Life Cycle Analysis for The Production of Urea Through Syngas

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Abstract. For optimum growth of the agriculture industry certain urea-based fertilizers are used to provide better Nitrogen content to the soil, but this growth comes with a cost in terms of carbon footprint. In this paper, life cycle assessment (LCA) is conducted for urea production having a minimum of 46% nitrogen content. For LCA, a fertilizer industry with 3850 MTPD urea production capacity is considered with an annual target of 1.27 MMTPA, while the functional unit is taken as 1MT of urea production. This paper is concerned about finding the MT equivalent CO₂ required per MT urea production. The coal used for syngas preparation is from G9 to G14 meaning the gross calorific value (GCV) ranges from 4601 to 3400 GCV per kilocalories. The carbon footprint of catalyst is considered and showed its importance when it comes to larger production size. In this analysis, MT CO₂ equivalent per MT urea is 0.714 and this result is also compared with the data of the developing countries.

Keywords. Life cycle assessment, Life cycle impact assessment, Carbon footprint, Global warming potential, Urea, Syngas.

Abbreviations. BFW : Boiler feed water, CH₄ : Methane, CO₂ : Carbon-di-oxide, CPP : Captive Power Plan, CT: Cooling tower, EIL: Engineers India Limited Eq: Equivalent, FCIL: Fertilizer Corporation of India Limited, GCV: Gross calorific value, GJ: Giga Joule, GWP: Global warming potential, kg: kilogram, kL: kiloliters, kWh: kilo Watt hour, LCA: Life cycle analysis, LC1: Life cycle Inventory, LCIA: Life cycle Impact assessment, MMTPA: Million metric tonne per annum, MT: Metric tonne, NFL: National Fertilizers Limited, NO₂: Nitrogen-di-oxide, PSA: Pressure swing adsorption, Ppmw: Parts per million weight, RFCL: Ramagundam Fertilizers and Chemicals Ltd., SEC: Specific energy consumption, SWC: Specific water consumption, SWC: Specific water consumption, TPD: Tonne per day

1. Introduction
India is an agriculture dominant country, where nearly 600 million peoples are dependent on agriculture for their livelihood. Nearly 96 million hectares of land is irrigated, which is largest in the world [1]. Urea has the highest nitrogen content among all solid nitrogenous fertilizers which are commonly used in the agriculture sector. Urea studied in this paper would have nitrogen content greater than 46.3% by weight which is very economical from the point of view of fertilizer
transportation per unit Nitrogen content. Since 2004 there is production gap in Indian urea production, due to lack of cutting-edge technology by which carbon emission can be reduced and optimum use of coal but after coal gasification is carbon footprint for urea production comparatively lesser as compared to other processes. Ramagundam Fertilizers and Chemicals Limited (RFCL) in Andhra Pradesh, India uses coal gasification-based fertilizer production.

1.1 Production of Urea through coal Gasification
In process of Coal gasification carbon (coal), oxygen, steam and carbon-di-oxide is reacted to form Hydrogen molecule and carbon-monoxide as product [2]. A water gas shift reaction is conducted to obtain purest form of hydrogen, and CO₂ which are used in production of Urea.

\[ 3C + O_2 + H_2O \rightarrow H_2 + 3CO \]
\[ CO + H_2O \rightarrow CO_2 + H_2 \] (WGS)

For syngas production coal grade used in this paper is G9 to G14 [3] and gross calorific value per kilo calories for different grades is shown in table 1.

| Gross calorific value based coal grades | GCV/kcal     |
|----------------------------------------|-------------|
| G9                                    | 4601 to 4900|
| G10                                   | 4301 to 4600|
| G11                                   | 4001 to 4300|
| G12                                   | 3701 to 4000|
| G13                                   | 3401 to 3700|
| G14                                   | 3101 to 3400|

In the process of gasification, the sulphur of coal is released as hydrogen sulphide rather than sulphur-di-oxide, hydrogen sulphide is itself poisonous, corrosive and flammable gas which could be toxic, although it has a very pungent rotten egg-like smell it quickly deadens the sense of smell so the victim may be unaware of its presence. So chemical treatment of H₂S is required for the safety of the environment and workers working in Industrial plant. It can remove by Amide gas treating technologies. The hydrogen sulphide is first converted to an ammonium salt, whereas the natural gas is unaffected [4].

\[ RNH_2 + H_2S \rightleftharpoons RNH_3^+ + SH^- \] (where 'R' is an alkali group compound)

1.2 Gas clean-up (CO₂ and H₂S Removal)
For removal of H₂S and other dust particles a three-stage gas treatment process is deployed, which consist of gas inlet filter, self-cleaning candle filter and polishing filter. In gas inlet filter majority of solid and hydrocarbon are removed, self-cleaning candle filter consists of strainers up to 30 microns, particle filter and activated carbon filter and last polishing filter have two stages where the first stage having concentrated suspension with activated carbon and in the second stage a slurry is formed for further removal[5].

1.3 Air separation (Nitrogen extraction)
PSA technique used to separate a particular gas from a mixture of gases, it works the principle of difference in pressure on applied gas i.e., higher the pressure more the gas is attracted to a solid surface or adsorbed and the absorbent material (activated carbon, zeolite etc) attracts nitrogen more strongly,
thus adsorbed nitrogen can be released by a reduction in pressure [6]. This extracted nitrogen is further reacted with hydrogen molecule form syngas to form Ammonia as a product [7].

In urea production first Ammonia is produced through syngas and then Ammonia is reacted with CO$_2$. In the process of ammonia production using Syngas as a feed following steps are followed [8].

i) Feed Gas Desulfurization
ii) Primary Reforming
iii) Process air Compression
iv) Secondary Reforming
vi) Carbon Monoxide Shift Conversion
vii) Carbon Dioxide Removal
viii) Methanation
ix) Drying
x) Cryogenic Purification
xi) Compression
xii) Ammonia Synthesis
xiii) Loop Purge Ammonia Recovery
xiv) Ammonia Refrigeration
xv) Process Condensate Stripper
xvi) Steam System

In the process of urea production using NH$_3$ and CO$_2$ as feed following steps are followed [8]

\[
2\text{NH}_3 + \text{CO}_2 \rightarrow \text{NH}_2\text{COONH}_4 \\
\text{NH}_2\text{COONH}_4 \leftrightarrow \text{NH}_2\text{CONH}_2 + \text{H}_2
\]

xvii) Urea synthesis and NH$_3$, CO$_2$ recovery at high pressure
xviii) Urea purification and NH$_3$, CO$_2$ recovery at medium and low pressures
xix) Urea Concentration Section
xx) Urea Prilling Section.

• Ammonia produced by the above process includes ammonia content 99.9 min by weight%, water 0.1 max by wt%, oil 0.3 ppmw.
• Removed CO$_2$ contain 99.3% dry volume and water vapour.
• Urea constituent’s total nitrogen 46.3% min, biuret 1 % max, moisture 0.3 % max by weight % of urea and free ammonia 100 max ppm.

2. Life Cycle Assessment (LCA)

LCA evaluates environmental impacts of products throughout cradle to grave i.e., from extracting raw material, material processing, manufacturing, distribution, actual use, repair, maintenance and disposal or recycling. LCA helps us understand both the positive and negative impact of any product. International Standards Organisation (ISO) standardise LCA in ISO 14040 series. System boundaries for conducting an LCA is characterised mainly in three categories:

i) Cradle-to-gate: system boundary includes raw material extraction to production phase in an industry.
ii) Cradle-to-grave: system boundary includes from raw material extraction to its usefully life and disposal.
iii) Gate-to-gate: system boundary only includes selected production process; it can be linked together to form Cradle to gates analysis.

LCA is performed in four basic interdependent stages [9]. The interdependencies of these stages are shown in figure 1.
4. **Interpretation**

- **Goal and Scope**: include specifying reasons for conducting the study, defining the functional unit, setting system boundaries, study limitation, data required for study and target audience.
- **Inventory analysis**: includes collection and validation of Input and output data to quantify material use, energy use, environmental discharges, and waste associated with each life cycle stage.
- **Impact assessment**: includes using Impact categories, category indicators, characterisation model, equivalency factors, and weighing values to convert raw data into the potential impact on human health and environment.
- **Interpretation**: includes an iterative process between the above three stages where methods can be suggested to reduce material and impact on environment and based on that conclusions and verification of result is done.

3. **Determination of Goal and Scope for Urea production**

Goal and Scope are determined in primary stage of LCA because it determines and guide the alternatives can be made within other phase of study, LCA has done in this paper for the Industrial production size of Ammonia 2200 TPD, Urea 3850 TPD and a yearly production of 1.27 MMTPA of Prilled urea. Definition of Functional unit is slightly complicated but it has to be comparative for e.g., production of 1-tonne urea, for this production there can be many possible technologies, total resources used and their potential impacts on the environment are calculated and a comparative study is conducted. Hence function unit for our paper is production of 1 tonne using syngas as a feed [10]. The system boundary for this paper would be Cradle to gates as shown above in figure 2, Cradle may be expressed as initial step such as extraction of syngas from Coal (G9 to G14) as a raw material for production of ammonia, urea to gates i.e., factory gate.

4. **Life cycle Inventory Analysis for Urea Production**

A statistical database is maintained in this stage which includes process/progress of work, source of data and other information including technical process, normalizing factor, weight factor. This data is maintained iteratively between inventory data collection, impact assessment and interpretation, quality of this data is mainly depended on consistent availability of inventory data, the appropriate methodology used in process, correctness of normalising and weight factor [11]. Generally getting an accurate data is not easy due to certain issues such as copyright protection or their trade secrets and sometimes industries feel insecure because if research conducted some unknown values of environmental impacts can be discovered which could be a threat to them. For our analysis resources quantified as electricity, catalyst for various process, water requirement and syngas, these are shown in tables 2-5 respectively.
Figure 2. System boundary for Urea production (cradle to gates)
5. Life cycle Impact assessment (LCIA)

Life cycle impact assessment (LCIA) is the part of the process of an LCA where the database of inventory is translated into impact categories related to resource depletion, human health and natural environment. Steps in LCIA are a selection of impact category, characterization, normalisation and valuation. Life cycle Inventory (LCI) data are multiplied with the respective characterisation factor is to calculate LCIA [11]. The LCIA results for respective impact categories are expressed as kg equivalent of CO$_2$ for global warming potential (GWP).

The energy emission absorbed by 1-tonne gas over a given period of time for example with standard time period of 20 or 100 years is compared with 1 tonne of CO$_2$ energy emissions. Greater the value of GWP, greater gas will increase the environment temperature as compared to CO$_2$ over that time period. An iterative study among previous stages is conducted in LCIA so that net GWP of end product is lesser as possible and policymaker have a better understanding of product emissions.

Reference value of GWP is considered in terms of CO$_2$, because CO$_2$ emissions remain in climate over 1000 years, So GWP of CO$_2$ is 1, where CH$_4$, N$_2$O have GWP of 25 and 298 respectively over a period of 100 years, both of these gases have a shorter life span of few decades [12].

5.1. Electrical power required per tonne urea production

In production phase, electricity is used to convert raw water into steam in boilers and run industrial equipment. Source of electricity for the various purpose (table 2) in production phase is assumed by a thermal power plant which has carbon factor of 0.85 kg eq CO$_2$ per kWh, losses in transmitting power and leakages are neglected. For calculation of power required per tonne Urea production, the total power required for the particular process is divided by total Urea produced per day.

| Systems                        | Power requirement (kWh)/MT urea | Carbon Factor | kg CO$_2$ eq/ MT urea |
|--------------------------------|---------------------------------|---------------|-----------------------|
| Ammonia Unit + Cooling Tower   | 66.68                           | 0.85          | 56.67                 |
| Prilled Urea Unit + Cooling Tower | 65.32                         | 0.85          | 55.52                 |
| Others                         | 47.36                           | 0.85          | 40.26                 |
| Total                          | 179.36                          | 0.85          | 152.45                |

Figure 3. Pollutant emissions for global warming potential [12]

Table 2. Power requirement and eq. carbon-di-oxide emission for 1 tonne urea
5.2. Catalyst required per tonne urea production
The catalyst used in a chemical reaction as to increase or decrease the rate of reaction by not taking part in reaction but this doesn’t mean that catalyst can be used forever, catalyst have their life period in which they perform effectively so An assumption is taken in the calculation of catalyst (table 3) used in particular reaction i.e. if a catalyst has a life of let’s say X years and Y quantity used to produce reactant for the desired lifetime then the catalyst required to produce 1-unit quantity would be Y divided by X. so for our calculation’s catalyst quantity required to produce 1-tonne urea is divided by lifetime in days. Here catalyst has a range of their bulk density and for calculation of their mass required an average bulk density is considered [8].

Table 3. Eq. carbon-di-oxide emission due to catalyst

| Section                          | Catalyst Life (Years) | Bulk Density Kg/m^3 | Per tonne Urea (kg) | Carbon Factor | kg eq CO_2/MT Urea |
|----------------------------------|-----------------------|---------------------|---------------------|---------------|---------------------|
| Hydro- desulphurization (Zinc oxide) | 5                     | 450-650             | 3.6                 | 2.91          | 0.006              |
| De-Sulfurization (MoS_2)         | 1                     | 950-1150            | 12.6                | -             | -                  |
| Primary Reformer ((Ca_2Al_2SiO_7) | 6                     | 700-900             | 8.46                | -             | -                  |
| Secondary Reformer (Ni)          | 7                     | 900-100             | 18.99               | 11.53         | 0.086              |
| HT Shift (CuNi, Fe_2O_3)         | 5                     | 1020-1220           | 27.47               | 1.025         | 0.015              |
| LT Shift (Al_2O_3, TiO_2)        | 4                     | 1040-1240           | 35.09               | 1.23          | 0.03               |
| Methanation (Ni, Rh)             | 8                     | 800-1000            | 6.48                | 11.53         | 0.026              |
| Ammonia Synthesis (ferrite)      | 8                     | 2500-3000           | 189.64              | 1.025         | 0.067              |
| HTER (Ni)                        | 4                     | 900-1000            | 4.99                | 11.53         | 0.039              |
| **TOTAL kg CO_2 eq / t urea**    |                       |                     |                     |               | **0.268**          |

5.3. Water required per tonne urea production
Source of raw water is assumed to be from groundwater (Table 4) which doesn’t require much treatment so the carbon factor per litre is assumed 0.03 kg eq of CO_2. Leakage loss, approximately 80L water is considered as a loss per tonne urea, whereas service water, as well as drinking water consumed by working staff, is also considered. The maximum amount of water is consumed in the ammonia and urea production phase.

Table 4. Water requirement and eq. carbon-di-oxide emission per MT urea

| Purpose                                      | (KL)/ MT urea | Carbon Factor per Litre water | kg CO2 Eq/MT urea |
|----------------------------------------------|---------------|-------------------------------|-------------------|
| Raw water to DM plant                        | 1.17          | 0.03                          | 35.06             |
| Make-up water to Cooling Tower (Ammonia, CPP CT and Urea CT) | 6.11          | 0.03                          | 183.43            |
| Service Water                                | 0.12          | 0.03                          | 3.74              |
| Drinking Water                               | 0.12          | 0.03                          | 3.74              |
| Considering losses in the Raw Water Treatment Plant | 0.08          | 0.03                          | 2.34              |
5.4. Syngas required per tonne Urea production
Syngas gas contains mainly carbon mono-oxide and molecule of Hydrogen, hydrogen is one of the cleanest sources of energy. Syngas is produced through coal gasification and used as feed for ammonia production. For the treatment of carbon mono-oxide, Carbon Monoxide Shift Conversion and Carbon Dioxide Removal process is conducted. An assumption is considered that’s all the removed carbon-di-oxide is reused in production of urea when Ammonia is reacted with carbon-di-oxide in a molar ratio of 2.17(ammonia) to 1(CO₂). In table 5 Syngas flow rate nm³/hr is converted GJ/hr and carbon footprint for this GJ/hr is calculated.

Table 5. Syngas requirement and eq. carbon-di-oxide emission for 1-tonne urea

| Syngas (nm³/hr) required per tonne urea | conversion Nm³/hr to GJ/hr | carbon factor*for GJ/hr | kg CO₂eq per GJ syngas |
|----------------------------------------|---------------------------|------------------------|-----------------------|
| 151.48                                 | 5.94                      | 56.10                  | 333.26                |

(Carbon factor* syngas emission factor 56.1 kg CO₂eq/GJ and 1 GJ =25.5 nm³)

3.5CO₂eq and Global warming potential per tonne urea for all resources required to produce Urea

Table 6. Eq. CO₂ emission in different resources used for 1 tonne urea

| Resources | kg CO₂Eq/ MT Urea | GWP /MT Urea |
|-----------|-------------------|--------------|
| Catalyst  | 0.27              | 2.68×10⁻⁶⁴   |
| Electricity| 152.45         | 0.152        |
| Water     | 228.31           | 0.228        |
| Syngas    | 333.26           | 0.333        |
| Total     | 714.29           | 0.714        |

6. Life cycle interpretation (LCI) of Urea production through syngas
Life cycle Interpretation (LCI) is a technique to estimate outcomes of LCI and LCIA, these outcomes will lead to quantification, comparison and quality check of data. Significant impact factor and impact categories are Interpreted, where a quality check is performed to get consistency, sensitivity and completeness of data and a conclusion could be made with a certain level of confidence [13]. Applications of interpretation are as follows:

- Product research and development and further enhancement.
- Premeditated planning.
- Product management and supervision.
- A product could be made more eco-friendly by reducing the environmental burden.
- Risk analysis
- Pareto-optimisation between development and environment.

6.1 GWP of various resources for per tonne urea production
The specific electricity consumption ranged from 145.9 to 200.3 kWh per MT of prilled urea, with the mean average of 173.7 kWh per MT prilled urea [14] in comparison to this paper result specific energy consumption per MT prilled Urea production is 179.36 Kwh (table 2).
• The average specific water consumption (SWC) is in the range of 4.55 KL/ MT to 12.73 KL/ MT of urea produced. Based on the sector-wise assessment, public sector plants in India have the highest average SWC of 8.13 KL/ MT urea produced. In which plants which are mainly coal-based captive power plants (CPPs) are the most inefficient [15]. In comparison, the SWC for this paper is 7.61 KL/ MT urea production (table 4).
• 151.48 Nm³/hr Syngas per MT urea is required which is equivalent to 5.94 GJ energy.
• Here if we consider the order of magnitude GWP of catalyst can be neglected (Figure 4).

![GWP per tonne urea](image)

**Figure 4. GWP per MT urea**

6.2. Comparison of avg. CO₂ eq per MT Urea production
Carbon footprint is compared among the developing countries which produce Urea by coal gasification by our paper result i.e., “0.7143 MT CO₂/MT urea”[16]. In fig. 5 where it can be seen that urea produced through coal gasification has a lesser carbon footprint as compared to if coal used directly as a fuel for eg. China.

![Avg MT CO₂/ MT urea](image)

**Figure 5. Average MT CO₂/MT urea**
7. Conclusions

- SWC per MT urea production is 7.61 KL which contributes to 228.312 kg eq of CO$_2$ and GWP of 0.23.
- Various Catalyst required per MT urea production contribute 0.268 kg eq of CO$_2$ and GWP of 0.000268
- Although carbon footprint due to catalyst is very less and can be ignored if we see a bigger picture it cannot be ignored if we see a bigger production size. So, a separate data collection of GWP due to the catalyst to be made.
- Electrical energy per MT urea production is 179.36 kWh which contribute 154.454 kg eq of CO$_2$ and GWP of 0.154
- Syngas required per MT urea production is 151.48 Nm$^3$/hr which contribute 333.257 kg eq of CO$_2$ and GWP of 0.333.
- GWP for Urea industrial production in India in using syngas as a feed will be 0.714.

General principles of the life cycle assessment following ISO-14040 are considered in the present study. Comprehensive procedures for each of its phases are still under conversation, and the ambiguity arising from the variability of quantities or a lack of data or model assumptions remains one of the significant problems affecting the decision-making procedure, predominantly concerning the input data.

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