

## Revamping Urea Synthesis Reactor using Aspen Plus

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### Abstract

Urea is synthesized in commercial plants from ammonia, carbon dioxide and recycle ammonium carbamate at high pressures and temperatures. In this paper, revamp of urea synthesis reactor at Agritech Limited (Formerly Pak-American Fertilizers Ltd.) has been studied. The revamp includes capacity enhancement to 135% and a change of existing technology to Stamicarbon. A simulation model has been developed using ASPEN Plus (V7.2) and validated against existing plant data. Various simulation runs were carried out to investigate the effect of ammonia to carbon dioxide molar ratio (N/C ratio), temperature and pressure on CO<sub>2</sub> conversion and urea fraction in liquid phase. Then, the model is simulated for the Revamp Case (with an increase in reactor volume) and the results compared with the data provided by the licensor. The results show a good agreement with the licensor's data of the revamp case.

## 1. Introduction

Urea is used worldwide mainly in agriculture as fertilizer. Naturally, urea is synthesized in the human body as well as other mammals to get rid of the excess nitrogen.

Friedrich Wohler in 1828 first synthesized urea from cyanate decomposition. This led to further research of urea production through inorganic means. The basic process is the Bosch Meiser urea process which was developed in 1922 and is used worldwide today with different operating conditions.

Several attempts have been made for the modeling and simulation of urea process including Hamidipour et al. [1], Zhang et al. [2], Satyro et al. [3], Irazoqui et al. [4], Dente et al. [5,6] and Aspen Tech itself [7]. Aspen Tech have modeled a plug flow reactor (PFR) and used a Fortran subroutine for reaction kinetics, however, the length of reactor has little effect on conversion. Satyro et al. have attempted it on Hysys along with C++ whilst the others have used mathematical modeling techniques. Hamidipour et al. used CSTRs in series and calculated the number of CSTRs required for the reactor to reach equilibrium. Irazoqui et al. used two series of CSTRs for internal coil and main reactor. Zhang et al. have used a stage-by-stage technique to solve the reactor. Dente et al. have used a stage wise reactor and also considered fluid dynamics.

In the present work, the reactor is modeled using a series of CSTRs with each CSTR representing one tray. Reaction doesn't reach equilibrium at the end of the series. For the revamp case, three more CSTRs are added. The present work models two different processes (Existing Technology and Stamicarbon) and is good enough for revamp project evaluations.

### 1.1. Process

Urea is synthesized from carbon dioxide and ammonia along with recycle carbamate in a high pressure reactor. Two reversible reactions occur. The first one is the formation of ammonium carbamate from ammonia and carbon dioxide and the second is the decomposition of ammonium carbamate to urea and water.



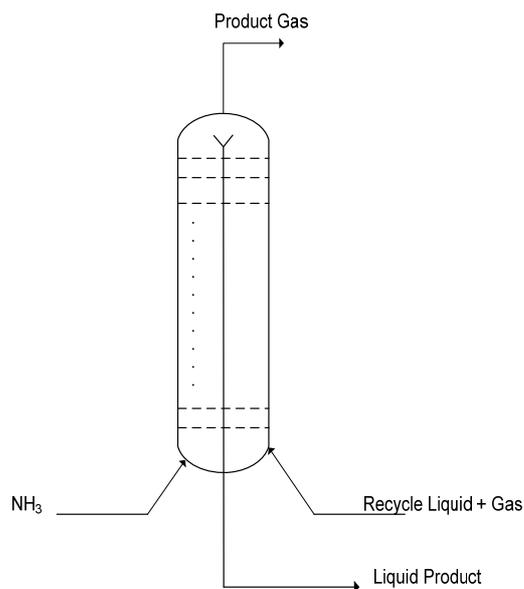
The first reaction is highly exothermic while the second reaction is endothermic, with the first reaction providing heat to the second reaction, however the reaction overall is exothermic. The first reaction is

assumed to attain equilibrium. The second reaction is slower and does not reach equilibrium. The N/C ratio is calculated assuming no biuret formation as [8]:

$$N/C \text{ ratio} = \frac{2 \times \text{wt\% urea}/60 + \text{wt\% NH}_3/17}{\text{wt\% urea}/60 + \text{wt\% CO}_2/44} \quad (3)$$

Usually, the N/C ratio is maintained higher than the stoichiometric ratio of 2, which is a consequence of thermodynamic reasons.

The pressure in the synthesis reactor is in the range 15~17 MPa and temperature 170 ~ 200 °C. The reactor is equipped with sieve plates in order to realize a number of CSTRs (Continuous Stirred Tank Reactors) by which plug flow regime is approached. The reactants (NH<sub>3</sub> feed, liquid and gas carbamate recycle streams) enter at the bottom of the reactor whereas the products leave from the top (Fig 1). Carbon dioxide is not introduced in the reactor directly but via the CO<sub>2</sub> stripper to the high pressure carbamate condensers and along with carbamate recycle. Separation of liquid and vapor streams occurs at the top of the reactor where vapors then enter the scrubber whereas liquid overflows to the stripper.



**Fig 1: Flow Diagram of Urea Reactor**

As a result of the revamp project (capacity enhancement to 135%), the conditions are changed such that the pressure is reduced to 14.7 MPa, the temperature is reduced to 183 °C, the N/C ratio reduced to 3.2 and the volume of the reactor is increased by about 23% with addition of three new plates. The CO<sub>2</sub> conversion in the outlet liquid stream of the reactor is defined as [8]:

$$CO_2 \text{ conversion} = \frac{\text{wt\% urea}/60}{\text{wt\% urea}/60 + \text{wt\% } CO_2/44} \quad (4)$$

The CO<sub>2</sub> conversion mentioned by the licensor is ~58% for the revamp case.

## 2. Simulation Model

The simulation model is made and validated using existing plant data and then used for predicting the revamp situation.

### 2.1. Hypotheses

Scant information is available from plant regarding the compositions of the liquid and gas carbamate recycle streams. Also, compositions and conversion of urea processes are usually mentioned as NH<sub>3</sub>, CO<sub>2</sub> and H<sub>2</sub>O called the initial-mixture composition [8]. Therefore, there is no accurate knowledge of carbamate present in any of the streams. The carbamate composition as well as the split between liquid and vapor in the recycle carbamate stream has been estimated (Tables 1 & 2) using data from literature and based on the following assumptions:

- Formation of biuret and other possible side reactions like hydrolysis have been neglected.
- No carbamate or urea is present in the vapor phase
- In the liquid stream, free CO<sub>2</sub> is present to a minimum extent [9] (1% of total CO<sub>2</sub> in liquid is assumed)
- N/C ratio of incoming liquid (including liquid ammonia) is equal to that in outgoing liquid
- All inert gases exist in gas phase and is composed of air only.
- The P& ID of the process shows separate lines for the recycle Gas and for the recycle liquid streams. The flows have been roughly estimated such that the stated pipe size is adequate for both the liquid and gas flows.

**Table 1**  
**Estimated Recycle Liquid Carbamate Composition**

Component	Wt. %
Urea	0.2%
CO <sub>2</sub> (free)	0.5%
Ammonium Carbamate	79.5%
NH <sub>3</sub>	0.7%
H <sub>2</sub> O	19.1%

**Table 2**  
**Estimated Recycle Vapor Carbamate Composition**

Component	Wt. %
CO <sub>2</sub>	37.2%
NH <sub>3</sub>	61.0%
Inert Gas	1.4%
H <sub>2</sub> O	0.4%

L/V ratio of the recycle stream is estimated as 1~1.5.

## **2.2. Thermodynamics**

Thermodynamic models have also been made [3,5,10] and in some cases existing models are modified (1,2,11). The thermodynamic model suggested by Aspen Tech [7] is SR-POLAR.

A study of the thermodynamic models revealed that SR-POLAR Equation of State Model suited well to fit the operating data; therefore the model in this study is based on the thermodynamics framework provided by Aspen Tech. The model deals well with highly non-ideal conditions of urea synthesis. The model contains extensions that enable an accurate description of the phase and chemical equilibria, the density and the other thermodynamic properties.

## **2.3. Reactor Model**

The reactor itself is a bubble column type reactor with trays and approaches the plug-flow type with complete mixing occurring at each tray of the reactor. The whole reactor has been modeled as a series of CSTRs (Fig.2). It has been assumed that each CSTR represents a tray (Tray 1 to Tray N). The composition of the inlet streams that are input to the simulator are also shown in Fig.2.

A volume of 20 m<sup>3</sup> has been used for each CSTR and a linear rise in temperature has been assigned to trays/CSTRs. The volume of CSTR used gave a total residence time matching with plant data.

A separator block (SUFOFLSH) has been used at the end of the CSTR series in order to separate the gas and liquid products. Actually, no such separate vessel is present at the reactor outlet. The separation of the liquid and vapour products occurs above the final tray in the existing process within the reactor under actual conditions. For the flash column the pressure drop, heat duty and liquid entrainment have been neglected.

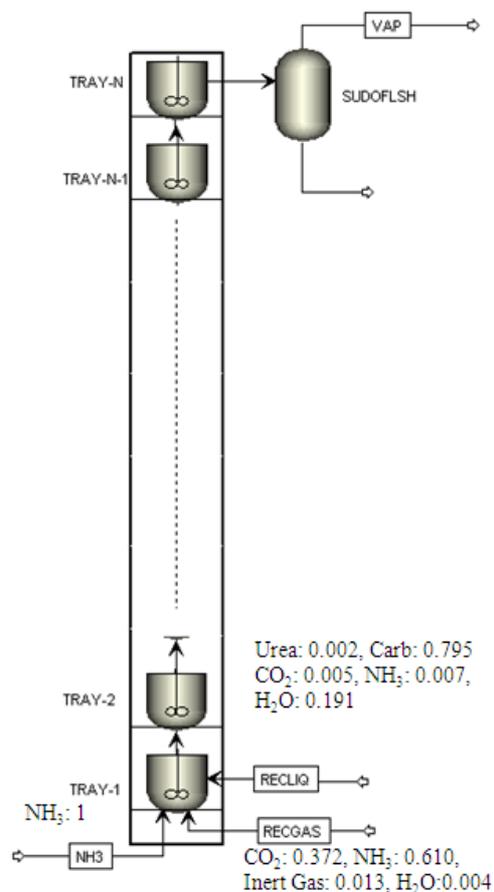


Fig 2: Aspen Tech Model of Urea Reactor

#### 2.4. Reaction Kinetics

Power Law has been used for kinetics of both the reactions:

$$rate = k(T/T_o)^n \exp\left(-\frac{E}{RT}\right) \prod_{i=1}^N C_i^{\alpha_i} \quad (5)$$

Where

- rate* = rate of reaction,
- k* = pre-exponential factor,
- T<sub>o</sub>* = reference temperature,
- T* = absolute temperature
- n* = temperature exponent
- E* = activation energy
- R* = gas law constant

- $\Pi$  = product operator  
 $N$  = number of components  
 $C_i$  = concentration of the  $i^{\text{th}}$  component  
 $a_i$  = exponent of the  $i^{\text{th}}$  component

The variables of power law are varied for both the reactions, and the model is simulated using different kinetics equations, till the result of the model matches with the plant operating data. The kinetics that gives the closest result is mentioned below.

**Reaction Kinetics for the Carbamate formation reaction:**

$$rate = 1628 \exp\left(-\frac{64001997}{RT}\right) C_{NH_3}^{1.4} C_{CO_2}^{-0.4} \quad (6)$$

The units of  $E$  are J/kmol, units of rate are kmol/m<sup>3</sup>s,  $n$  is assumed to be zero and the reaction is assumed to occur in the vapour phase.  $C_{NH_3}$  and  $C_{CO_2}$  represent the molar concentration of NH<sub>3</sub> and CO<sub>2</sub> respectively.

**Reaction Kinetics for the urea formation reaction:**

$$rate = 12000 \exp\left(-\frac{52801997}{RT}\right) C_{carb}^{0.92} \quad (7)$$

The units of  $E$  are J/kmol, units of  $rate$  are kmol/m<sup>3</sup>s,  $n$  is assumed to be zero and the reaction is assumed to occur in the liquid phase.  $C_{carb}$  is the molar concentration of ammonium carbamate.

Both reactions are reversible.

**3. Results and Discussion**

**3.1. Model Validation**

Data from the existing plant conditions and estimated data for recycle carbamate are used as input to the simulator and model is run and the results recorded. The simulator reports carbamate both in the liquid and vapor phase; however for the sake of comparison with plant data, ammonium carbamate is expressed as NH<sub>3</sub> and CO<sub>2</sub>.

For the existing reactor conditions the deviations from plant operating conditions are compared in Table 3.

It is noted that the simulator reports the possible presence of inert gas in the liquid product whereas nothing is indicated in the plant operating conditions, as it is not easy to measure. Secondly, from the simulator results, urea is found in vapor phase but again plant data doesn't indicate it as it will be negligible.

Deviations are more pronounced for the vapor product stream because of the smaller mass flows in vapor product stream than in the liquid product stream. A small difference in flows (from the simulator results and plant data) results in a higher deviation.

**Table 3**  
**Deviation of Material Balance (%) from existing plant Data for Model Validation**

	Urea	NH <sub>3</sub>	CO <sub>2</sub>	H <sub>2</sub> O	Total	Inert Gas	Density	Molecular Weight
Liquid Product	0	0	-3	0	0	--*	-8	0
Vapor Product	--**	-7	29	-32	-3	-24	-9	8

\* Inert Gas will be somewhat dissolved in Liquid phase but has not been reported.

\*\*Urea is not reported because the fraction is small, or it may have been reported as NH<sub>3</sub> and CO<sub>2</sub> in gas phase.

### **3.2. Residence Time Distribution**

Since, the volume of vapors decreases from bottom to top bottom and from tray to tray in the reactor therefore, residence time in the reactor increases from Tray-1 to Tray-N (Fig 3). A linear temperature rise is assumed resulting in linear residence time increase over the reactor length.

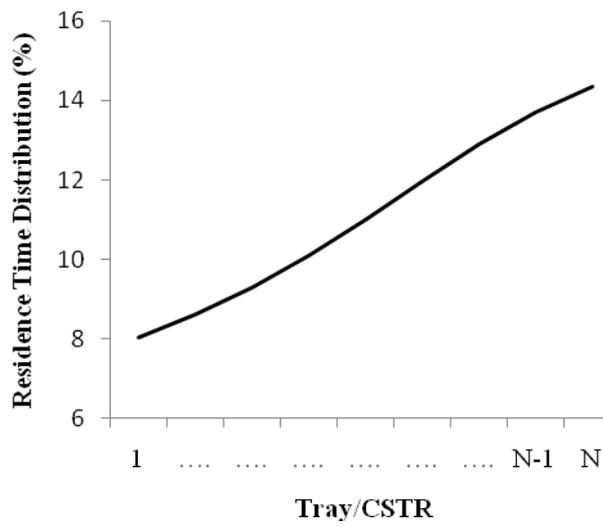
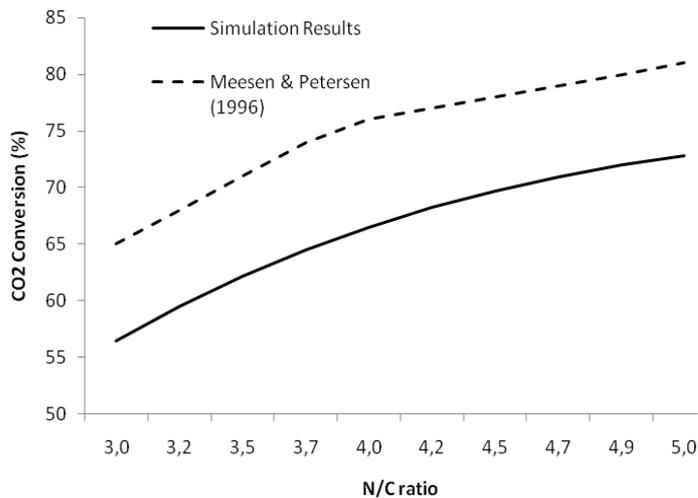


Fig 3: Residence Time Distribution in the reactor

### 3.3. Effect of N/C ratio on CO<sub>2</sub> Conversion and Urea Fraction in Liquid Phase

N/C ratio is varied from 3 to 5 and the effect on CO<sub>2</sub> conversion is observed. The relation is expressed in Fig 4 in comparison with data from Meesen and Petersen (1996). The deviation is because Meesen and Petersen have worked at lower H/C ratio of 0.25. H/C ratio (water to carbon dioxide in liquid product), is defined as:



$$H/C \text{ ratio} = \frac{\text{wt\% } H_2O / 18}{\text{wt\% urea} / 60 + \text{wt\% } CO_2 / 44} \quad (8)$$

Fig 4: Effect of N/C ratio on CO<sub>2</sub> conversion

The other effect studied is the urea fraction which is shown in Fig 4. Meesen & Petersen [12] report a similar graph, which passes through a maximum at N/C ratio of about 3 for an H/C ratio of 0.25. However, the H/C ratio is higher here and so, the maximum deviates to 3.4.

### 3.4. Effect of Temperature and Pressure on CO<sub>2</sub> Conversion

The effect of temperature and pressure on CO<sub>2</sub> conversion shows the trend is an increase with pressure and temperature till a maximum (Fig 6). Meesen and Petersen [12] report the graph as passing through a maximum at 192°C (N/C: 3.5 and H/C: 0.25).

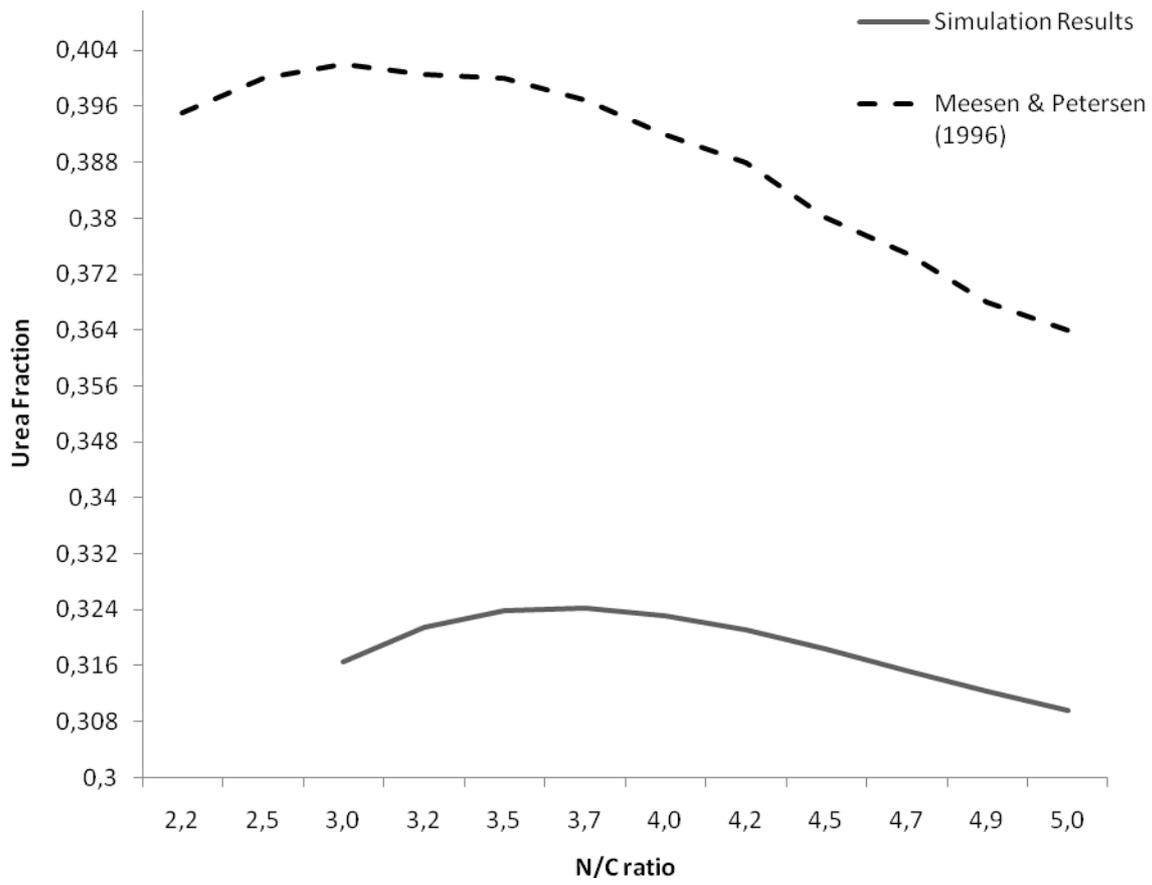


Fig 5: Effect of N/C ratio on urea fraction in final liquid

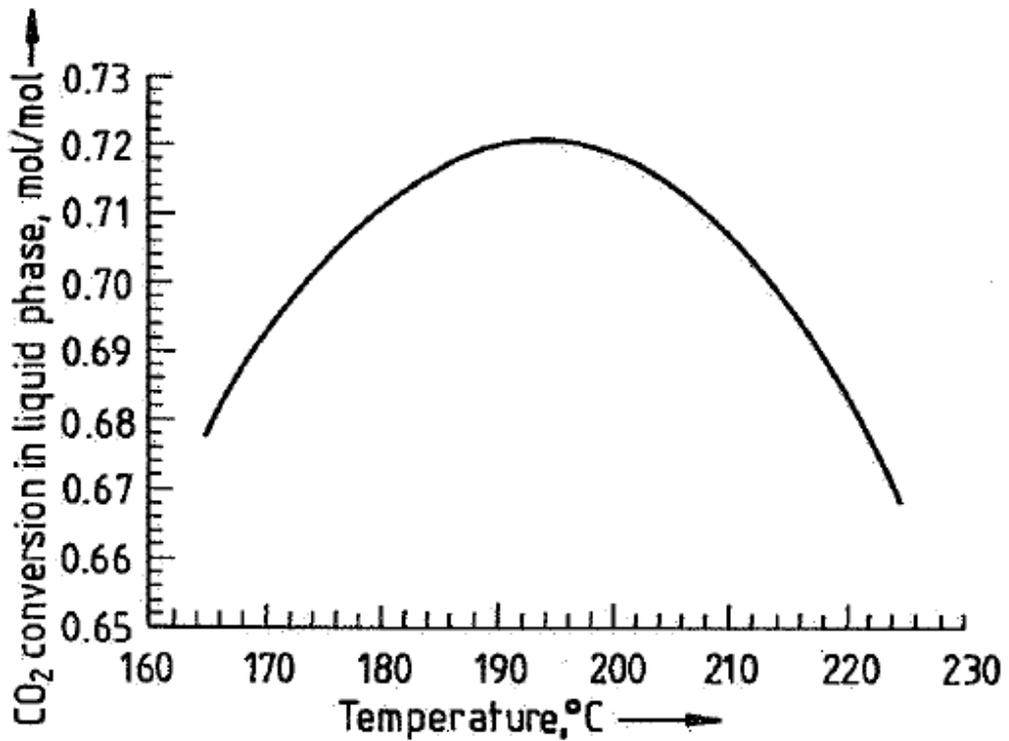
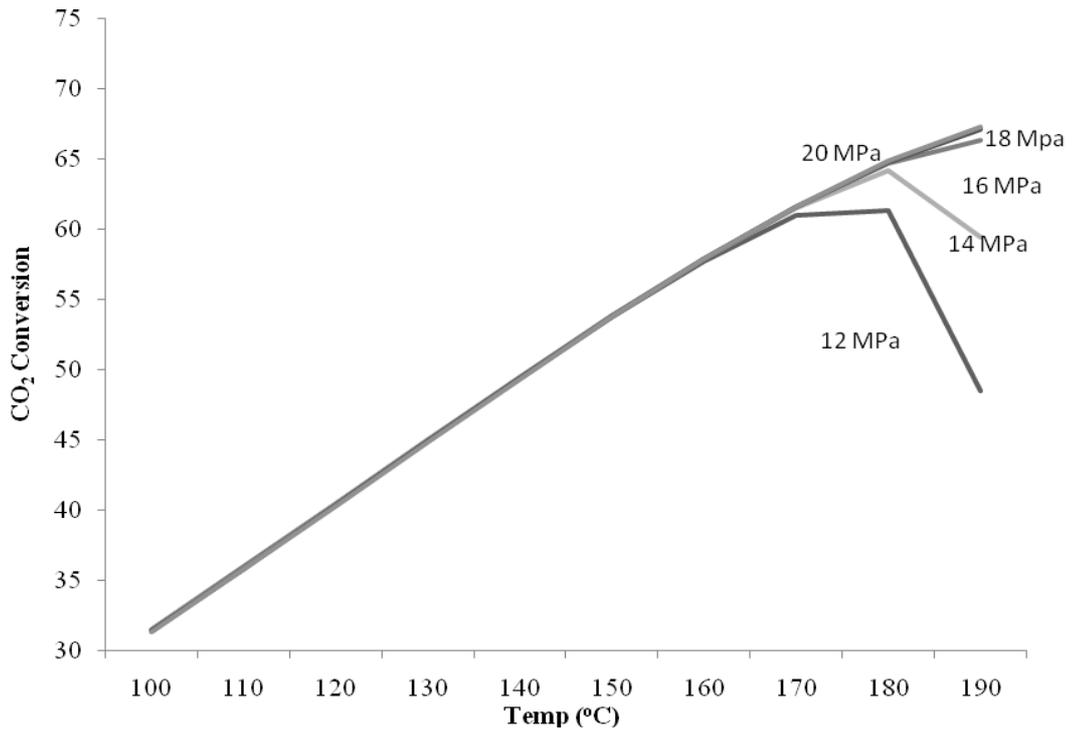


Fig 6: Effect of Temperature and Pressure (MPa) on CO<sub>2</sub> conversion  
(Above Aspen Results, below Meesen & Petersen (1996))

### 3.5. Conversion Results for Enhanced Capacity with Existing Reactor

For capacity enhancement to 135%, first the existing reactor with same volume is checked for the feasible CO<sub>2</sub> conversion with increased capacity. The CO<sub>2</sub> conversion is reported for two different cases in Table 4.

**Table 4**  
**Conversion Results for 135% Capacity with Existing Reactor**

Case	UREA	Fraction	CARB Out	CO <sub>2</sub>	NH <sub>3</sub>	Total NH <sub>3</sub>	Total CO <sub>2</sub>	CO <sub>2</sub>
	Out			OUT	OUT	OUT	OUT	Conv.
Existing Technology	0.27		0.24	.02	0.29	0.4	0.2	55.7
Stamicarbon	0.29		0.32	0.02	0.20	0.33	0.20	51.7

From the results, it is evident that, the existing reactor volume is insufficient to realise a sufficient conversion. The existing process technology has a higher CO<sub>2</sub> conversion because it has a higher N/C ratio and a higher pressure. However, higher N/C ratios require greater NH<sub>3</sub> input to the reactor and higher pressure cause higher energy consumption for rotating equipments and result in lower NH<sub>3</sub> conversion.

### 3.6. Conversion Results for Capacity Enhancement with increased number of Trays (increased reactor volume)

Next, the model is run for the Stamicarbon case for N+3 trays and 23% more reactor volume. Three more trays are added with volumes one with 12 cum, and the last two of 15 cum. The CO<sub>2</sub> conversion predicted by the simulation model is 61.7%. The results are shown in Table 5.

**Table 5**  
**% Deviation of Simulation Results with Stamicarbon Proposal**

	Urea	NH <sub>3</sub>	CO <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>	O <sub>2</sub>	Total	Density	Molecular Weight
Liquid Product	2	-1	-7	1	--*	--*	1	-5	0
Gas Product	--**	-7	13	-22	-10	-9	7	-3	4

\* Inert Gas will be somewhat dissolved in Liquid phase but has not been reported.

\*\*Urea is not reported because the fraction is small, or it may have been reported as NH<sub>3</sub> and CO<sub>2</sub> in gas phase.

The result in urea production from the reactor derived from the Aspen Plus simulation is slightly larger than that from Stamicarbon data (Fig 7). This difference is likely partly attributed to the model assumptions and the conservative approach of any licensor.

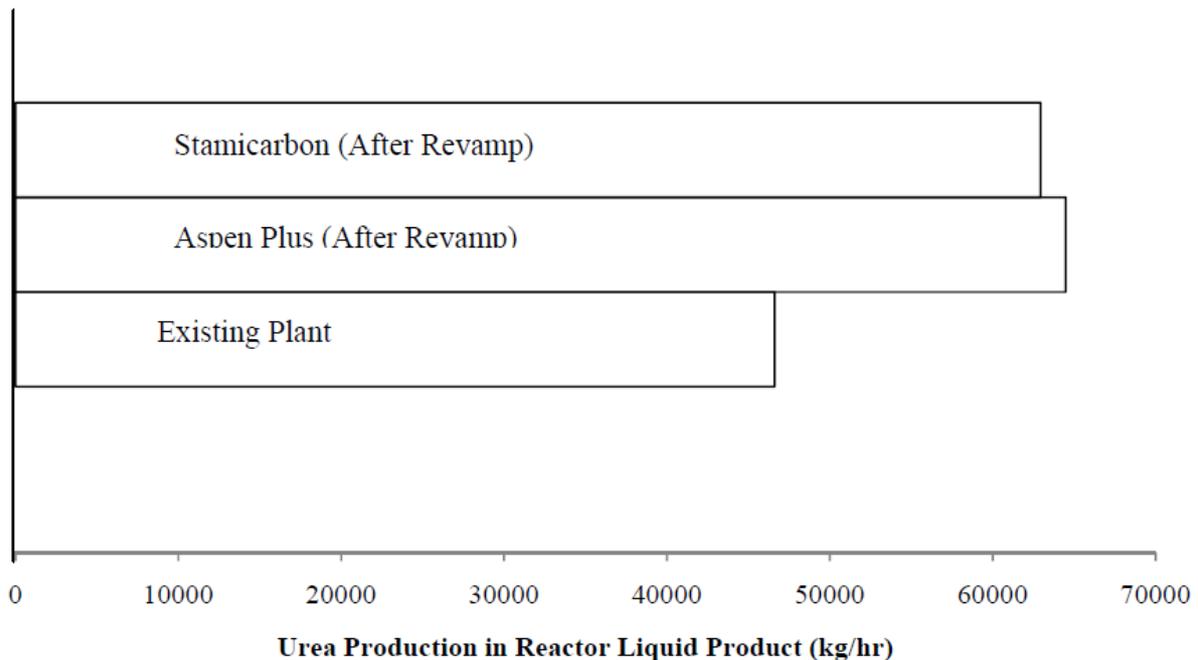


Fig 7: Urea Production (kg/hr) in Liquid Product Before and After Revamp

#### 4. Conclusions

The simulation model for the urea synthesis reactor developed using ASPEN Plus (V7.2) shows a good agreement with the licensor's data.

The simulation model has been used to investigate:

- The effect of N/C ratio on CO<sub>2</sub> conversion and urea fraction in liquid phase at the outlet of the reactor shows that conversion increases with increase in N/C ratio while urea fraction passes through a maximum.
- The effect of temperature and pressure on CO<sub>2</sub> conversion also shows a maximum conversion at a certain temperature for a certain pressure of system.
- The effect of more trays/ larger volume of the reactor increase conversion and enhance urea production, the modifications are enough for achieving 135% capacity enhancement.

## Remarks

1. This article is the excerpt of the MS Thesis of the author, which was completed under the supervision of Dr.-Ing Naveed Ramzan at University of Engineering and Technology, Lahore, Pakistan. At the time of writing of thesis, the technology hadn't changed. Currently, the technology has been shifted to Stamicarbon, but the plant is yet to be revamped to 135% capacity.
2. Due to confidentiality reasons, the name of 'existing technology' and plant/licensor data hasn't been mentioned.

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