifying step is by passing through activated carbon to remove odour and H2S and passing through dehydrator (molecular sieve dryer) to remove water content. Pure CO2 gas then compressed to about 18-19 kg/cm2g, and liquified in a column provided with refrigeration system to change the high purity carbon dioxide into its liquid form. Liquid CO2 as final product is at pressure 17 kg/cm2g, temperature -30°C.

To convert liquid CO2 to be dry ice needs two steps. First: the pressure is reduced. When this occurs some liquid carbon dioxide vaporizes, and this causes a rapid lowering of temperature of the remaining liquid carbon dioxide. As a result, the extreme cold causes the liquid to solidify into a snow-like consistency. Second: the snow-like solid carbon dioxide is compressed into larger blocks of dry ice.

8. Results and Discussion

In producing ammonia, PT Petrokimia Gresik choose to use lighter gas as feedstock, so Carbondioxide produced is less. This is done by splitting different gas quality from different sources, and use the light gas as feedstock, while the heavier gas is used as fuel. This step can reduce CO2 product about 7%. For 1350 ton/day ammonia production rate, CO2 product decrease from 72 ton/hour become 67 ton/hour.

To minimize CO2 release to atmosphere, 60% of CO2 is converted to urea fertilizer, 20% is used for producing ammonium sulfate by gypsum process, 7% is liquified and pressed to be dry ice, and some of them is vented in CO2 stripper as pressure control. By this route, CO2 vented to atmosphere is about 11% of total CO2 product.

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