TOYO’s latest innovation in urea synthesis technology and sustainable urea production

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Toyo Engineering Corporation (TOYO), a global leading engineering contractor and urea process licensor, has made continuous efforts to improve its own urea production technologies and has supplied reliable, efficient and economical urea plants since founded in 1961. TOYO’s latest urea process, ACES21® became ready for industrial application in late 1990s and has since been applied worldwide.

TOYO has been working on further improvements and innovations in its proprietary urea processes to realize further energy savings and plant cost reduction maintaining all salient features of current ACES21® by harvesting fruitages cultivated for years from “seeds” technologies. TOYO has developed the next generation ACES21® which achieves lowest urea synthesis pressure among modern urea process.

In addition, TOYO is launching a new concept “g-Urea®”, aiming at carbon neutral urea production utilizing renewable energies and feedstocks. One of promising solution is urea production from “Green Ammonia”. Another can be urea production from ammonia and carbon dioxide derived from biomass and/or waste gasification.

The paper introduces TOYO’s latest innovations in urea synthesis technologies and the sustainable urea production concept g-Urea®.

1. DEVELOPMENT AND SCALE-UP HISTORY OF TOYO UREA PROCESS

TOYO as a urea process licensor has developed TOYO urea processes since the development of partial recycle process in 1950’s. History of process development by TOYO from 1960’s is summarized in in Fig. 1.

TOYO has been concentrating urea process development activities on energy saving, pollution prevention and product quality improvement since 1970’s. As a result of these efforts, the ACES and Spout-Fluid Bed Urea Granulation Process were developed and came into operation in the early 1980’s. In the middle of 1990’s, TOYO commenced R&D work on a new urea process, aiming to reduce plant investment cost and reduce energy consumption further. The resulting new process, ACES21®, became ready for industrial application in late 1990s and has since been applied in 16 plants.

TOYO’s history, as a urea process licensor, over the past decades has also been in successful scale-up of its own urea processes in response to diverse and increasing demands of nitrogen fertilizer.

In June 2016, the world largest single train 4,000 MTPD urea plant (TOYO ACES21® and Spout-Fluid Bed Granulation) with 2,300 MTPD ammonia plant (KBR Purifier™ process) for Indorama Eleme Fertilizer & Chemicals.
Limited (IEFCL) in Nigeria commenced commercial operation. Following the successful operation of the plant, IEFCL awarded a contract to TOYO in 2018 to build No.2 Train with same capacity. The construction and the commissioning activities were successfully completed in 2021. The plant achieved really smooth start up; the urea plant accomplished the stable operation in 17 days from initial natural gas feed-in to the ammonia plant. First granular urea was produced on the same day of the initial feed-in of raw material from the ammonia plant. Subsequently, the provisional acceptance of Train-2 was attained within 2 months since natural gas feed-in and the plant has been operated steadily by the owner in a full load.

TOYO has already verified viability of 6,000 MTPD single train urea plant covering basic design and all EPCC activities, and now the 6,000 MTPD urea plant design is ready for commercial projects.

To contribute to the global sustainable growth, TOYO has been working on further improvements and innovations in its proprietary urea processes. TOYO has developed next generation ACES21®, “ACES21® Low Pressure Process; ACES21-LPTM” to realize further energy savings and plant cost reduction maintaining all salient features of current ACES21® by harvesting fruitages cultivated for years from “seeds” technologies. TOYO also has developed a new concept “g-Urea®”, aiming at carbon neutral urea production utilizing renewable energies and feedstocks.

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TOYO’s latest urea synthesis technology ACES21® is advantageous in low investment cost and low energy consumption for urea production. Using its own expertise, advanced technology and novel thinking, TOYO has established ACES21®, which achieves energy saving and plant cost reduction maintaining high performance and high efficiency of the urea plant. ACES21® has been developed together with P.T. Pupuk Sriwidjaja (PUSRI) of Indonesia as further Cost and Energy Saving version of the ACES (Advanced process for Cost and Energy Saving) Process.

Major features of this technology are given below. ACES21® becomes more advantageous as urea plant capacity increases because fewer and smaller high pressure (HP) equipment are used in ACES21® and laid out at low elevation leading to significant improvements in equipment manufacturability, transportability, constructability, operability and maintainability.

1) Low Investment Cost
   Reduction of construction cost (Low Elevation and Compact Layout)
   - Reactor at Ground Level
   - Vertical Submerged type Carbamate Condenser (VSCC)
   - Simple synthesis loop and no gravity flow
   Reduction of Equipment cost
   - Small reactor by two stage reaction
   - Less number of equipment in synthesis loop

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![Fig. 1: Development History of TOYO Urea Process](image-url)
2) Low Energy Consumption and Running Cost Saving
   The operating condition of synthesis section is optimized at lower operation pressure than the previous process. As a result, a remarkable reduction in energy consumption is achieved.

3) Easy Operation and High On-stream Factor
   Forced flow of synthesis loop circulation by ejector and no gravity flow

4) Maintenance Cost Saving
   - Milder operating condition in synthesis loop (Less corrosion risk)
   - Advanced and proven material developed by TOYO for high pressure vessel

Fig. 2 shows a schematic flow sheet of ACES21® synthesis section.

![ACES21® Synthesis Section with Current Operation Parameters](image)

### 2.1 ACES21® Process Description with Current Operation Conditions
Liquid ammonia is fed to the reactor via HP Carbamate Ejector which provides the driving force for circulation in the synthesis loop instead of gravity for the original ACES Process. Most of the carbon dioxide with small amount of passivation air is fed to the stripper as a stripping medium for urea synthesis, while the rest is fed to the reactor to passivate the reactor. The reactor is operated at NH₃/CO₂ molar ratio (N/C ratio) of 3.7, 182 - 185°C and 152 barG. CO₂ conversion to urea is as high as 63% at the exit of the reactor. Carbamate solution from the carbamate condenser is fed to the reactor after being pumped by the HP ejector that is motivated by high pressure liquid ammonia. Urea synthesis solution leaving the reactor is fed to the stripper where unconverted carbamate is thermally decomposed and excess ammonia and CO₂ are efficiently separated by CO₂ stripping. Stripped urea solution is sent to MP decomposition stage to be purified further. Stripped off gas from the stripper is fed to Vertical Submerged Carbamate Condenser (VSCC), operated at an N/C ratio of 3.0, 180 - 182°C and 152 barG. Ammonia and CO₂ gas condenses to form ammonium carbamate and subsequently urea is formed by dehydration of the carbamate in the shell side. Reaction heat of carbamate formation is recovered to generate 5-5.5 barG steam in the tube side. Packed bed is provided at the top of VSCC to absorb uncondensed ammonia and CO₂ gas into recycle carbamate solution from MP absorption stage. Inert gas from the top of the packed bed is sent to MP absorption stage.

### 3. NEXT GENERATION ACES21®
TOYO has developed next generation ACES21®, “ACES21-LPTM” to realize further energy savings and plant cost reduction maintaining all salient features of current ACES21® by harvesting fruitages cultivated for years from “seeds” technologies.

Fig. 3 shows the history in lowering urea synthesis pressure by TOYO in past 60 years. The urea synthesis pressure has lowered step-by-step from around 240bar to around 152bar as technology advances. ACES21-LP™ concept
further lowers it to 136bar. **Table 1** summarizes key factors of synthesis section in comparison between ACES21® and ACES21-LPTM.

The key to realize ACES21-LPTM is a sophisticated application of DP28W™, conventional duplex SS and 316L SS to synthesis section in combination with reduced passivation air.

The simple and sophisticated concept of ACES21-LPTM enhances distinguished features of current ACES21® as follows:

- Lowest synthesis pressure among commercial urea processes owing to uniquely optimized synthesis conditions and reduced passivation air requirement
- Highest CO₂ conversion among advanced modern urea processes
- Further energy savings (less OPEX) owing to less power requirements in CO₂ compressor, ammonia & carbamate pumps by 5-10%
- Less CAPEX owing to relaxed mechanical design conditions of synthesis equipment (synthesis section HP equipment cost reduction by 5-10%.

![Fig. 3: History in Lowering Urea Synthesis Pressure](image)

<table>
<thead>
<tr>
<th>Process</th>
<th>ACES21®</th>
<th>ACES21-LPTM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure [barg]</td>
<td>152</td>
<td>136</td>
</tr>
<tr>
<td>Reactor</td>
<td>Two-stage Reaction</td>
<td>Two-stage Reaction</td>
</tr>
<tr>
<td>N/C Ratio [mol/mol]</td>
<td>3.7</td>
<td>3.7</td>
</tr>
<tr>
<td>CO₂ Conversion [%]</td>
<td>63</td>
<td>62</td>
</tr>
</tbody>
</table>

**3.3 DP28W™ TOYO's Proprietary Super-Duplex Stainless Steel for Urea Plant**

TOYO and Sumitomo Metal Industries (current Nippon Steel Corporation) developed a new super duplex stainless steel DP28W™ specially for application in urea synthesis section. DP28W™ has been used in commercial urea plants since early 2000s because of a number of remarkable advantages. DP28W™ shows excellent corrosion resistance even in weld metal and heat affected zone because of optimized alloying design of base metal and welding material. DP28W™ can be easily passivated with little oxygen concentration in urea-carbamate solution. Application of DP28W™ contributes to reducing required passivation oxygen concentration.

DP28W™ is best material for urea plant owing to following advantages.
• Excellent corrosion resistance
  ➢ improves reliability and maintainability
  ➢ contributes to less maintenance cost
  ➢ prolongs life of equipment and plant

• Excellent passivation property
  ➢ eliminates risk of active corrosion
  ➢ requires less passivation air injection
  ➢ improves safety and operability

• High mechanical strength
  ➢ reduces thickness & weight of pressure parts
  ➢ reduces required surface area of tubes

3.4 Optimum Application of Materials for HP Equipment and Piping
A passivation air is mixed in raw material CO₂ and fed to urea synthesis section together and oxygen in air is distributed in synthesis section for passivation. The oxygen concentration in process fluid in each equipment and piping was obtained using process simulator with regard to oxygen concentration in CO₂ which is fed to synthesis section as raw material. The simulation results confirmed that the oxygen concentration is in lowest at Stripper and Stripper outlet gas among the HP synthesis section. Thus, severest location in view of corrosion is Stripper and Stripper outlet because of lower oxygen concentration.

TOYO has identified the minimum required oxygen concentration for passivation in gas phase to prevent active corrosion for each material based on TOYO’s intense R&D and electrochemical studies. Fig. 4 shows the results. Based on these studies, oxygen concentration can be reduced by applying material in accordance with an oxygen concentration at each point without paying high cost for material. Material of DP28WTM or 25Cr duplex stainless steel (S31260) which is passivated at low oxygen concentration is applied for Stripper outlet piping where the oxygen concentration is lowest in synthesis section, required oxygen concentration can be reduced drastically. Maximum application of DP28WTM and duplex stainless steels to synthesis section further reduces passivation air requirement.

![Fig. 4: Min. Required Oxygen Concentration for Passivation](image)

3.5 Suitable for Revamp Application
Since basic process scheme of current ACES21® is maintained, currently operating ACES21® plants can be easily up-graded to ACES21-LP™ with very minor modifications, receiving full benefits such as OPEX saving, additional capacity margins of CO₂ compressor, ammonia pump and carbamate pump.
4. TOYO’S APPROACH FOR SUSTAINABLE UREA PRODUCTION

Net-zero or negative emissions of greenhouse gas (GHG) to prevent global warming is a common goal for all humankind. With the ambition to achieve a carbon-neutral society, TOYO is working to provide a wide range of solutions, including technology and business development support, ranging from the capture of CO₂ to the utilization and storage of CO₂ (CCUS), through collaboration with leading-edge technology partners and through TOYO’s expertise established in the plant engineering business. TOYO is also working on establishing chemicals and synthetic fuel production system in combination with renewable feedstock and/or waste gasification technologies. Urea is one of the final products.

TOYO (and most probably most of fertilizer producers) believes carbon footprint by fertilizer production and usage must be considered by “scientific fact-based, comprehensive and quantitative approach”, NOT “ideological or political approach”. Followings are TOYO’s views on this issue:

1. CO₂ emissions by N-fertilizer production simply depends on feedstock for ammonia (hydrogen in nature) production, NOT N-fertilizer itself. As far as N-source is grey NH₃ from fossil feedstocks, CO₂ footprint in the N-fertilizer production is totally attributable to ammonia production. On the contrary, N-fertilizer produced from “Green NH₃” and renewable energies/feedstocks must be regarded as “Green”.

2. As far as fossil feedstock is used, there is no significant difference of GHG footprint between urea and ammonium nitrate, another typical N-fertilizer. Ammonium nitrate production does not utilize any CO₂ emitted by ammonia production. On the contrary urea production utilizes CO₂ by ammonia production as a feedstock. It is also noted that utilized CO₂ during urea production stage will not be totally emitted to atmosphere at use stage. Emission of all CO₂ (0.733t-CO₂/t-urea) is a conservative expedient assumption to omit more detailed models or measurements that incorporate the possibility of bicarbonate leaching to deep groundwater, and/or lakes and oceans as stated in IPCC guideline[1].

3. It will lead to carbon reduction when urea is synthesized from green NH₃ and CO₂ captured from CO₂ at emission source and/or CO₂ from direct air capture (DAC) based on renewable energies and even a part of CO₂ leached to deep groundwater, lakes and/oceans at use stage. Even in case all CO₂ in urea is emitted at use stage, it is regarded as carbon neutral and leads to reduce equivalent CO₂ emission which would be emitted in case same quantity of urea were produced from fossil feedstocks.

4. Urea contains highest nitrogen among any N-fertilizers, thus GHG emissions attributable to the transportation of urea must be minimum from life cycle assessment (LCA) point of view of which aspect is mandatorily accounted when evaluating GHG emissions on a fair manner.

5. In addition, urea is easy for handling, storage and transportation since it is not classified as a hazardous substance and has provided great benefits to fertilizer logistics and farmers. On the other hand, ammonium-based fertilizer requires careful handling and storage, especially ammonium nitrate has explosive potential.

4.1 Concept of g-Urea®

It is supposed there is no established definition for green urea, but in this paper TOYO define it as “carbon neutral (or negative) urea production or process utilizing renewable energies and feedstocks” and named it g-Urea®. g-Urea® can be produced from green ammonia synthesized from electrolysis hydrogen and nitrogen from air separation (Fig.5). CO₂ will be sourced separately from CO₂ production, for example, sourced from thermal power plants, refineries, and other industrial facilities. In those facilities, CO₂ is anyhow finally emitted from stacks. Utilization of those waste CO₂ for urea production from green ammonia reduces equivalent CO₂ emission in case urea is produced from fossil feedstocks. TOYO is ready to integrate CO₂ capture technologies such as post combustion capture etc. with green ammonia and urea production system in order to source CO₂ from stacks and/or direct air capture (DAC); crucial components to harmonize fertilizer industry with “circular carbon society”.

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Nitrogen + Syngas 2022 International Conference & Exhibition (Berlin 28-30 March 2022)

Fig. 5: g-Urea Production from green-Ammonia

g-Urea® is also produced by gasification-based ammonia-urea production. Biomass and/or MSW (Municipal Solid Waste) could be the feed(s) for gasification (Fig.6). Biomass or MSW feedstock is converted by partial oxidation reaction to “syngas” containing H₂, CO, CO₂ and CH₄ mainly in gasification process at high temperature using oxygen from an air separation unit (ASU) and steam. Impurities contained in gasified gas originated from feedstock are removed in gas purification step then CO is converted to CO₂ and H₂ at CO shift reaction step with H₂O injected to the gas. CO₂ and H₂ are separated in CO₂ separation step and CO₂ is used for urea synthesis. A part of obtained CO₂ may be utilized for CCU or CCS. Ammonia is synthesized from obtained H₂ and N₂ from ASU. Some H₂ may be supplied supplementary from the outside for example water electrolysis using renewable energies. Overall process scheme is basically very similar to conventional gasification-based ammonia-urea production from coal, heavy oil, etc.

Fig. 6: g-Urea Production from Ammonia / CO₂ derived from Biomass / MSW

4.2 Production plant for g-Urea®

g-Urea® production plants would be likely smaller than natural-gas-based ones, due to limited availability of carbon neutral feedstocks and renewable energies. TOYO is ready to provide urea production technologies suitable to small-to-medium scale plants.

The primary solution is “Simplified ACES21®” with Unified Urea Reactor. This ultimately simplified urea process consists of only two HP equipment in synthesis section as shown Fig.7. The unified urea reactor is a self-supporting vertical tower installed on ground level, combining carbamate condensation and dehydration to urea in a single tower. It eliminates structure for heavy equipment, significantly reduces HP piping, resultantly reduces CAPEX, and operation and maintenance become much easier. Its energy consumption is comparable to current ACES21®. The Simplified ACES21® will soon be ready for technology licensing and engineering on commercial basis.
Besides the simplified ACES21®, TOYO is also ready to provide “advanced solution recycle urea production plants”, typically for very small plants as 500 t/d or smaller. This concept aims at lowest CAPEX rather than energy efficiency, modernizing traditional solution recycle process (like Total Recycle C-Improved) by incorporating state-of-the-art elemental technologies such as advanced MOC, digitalization, advanced process control, vibropriller, etc.

5 **N₂O EMISSION BY N-FERTILIZER APPLICATION TO FIELDS**

Application of livestock manure, crop residues, organic fertilizers, synthetic fertilizers and so on to fields leads N₂O emission. Fig. 8 shows a break of N₂O emission from agriculture in the world in 2017 based on data sourced from FAO (Food and Agriculture Organization of the United Nations)[2]. N₂O is emitted from soil as a by-product of two processes by which soil microbes convert ammonia back to nitrogen gas; nitrification which converts ammonium to nitrate; and denitrification which converts nitrate to nitrogen gas. Urea is no exception of these processes. However, N₂O emission from soil per unit of N-fertilizer is highly dependent on application practice, soil type and conditions humidity and other weather condition. Further scientific research and analysis in a fair manner are required to evaluate N₂O emissions from nitrogen-fertilization.

Nitrification inhibitors reduces N₂O emission. Slow-release fertilizers or controlled release fertilizers can lower the amount of fertilizers for a crop thus reduce N₂O emissions. Intensive studies are on-going and further research and development is expected in this area.

6. **CONCLUSION**

TOYO Engineering Corporation (TOYO), a global leading engineering contractor and urea process licensor, has newly developed the next generation of ACES21®, “ACES21-LPTM” to realize further energy savings and plant cost reduction by lowering urea synthesis pressure to 136bar, maintaining all salient features of current ACES21®.
In addition, TOYO is launching a new concept “g-Urea®”, aiming at carbon neutral urea production utilizing renewable energies and feedstocks; urea production from green ammonia synthesized from electrolysis hydrogen and nitrogen from air separation and captured CO₂ from waste flue gas or DAC, and urea production from ammonia and CO₂ by biomass and/or MSW (Municipal Solid Waste) gasification.

When evaluating carbon footprint by fertilizer production and usage, scientific fact-based, comprehensive and quantitative approach must be considered.

TOYO will continue contributing to fertilizer industry by improving its proprietary urea technologies and delivering technologies for the sustainable growth of the global community.

References
[1] 2006 IPCC Guideline for National Greenhouse Gas Inventory. Vol.4 Ch. 11.4.1

ACES21® and g-Urea® is a registered trademark of Toyo Engineering Corporation in Japan (Registered Number 4309123 and 6390485.)