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# Aqueous Urea Decomposition Reactor: Reaction Modeling and Scale Up

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### Abstract

This Article will illustrate an application of the principles discussed in previous sections such as scale-up, reaction modeling, and rate coefficient estimation. The example to be discussed involves the production of ammonia gas by decomposition of an aqueous solution of urea reactant at about 40 wt% urea to be used for reduction of NOx in Power plants.

**Keywords:** Aqueous urea; Chemical kinetics

## Outline of the Problem

A large commercial size reactor of the kettle type (Figure 1) was designed based on data gathered from smaller size demonstration reactors and a laboratory scale unit.

The reactor was designed to decompose an aqueous solution of urea into ammonia (2,000 lbs/hr) and carbon dioxide gas. Ammonia gas was to be used as a reducing agent in a power plant. Steam is used as the source of heat since the decomposition is endothermic.

(1) Unfortunately, the commercial unit's performance was poor and the reactor had to operate at higher temperatures relatively speaking. The smaller units (400 lbs/hr ammonia magnitude) operated at 300°F (about 100 psig pressure) while the larger commercial units operated at 320°F. Nevertheless, the commercial reactors did not achieve design conversion of urea.

(2) Also the reactor was sized with a large safety factor because of uncertainty in the scale-up from the smaller units.

(3) There seemed to be discrepancies in the performance data that had been collected from the lab and demonstration size reactors.

(4) There were issues with the scale-up of the urea reactant into the kettle reactor.

### The main objectives of the analysis are:

To review the basis for scale-up and then design of the reactor to improve performance to achieve higher conversion of urea to ammonia gas Model and recommend proper urea feed reactant assembly into the kettle reactor at commercial sizes. Review the chemical kinetics for the reactor design. As well as to be able to reduce the size of the reactor for cost savings.

## Analysis of Exiting Scale-up and Design

### Aqueous urea decomposition chemistry

Without the development of relevant chemistry for aqueous urea decomposition, the reactor modeling and design would mean very little. This this is the first step in the analysis [1].

The overall decomposition of urea in water is known to occur according to the following reaction,
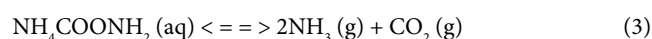
$$NH_2CONH_2 \text{ (aq)} + H_2O \text{ (l)} <==> 2NH_3 \text{ (g)} + CO_2 \text{ (g)} \qquad (1)$$

$$\Delta H = +113 kJ / mol$$
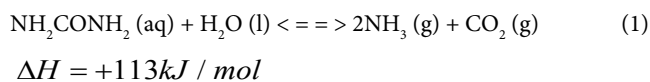
However, there is evidence that the reaction takes place in two major steps [2,3],

$$NH_2CONH_2 \text{ (aq)} + H_2O \text{ (l)} <==> NH_4COONH_2 \text{ (aq)} \qquad (2)$$
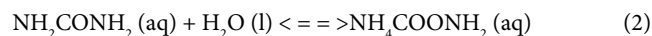
$$\Delta H = -23 kJ / mol$$

which leads to the formation of ammonium carbamate, and

$$NH_4COONH_2 \text{ (aq)} <==> 2NH_3 \text{ (g)} + CO_2 \text{ (g)} \qquad (3)$$

$$\Delta H = +136 kJ / mol \quad \text{(By difference)}$$

Where decomposition of carbamate leads to ammonia and carbon dioxide in the gas phase.

The overall reaction (1) is highly endothermic, or +113 kJ/mol. Similarly, the decomposition of carbamate to ammonia (reaction 3) is endothermic or +136 kJ/mol. The formation of Carbamate by reaction (2) is slightly exothermic.

The literature value for the heat of reaction (1) represents 809 btu/lb Urea. This value is lower by 12% than the value used during design of the commercial units. The source of this difference could not be determined.

### Aqueous urea decomposition chemical kinetics

It has been determined that reaction (2) is a very slow reaction and it is kinetically controlling the decomposition of urea into ammonia gas [1]. Thus the rate of decomposition of urea is given by equation 4.

Decomposition Rate,

$$R = k * [H2O] * [Urea] \qquad (4)$$

Where $[H_2O]$ is the concentration of water, and [Urea] is the concentration of urea.

Note that the rate coefficient is given by the expression,

k= A*exp(-E/RT)

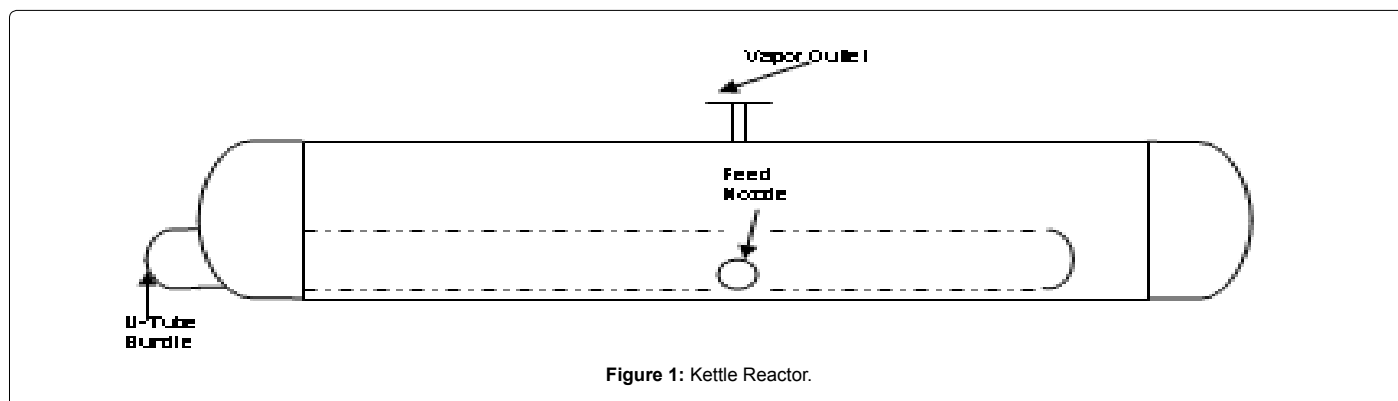A is the pre-exponential factor, E is the activation energy, R is the

**Figure 1:** Kettle Reactor.

gas constant, and T is the thermodynamic temperature. Experimental data confirms that the reaction is first order with respect to urea concentration [3].

For purposes of modeling the Urea Hydrolyzer, the following expression taken from Sahu et al. [4] is utilized,

$$\text{Rurea} = 4.295 * 10^5 * e^{\frac{60.93KJ/gmole}{RT}} * [\text{Urea}]_R, \text{gmole / liter} - \min \quad (5)$$

Where the concentration of Urea is within the kettle reactor and the expression implicitly includes the concentration of water as constant in the pre-exponential factor.

### Kettle reactor mass balance design equation

If the kettle reactor is treated as a well-mixed reactor (Figure 2), an overall mass balance results in the following sizing criteria,

$$\sum_i Ri = \frac{u}{Vo} * [Co] \quad (6)$$

$R_i$, rate of disappearance of urea by reaction i, mole/l-sec

u, volumetric feed rate urea solution, liters/sec

[Co], concentration of urea in feed, mol/liter

Vo, reactor volume, liters

The summation term on the left of equation (6) represents the disappearance of urea in the reactors by all reactions i, in mole/liter-sec units. The term on the right represents the volumetric feed-rate of urea divided by the reactor volume Vo. If the main reaction is the decomposition of urea, then

$$\text{Decomposition Rate}, Ri = k * [H2O]_R * [\text{Urea}]_R, \text{mole / l} - \sec \quad (7)$$

It is important to note that the concentration of urea in equation (3), [Urea] R, corresponds to the concentration of this component in the Hydrolyzer inventory or volume, and not in the feed solution. The rate coefficient for the reaction is given by k. Equation (7) is general, for the reaction under consideration; the values in equation (5) are used for sizing purpose.

In essence what the urea mass balance equation (6) describes is that the rate of urea decomposition in the Hydrolyzer must equal the feed-rate of urea with the solution.

Equation (6) corresponds to the idealized situation where there are no concentration gradients or differences within the reactor, and it leads to the maximum production of ammonia gas. In the event that the urea feedstock solution is not well distributed into the reactor, the rate of urea production would diminish since there are localized areas of the reactor where the concentration of reacting urea is depleted.

### Reactor performance data: theoretical, pilot plant, small demonsration units

Figure 3 below depicts the urea decomposition rates according to equation 5 for an ideal reactor, a pilot plant unit, and finally for three different small size commercial or demonstration units. It is obvious because of the kettle configuration for the reactor that the ideal reactor model results in significantly higher rates because of perfect mixing (equation 5). Moreover, there are significant differences in the rates of decomposition measured in the pilot unit and the small commercial units, especially at the higher temperatures. An inspection of the tabulated date from which the figure is derived showed that the spread in the measured rates is too large. This is a strong warning of some problems with scaling-up the reactors or significant differences in the extent of mixing amongst the reactors shown for the study.

The reasons will be made clearer in the discussions that follow concerning scale-up and mixing.

### Reactor scale-up

Inspection of the data available during development of the urea decomposition reactor showed the following:

The bench scale unit was a ¾" dia. pipe tubular reactor and about 1 foot long.

The Pilot scale unit was a 4" dia. pipe with a reduced section or 3" dia. Pipe. The reactor was over 3 feet long and also tubular type.
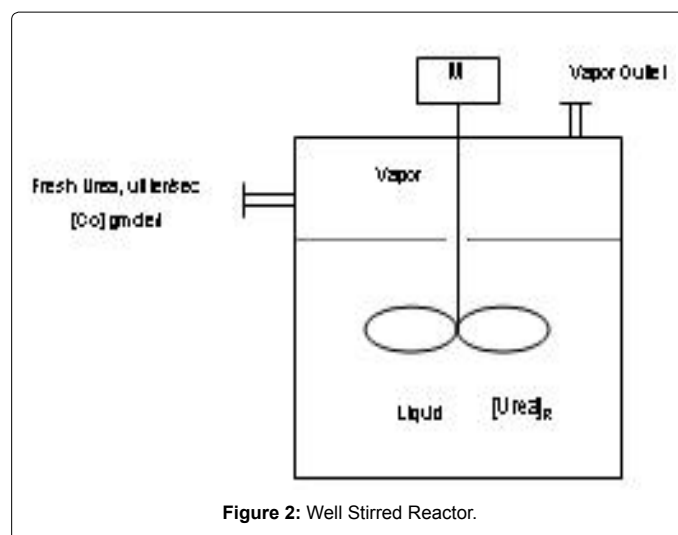


**Figure 2:** Well Stirred Reactor.

The smaller size commercial units produced about 400 lbs/hr of ammonia gas but were kettle type reactors

The large size commercial reactor produced 2,000 lbs/hr of ammonia and it also was a kettle type reactor.

The reactors were scaled-up by the method of extrapolation thus the following are the most important factors to consider during sizing:

- Geometric similarity

- Reaction Time

- Mixing

It should be obvious that the differences in chemical reaction rates between the pilot reactor (tubular) and the kettle commercial reactors is due to the lack of geometric similarity of most importance for extrapolation. Even the bench scale reactor was of the tubular type. This explains the differences in the data shown in Figure 3.

Unfortunately, there is also too much spread in the measured decomposition rates with the smaller size commercial units in Figure 3. This is probably due to the lack of consideration to mixing during design of the reactors which becomes most significant with the large size commercial reactor at 2,000 lbs/hr production target.

In order to understand this problem, it must be noted that both small size kettle reactors and then the larger size commercial kettle reactor were designed with one single feed line located at the bottom of the reactor and centered along its length. Thus, it should be obvious that mixing in the larger reactors would be considerably worst.

The kettle reactor will have due to temperature differences within the reactor natural convection fluid circulation patterns. See Figure 4 for example.

In order to improve mixing of the urea feed with the contents of the reactor, especially with much larger or longer reactors, the urea feed pipe must be able to disperse the urea solution into the reactor (using a bladder or multiple entry feed-pipe for example), but also consideration must be given to the location of the urea solution feed with respect to the circulation currents within the kettle as shown in Figure 4.
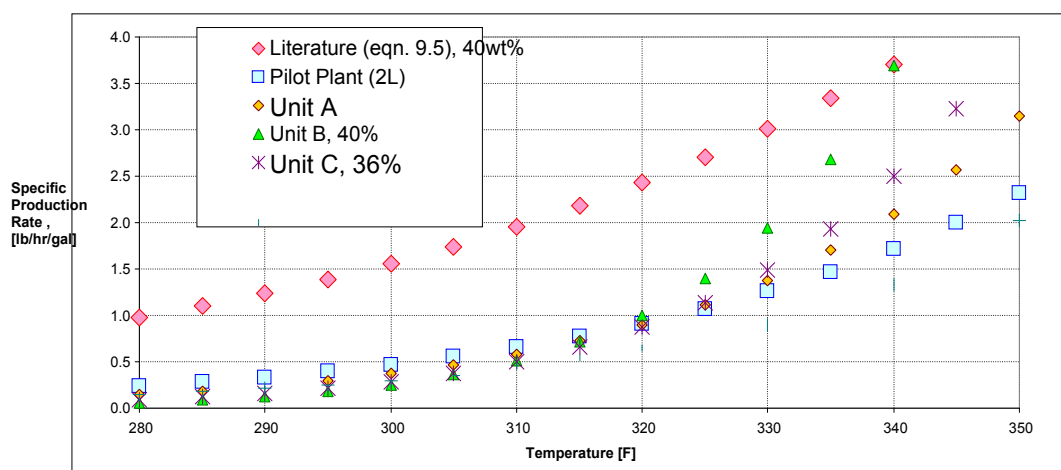


**Figure 3:** Urea Decomposition Rate (Theoretical, Pilot, Small Size Commercial) Comparison.
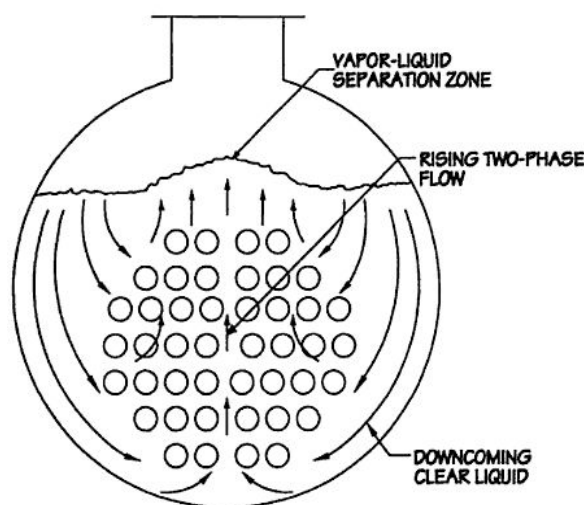


**Figure 4:** Kettle Re-boiler Circulation Pattern.

This issue will require CFD modeling of the reactor with special attention to the feed assembly.

## Recommendations for kettled reactor improved performance

Based on the discussion and analysis present in this report, the following is a summary of the major recommendations for improvement of the design of Urea Hydrolyzer: Better define Chemical Reaction Rate for the Urea decomposition with a pilot kettle reactor.

(1) As a result of fundamental chemical reactor theory and CFD modeling (to be conducted as part of the pilot unit work), it is recommended that urea feedstock solution be fed into the hydrolyzer at multiple points (possibly four) to maximize the dispersion of urea into the inventory.

(2) Furthermore, it is important to inject the urea solution into the mixing zone of the reactor. This will require the injector nozzles to protrude inside the vessel some distance away from the wall. This will be better defined as a result of CFD modeling.

**The proper scale-up of urea hydrolyzers will involve "extrapolation", thus requirements are:**

- Vessel geometric similarity (as well as similar aspect ratio),
- Scaled Reactor volume or residence time,
- Equal Reactor temperature,
- Geometrical/Dynamic similarity for urea feedstock assembly.

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