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Ammonia/Urea Production Process Simulation/Optimisation Applied Techno-Economic and Stochastic Analysis

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To support the demand growth in the agriculture sector from increasing population, ammonia and urea productions have been continuously increasing. Methane from natural gas can be used as feedstock in the production process. The conventional plant using natural gas feedstock produces cabon dioxide as a by-product of the process. This proposed plant contains two processes, producing ammonia and urea can be more efficient in the production, where the by-products of CO_2 can be used to produce more urea and reduce CO_2 emission. This research proposes ammonia and urea synthesis process using PROII software to simulate workflow and estimate the energy consumption. To be marketable and profitable for the agricultural industry, the techno-economic and stochastic analysis are applied to deal with uncertain demand from the market. This work is comprised of three main parts; the first part is the simulation of the base case process of the proposed ammonia/urea plant. The input data and parameters are obtained from the petrochemical industry in Thailand. In the second part, techno-economic analysis is significant for a feasibility study to estimate expenditure and the profitability of the project. The stochastic analysis is applied to optimise the production rate and supply chain of the products from various demands of the markets. The optimised supply chain network has been investigated on the production rate, the effect of penalty, and profit feasibility through profit accumulative curve. The conceptual design of manufacturing processes attempts to produce ammonia and urea, based on 1,930 t/d of natural gas feedstock.

1. Introduction

Ammonia is one of the most important chemicals. The use of ammonia to produce fertilizer has increased every year related to the global population growth, increasing in demand for agriculture. Ammonia and CO_2 are feedstock substances in production of urea, the important component of nitrogen-based fertilizer, and a widely used intermediate in the chemical industry. Mass production of Ammonia mostly utilises the Haber–Bosch process, reacting hydrogen (H_2) and nitrogen (N_2) at a moderately-elevated temperature and high pressure (Chisholm, 1911). The main process initially produces ammonia and carbon dioxide from natural gas. Synthetic ammonia and carbon dioxide are used in one of the urea synthesis processes. Based on pure N_2 and H_2 produced by the chemical looping process, a conceptual ammonia production plant was also proposed (Edrisi et al., 2014). This plant can be used as a new pathway to simultaneously provide both the needed CO_2 and ammonia for urea production (Edrisi et al., 2016). Based on the results and achievements in the previous research, this research proposes a conceptual design of ammonia and urea manufacturing process from main natural gas feedstock consisting of 97.47 % mole of methane and optimisation of production rate from the supply chain. The techno-economic and stochastic analyses were applied to deal with uncertain demands from the markets under effects of production rate, transportation cost, and penalty fee. The stochastic analysis method as a probabilistic approach provides more accurate and dependable results considering the effect of randomness in the input variable (Juheon et al., 2019). The optimal supply chain from stochastic apporch sastified demand rather than the deterministic model solution (Yue and You., 2016).

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2. Properties and specifications

The main feedstock of natural gas, obtained from industrial, is 1,930 t/d. The properties of natural feedstock, and products specifications are shown in Table 1.

Table 1: The properties of natural gas feedstock and products specifications

Component	% mole	Products specification	Ammonia	Urea
Carbon dioxide	0.028	Purity (% mole)	99.90 %	99.90 %
Nitrogen	2.105	Flowrate (t/d)	3,870	5,472
Methane	97.471	Temperature (°C)	-27.04	93.99
Ethane	0.395	Pressure (psia)	4,450	-
Propane	0.001			

2.1 Ammonia and urea synthesis reaction

Ammonia is produced from nitrogen and hydrogen. Hydrogen is obtained from natural gas (methane) reacting with steam. Nitrogen is obtained from burning air. The ammonia manufacturing process consists of 4 main stages, 1. Catalytic reforming stage, 2. Shift conversion and CO_2 removal stage, 3. Compression stage, and 4. Ammonia converter stage. The CO_2 removed from second stage will be feedstock substance of urea synthesis by main reaction between ammonia and CO_2. The overall reactions of ammonia and urea production are shown as following equations.

Primary reforming reactions :

$$CH4 + H2O \leftrightharpoons 3H2 + CO \quad (1)$$

$$CH_4 + 2H_2O \leftrightharpoons 4H_2 + CO_2 \quad (2)$$

Secondary reforming reactions

$$CO + H_2O \leftrightharpoons CO_2 + H_2 \quad (3)$$

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 \quad (4)$$

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 \quad (5)$$

Shift conversion reaction

$$CO + H_2O \leftrightharpoons CO_2 + H_2 \quad (6)$$

Ammonia Convertion reaction

$$N_2 + 3H_2 \leftrightharpoons 2NH_3 \quad (7)$$

Urea synthesis reactions

$$8NH_3 + 4CO_2 \leftrightharpoons 3CH_4N_2O + 3H_2O + NH_2COONH_4 \quad (8)$$

$$2NH_3 + CO_2 \leftrightharpoons NH_2COONH_4 \quad (9)$$

$$NH_2COONH_4 \leftrightharpoons NH_2CONH_2 + H_2O \quad (10)$$

2.2 Techno economic analysis

The Techno-Economic model in this research is considered on variable operation cost. The equipment costs were estimated by a guide to chemical engineering process design and economics book as shown in Eq(11) (Gael and Palligarnai, 2004). The utility cost coefficients consists of electricity, process steam, cooling water, and refrigerant are shown in table 2.
Utility price ($ per unit design)

$$C_S{,}u = a\,(CE\ PCI) + b\,(C_S{,}f) \quad (11)$$

where C_S,u is the price of the utility, a and b are utility cost coefficients, C_S,f is the price of fuel in $/GJ, and CE PCI is an inflation parameter for projects in the U.S.

Table 2: Utility cost coefficients

	Utility cost coefficients	
	a	b
Electricity ($/kWh)	$1.1 \cdot 10^{-4}$	0.011
Process steam ($/kg) *a	$2.3 \cdot 10^{-5} \cdot m_s^{-0.9}$	$0.0034 \cdot p^{0.05}$
Cooling water ($/m³) *b	$0.001 + 0.3 \cdot 10^{-5} \cdot q^{-1}$	0.003
Refrigerant ($/kJ) *c	$0.5Q_c^{-0.9} \cdot (T^{-3})$	$1.1 \cdot 10^{6} \cdot T^{-5}$

*[a] m_s is total auxiliary boiler steam capacity (kg/s) p = pressure (bar) *[b] q is total water capacity (m^3/s)
*[c] Q_c is total auxiliary cooling capacity (kJ/s), T is absolute temperature (K).

3. Methodology

The methodology consists of three main parts: Base-case simulation for ammonia process, Base-case simulation for urea process, and stochastic analysis of products supply chain.

3.1 Process flow diagram (PFD) – A conceptual design of ammonia production

This ammonia production process has been simulated by commercial software PRO/II program version 10.0 using SRK and AMINE01 thermodynamic models to achieve the ammonia specification. The ammonia process simulation is shown in Figure 1.

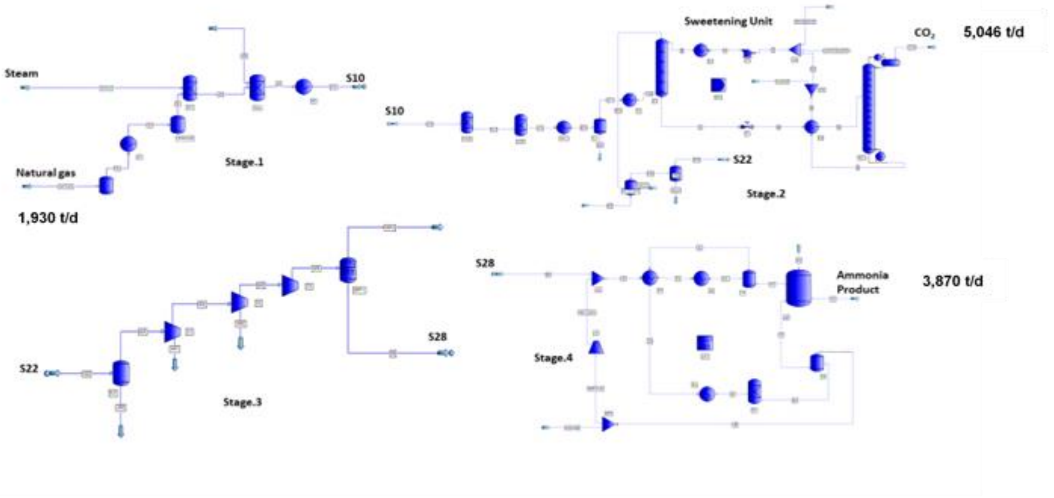
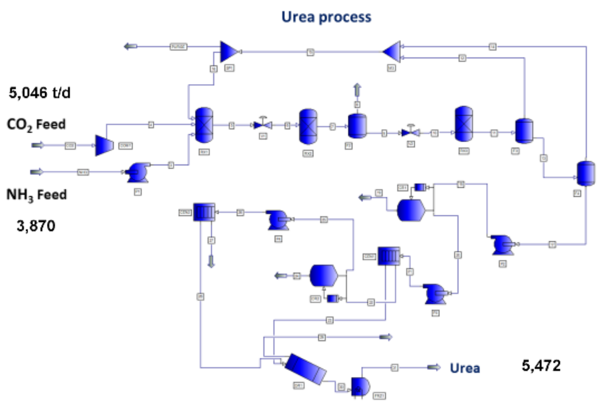


Figure 1: Pro II simulation program of ammonia production process

3.2 Process flow diagram (PFD) - A conceptual design of urea production

The urea production process has been simulated using NRTL thermodynamic model. This process is to convert CO_2, from sweetening unit of ammonia stage 2 process, and synthetic ammonia into urea. There are 3 main equilibrium reactions in the urea synthesis as shown in Eq(8), Eq(9) and Eq(10). The urea process simulation is shown in Figure 2.



Nomenclature

$Price_{amm}$	ammonia price ($/t)
$Price_{Urea}$	urea price ($/t)
$CAmm_i$	capacity of ammonia plant (t/d)
$CUrea_i$	capacity of urea plant (t/d)
$AmmIn_i$	Initial ammonia capacity (t/d)
AmmFeed (t/d)	ammonia feed to urea process
x_{ij} (t/d)	ammonia transported amount
y_{ij}	urea transported amount (t/d)
$DAmm_j$	ammonia demand (t/d)
$DUrea_j$	urea demand (t/d)
$PAmm_{ij}$	ammonia lacked penalty (t/d)
$PPAmm_j$	ammonia oversupply penalty

Figure 2: Pro II simulation program of urea production process

3.3 The stochastic analysis of products supply chain.

The supply chain can be defined as the flow of materials from raw materials to final products for end-customer through processes linked together. The stochastic programming approach for supply chains optimisation under uncertainty in market demand (Gao and You., 2017). The urea production capacity and urea production cost are optimised to satisfy the demand of markets by mathematical programming. In this work, the network has 2 echelons; Plant (i) with 2 products (ammonia and urea), and Market (j) with 2 products (ammonia and urea). The mathematical model for designing the network is expressed as shown below

$$\text{Maximise } Z = Price_{Amm} \cdot \Sigma_i\Sigma_j\, x_{ij} + Price_{Urea} \cdot \Sigma_i\Sigma_j\, y_{ij} - [Cost1 + Cost2 + Cost3] \tag{12}$$

Subject to constraints,

$$CAmm_i = AmmIn_i - AmmFeed \tag{13}$$

$$CUrea_i = 1.4683 \cdot AmmFeed_i + 0.147 \tag{14}$$

$$\Sigma_j\, x_{ij} = CAmm_i \tag{15}$$

$$\Sigma_j\, y_{ij} = CUrea_i \tag{16}$$

$$\Sigma_i\, x_{ij} + \Sigma_i PAmm_{ij} - PPAmm_j = DAmm_j \tag{17}$$

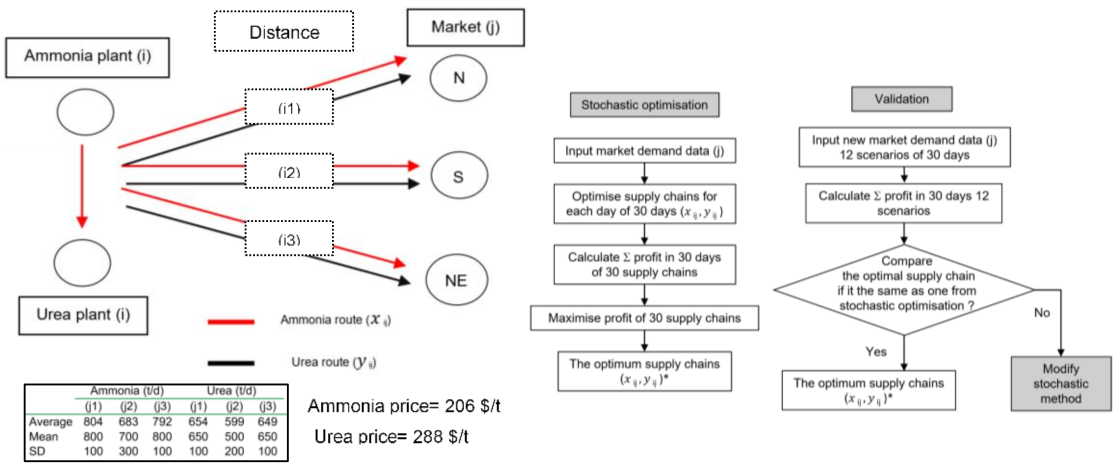
$$\Sigma_i\, y_{ij} + \Sigma_i PUrea_{ij} - PPUrea_j = DUrea_j \tag{18}$$

$$Cost1 = 647632 + \Sigma_i\, CUrea_i \cdot 72.114 + 3.7065 \tag{19}$$

$$Cost2 = (\Sigma_i\Sigma_j\, x_{ij} + \Sigma_i\Sigma_j\, y_{ij}) \cdot \text{transport cost} \tag{20}$$

$$\begin{aligned} Cost3 = {} & \Sigma_i\, \Sigma_j\, PAmm_{ij} \cdot PAmmCost + \Sigma_i\, \Sigma_j\, PPAmm_j \cdot PPAmmCost \; + \\ & \Sigma_i\, \Sigma_j\, PUrea_{ij} \cdot PUreaCost + \Sigma_i\, \Sigma_j\, PPUrea_j \cdot PPUreaCost \end{aligned} \tag{21}$$

The main objective of this model is to maximise profit from sale products. The objective function is profit as function of 3 parts; revenue, transportation cost, and penalty cost as shown in Eq(12). Eq(13) and Eq(14) calculate ammonia and urea production capacities. The urea production capacity is correlation between ammonia feed and urea product as shown in Eq(14). The penalty cost is considered from products shipping amount not satifying market's demand. The transported products amount greater than demand of the market (j) or oversupply product will be sold with cheaper selling price about 25 % of product selling price. The transported products amount lower than demand of the market (j) or lacked product will have penalty cost about 50 % of product selling price. The transportation cost is calculated from distance between plant and market and amount of product transported to market. The distance between plant and markets N(j1), S(j2), and NE(j3) are assumed as 531, 684, 208 mi. The transportation cost for products is 0.05 \$/t/mi. The supply chain model is shown in Figure 3a. The stochastic optimisation programming algorithm is shown in Figure 3b.



	Ammonia (t/d)			Urea (t/d)		
	(j1)	(j2)	(j3)	(j1)	(j2)	(j3)
Average	804	683	792	654	599	649
Mean	800	700	800	650	500	650
SD	100	300	100	100	200	100

(a) (b)

Figure 3: The optimisation progamming chart diagram of (a) products supply chain network and (b) stochastic algorithm step

4. Result and discussion

4.1 Energy consumption and economic assessment of the process

The ammonia process in Figure 1, is divided into four stages; stage 1 to 4. Stage 1 consists of 5 units consuming hot utility of 8.718 x 10^7 kJ/h with expenditure of 8,113,867 \$/y and cold utilities of 1.050 x 10^9 kJ/h with expenditure 4,806,700 \$/y. Stage 2 consists of 15 units consuming hot utilities of 4.205 x 10^8 kJ/h with expenditure of 19,046,559 \$/y and cold utilities of 1.224 x 10^9 kJ/h with expenditure of 9,904,655 \$/y. Stage 3 consists of 5 units without hot utilities usage consuming cold utilities of 3.445 x 10^8 kJ/h with expenditure of 1,576,131 $/y. The shaft work from compressor in stage 3 is 9.49 x 10^4 kW with expenditure of 110,693,413 $/y. Stage 4 consists of 10 units consuming hot utilities of 2.429 x 10^8 kJ/h with expenditure of 22,607,138 $/y and it consumes refrigerant utilities of 9.2539 x 10^8 kJ/h with expenditure of 75,776,264 $/y. The urea synthesis process in Figure 2, consists of 21 units consuming hot utilities of 3.6204 x 10^8 kJ/h with expenditure of 33,693,506 $/y and cold utilities of 4.6607 x 10^8 kJ/h with expenditure of 2,132,618 $/y. The shaft work of urea process is 8.49 x 10^4 kW with expenditure of 98,990,173 $/y. According to the result of economic evaluation in Figure 4, the highest expenditure of overall process is from shaft work or electricity used for cooler pumps which require high pressure in ammonia synthesis process. The expenditure of urea process can be varied from different energy consumption due to different amount of ammonia feed and urea production rate. To be economical, the correlation between urea production rate and ammonia feed is considered. The maximum production capacity of ammonia produced from 1,930 t/d of natural gas feed is 3,870 t/d. The correlation between urea and ammonia feed is shown in Eq(14). For additional benefit, this research also includes the stochastic optimisation of supply chain from plant to markets with optimal production rate of ammonia and urea.

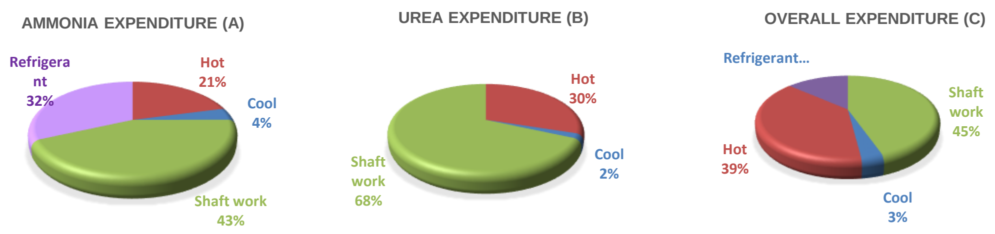
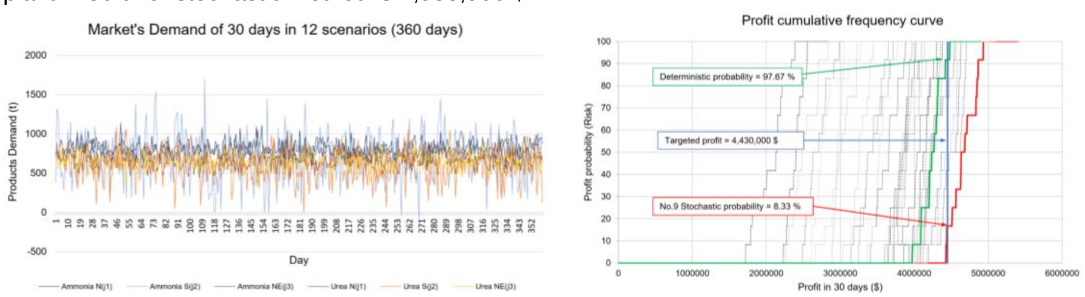


Figure 4: Process utilities expenditure of (A) Ammonia production process, (B) Urea production process, (C) combination of ammonia and urea process (overall process)

4.2 Stochastic analysis of products supply chain

In this research, 3 markets with uncertainty in market demand (j) of ammonia and urea are assumed as historical data for 30 d. The related parameters, raw material and products price, are assumed to be constant. For deterministic analysis method, average demands are representative for the data set to program assessment. The average demand are considered to find optimal ammonia and urea shipping amount for maximum profit. According to optimal results in Table 3, The overall profit of supply chain in 30 d for deterministic method is 4,657,825 $. For stochastic analysis method, demand of each markets in 30 d is considered instead using average representative data set. There are 30 optimal supply chains with optimal value of products shipping amount. The highest profit supply chain is provided from the optimum shipping value of method. The profit of plant in 30 d for stochastic method is 4,938,966 $.



(a) (b)

Figure 5: The data for validation part; (a) New uncertain market demand, (b) Profit cumulative frequency curve

For more accuracy, the validation part is performed by using new data set of uncertain demands of market (j) using statistic values, mean and standard deviation, as same as ones from historical data (j) as shown in Figure 5a. The market's demands (j) are divided into 12 scenarios of 30 d (360 d of various data). The summation of profit in 30 d of each scenarios are reported in profit cumulative frequency curve for evaluated profit probability and expected profit risk of each supply chains. The upper and lower limit of profit for each supply chains are presented in Figure 5b. According to the results in Figure 5b, at the targeted profit of 4,430,000 $, the stochastic supply chains No.9 has 8.33 % risk giving profit less than targeted proft and its upper limit of profit is 4,935,000 $ while the deterministic supply chain has higher risk of 91.67 % giving profit less than targeted profit and its upper limit of profit is 4,480,000 $. The stochastic analysis will help plant manager make decision to manipulate production rate and products transportation amount for minimising penalty cost and maximising profit of the supply chain.

Table 3: The optimised programming results

	Ammonia (t/d)			Urea (t/d)			Ammonia production rate (t/d)	Urea production rate (t/d)	Σ Profit in 30 d ($)
	(j1)	(j2)	(j3)	(j1)	(j2)	(j3)			
Deterministic	813	679	814	673	565	1,111	2,306	2,349	4,657,825
Stochastic	825	674	743	771	805	867	2,242	2,443	4,938,966

5. Conclusions

Ammonia is a significant material used in a urea production by reacting with CO_2. This conceptual ammonia and urea processes are more efficient in the production of urea, when by-products of each process is used to produce more urea and reduce CO_2 emission. From 1,930 t/d of natural gas feed, the production capacity of the ammonia is 3,870 t/d and the production capacity of the urea is 5,472 t/d. From energy consumption and economic assessment, the most expenditure of overall process is from electricity about 45 %. Improving this section can highly affect economic of the process. The expenditure of urea process can be varied with different energy consumption due to different amount of ammonia feed and urea production rate. The correlation between urea production and ammonia feed is essentially considered. For stochastic analysis, the validation part approves that optimisation with stochastic method provided more optimal value compared with deterministic method. The profit cumulative curve shows that stochastic method provides supply chain with a lower risk to achieve profit less the targeted one than deterministic method does. Consideration of both deterministic and stochastic analyses can provide more effective results.

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