Process Synthesis and Global Optimization of Novel Ammonia Production Processes

C. Doga Demirhan\textsuperscript{1,2}, William W. Tso\textsuperscript{1,2}, Efstratios N. Pistikopoulos\textsuperscript{1,2}

1. Artie McFerrin Department of Chemical Engineering
2. Texas A&M Energy Institute

November 2, 2017
Introduction & Motivation

- World population is expected to reach 8.6 billion by 2035 and 9.4 billion by 2050 and the world GDP will double!
- Ammonia will continue to be produced and used in extensive amounts.
- Biomass is an environmentally friendly alternative hydrogen source to natural gas with no net CO$_2$ emissions

365 million tons/year of solid biomass was available in 2015!
Possible >1 billion tons/year will be available by 2040!
Aims of this Work

**Aim 1:** Mathematical modeling of the processes in fossil- and/or renewable fuel-based (hybrid fuel) ammonia production processes

- Develop a data-driven model for ammonia converter
- Present models for process alternatives for syngas generation, syngas cleaning, and ammonia synthesis loop sections

**Aim 2:** Process synthesis and global optimization of ammonia production processes

- Incorporate all process alternatives in a process superstructure with simultaneous heat, power, and water integration
- Apply global optimization methods to find the globally optimal topologies for different feedstock availabilities, greenhouse gas emission reductions, and plant scales
Ammonia Converter Modeling

Challenges of building data-driven models:
- How to find the best fitting model?
- Which terms should be included in the model?
- Overfitting?

Our solution:
- We prepared train/validation/test sets
- 5-fold cross-validation approach is applied to create 5 models
- These 5 models are tested with new data (test set)
- Below are the scattered results of an example train/validation/test with 55 total points (40-10-5)

![Graphs showing model training, validation, and testing results.](image)

Conversion = \( \beta_0 + \sum \beta_i x_i \)

Linear model is selected!

Quadratic pressure term is found to be insignificant!

Addition of quadratic terms of temperature and pressure resulted in overfitting!

Now we can move on to the process alternatives!
Natural Gas-Based Ammonia Production

Primary Reforming

Secondary Reforming

Water-Gas-Shift

Air Separation Unit

Syngas Purification

Natural gas → Water

Syngas

Air

Oxygen

Nitrogen

Ammonia Synthesis

Compression

Ammonia Synthesis Gas

Carbon dioxide

Purge

Recycle

Air

Nitrogen

Ammonia
Biomass-Based Ammonia Production

- Biomass: Switchgrass, Hardwood, Corn Stover, Municipal Solid Waste
- SynGas Cleaning: Carbon dioxide, Oxygen
- Air Separation Unit: Nitrogen
- Ammonia Synthesis: Ammonia Synthesis Gas
- Compression: Ammonia Synthesis Gas
- Water-Gas-Shift: H₂-rich Syngas
- Purge: Carbon dioxide
Optimization Problem

- Process synthesis problem is a large-scale nonconvex mixed-integer nonlinear optimization (MINLP) problem
- Binary variables are used for technology/reactor type selection
- Model includes:
  - Mass & energy balance equations
  - Thermodynamic relations (phase and chemical reaction equilibria)
  - Simultaneous heat and power integration
  - Concave cost functions for calculation of unit investment costs
- Nonlinearity comes from the following terms:
  - Bilinear: equilibrium reactors, splitters, flash calculations, stream compositions, etc.
  - Trilinear and quadrilinear terms: Thermodynamics and equilibrium calculations
- Objective function is minimizing the levelized cost of ammonia production:

\[
\text{MIN } \sum_{\text{feed}} \text{Cost}_{\text{feed}} + \text{Cost}_{\text{electricity}} + \text{Cost}_{\text{CO}_2\text{sequestration}} - \text{Cost}_{\text{LPG}} + \sum_{u \in \text{INV}} \text{Cost}_{\text{units}}
\]
Global Optimization Algorithm

- We use a tailored branch-and-bound algorithm combined with advanced term-based relaxation techniques to solve the problem to global optimality.
- Piecewise linear underestimators are used with logarithmic partitioning scheme.
- The problem is decomposed into an MILP lower bound and an NLP upper bound problem.

- Feasibility- and optimality-based bounds tightening (FFBT and OBBT) methods are used to obtain good quality bounds.
- Branching is done on the variable with the largest relaxation error.
- The aim is the get a solution within a few percent of the best possible value.

Global optimality is theoretically guaranteed!
Conclusions

- A data-driven mathematical model is developed for ammonia converter
- A process superstructure is synthesized and modeled for biomass-based ammonia production and solved to global optimality
- Case studies showed that for single type of feedstock:
  - Ammonia produced from hardwood type biomass had the lowest break-even price of ammonia with 50% reduction in GHG emissions being possible
  - At smaller plant size, NG-based production has lower break-even price; as the plant size becomes larger, biomass-based process has the lowest break-even price

Acknowledgements