

Reaction engineering of urea alcoholysis: Alkyl carbamates

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Urea alcoholysis is a reversible reaction generating alkyl carbamate and ammonia as products. The reaction can be performed non-catalytically or in presence of catalyst. The first step in Reaction engineering analysis is to finalize the reactor configuration. In this case it is important to determine the necessity of reactive separation (simultaneous reaction and separation). This has been addressed by first establishing the reversibility of the reaction through theoretical and experimental investigation. Based on this analysis, an experimental setup comprising tubular reactor and a separator has been built. Experiments have been performed for different alcohols at different flow rates and temperatures. The experimental data is used to establish kinetic parameters. Systematic reaction engineering analysis based on multi-stage ideal reactors with and without simultaneous mass transfer is then carried out in terms of three dimensionless numbers. The analysis presented in this work can be readily applied to a general class of reversible reactions with volatile products and the methodology can be used to develop and design reactors for them. The approach and results presented here will be useful to establish optimal reactor configuration and design for urea alcoholysis reactions.

Keywords: Reactor, Process intensification, Alcoholysis, Reaction engineering, Alkyl carbamate, Urea

Organic carbamates and carbonates are a class of compounds having variety of applications. These carbonates can be acyclic or cyclic. Acyclic carbonates are basically Dialkyl carbonates (DAC) e.g. Dimethyl carbonate (DMC), Diethyl carbonate (DEC) and their higher homologues. DAC's are considered as chemical feedstock fulfilling the requirements of 'green' chemistry¹. They form an important branch of these organic carbonates and are mainly used as precursor to synthesize higher organic carbonates and polycarbonates. Apart from this, DMC is used as a methylating agent in organic synthesis as a more benign replacement for presently used methylating agents which are hazardous such as Dimethyl sulphate etc. DMC is also known in organic synthesis as an effective carbonylating, methoxylating and methylolating agent with active chemical properties. Di-alkyl carbonates have several applications as solvents in paints, coatings, adhesives and inks, as electrolytes, as fuel additives or lubricants²⁻⁴.

Synthesis of DAC's by urea alcoholysis is an attractive 'green' route and has recently received a lot

of attention. Urea alcoholysis i.e. reaction of urea with alcohol produces dialkyl carbonates in stepwise manner. In the first step urea reacts with alcohol and forms the corresponding alkyl carbamate (AC) and in the second step this alkyl carbamate reacts further with another molecule of alcohol to yield dialkyl carbonate. In this work we have investigated the reaction engineering aspects of the first step of urea alcoholysis i.e. formation of methyl carbamate. Recently Ranade *et al.*⁵ have analyzed this problem in detail.

Urea to carbamate reaction is mildly endothermic in nature and is reversible. Urea to MC reaction can be performed both catalytically as well as non-catalytically and information about the reaction kinetics for both approaches is sporadically available. Sun *et al.*⁶ have carried out urea alcoholysis to MC in semi-continuous mode in an autoclave without any catalyst. Ammonia was removed in situ by continuously vaporizing and feeding liquid methanol into the reactor. Authors have reported pseudo-first order kinetics of the process and the reaction was considered irreversible. Zhang *et al.*⁷ have reported

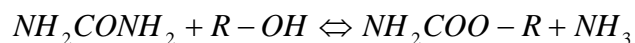
the kinetics of direct urea alcoholysis to DMC in the presence of ZnO catalyst. The reaction was carried out in a packed column type reactor with catalytic distillation. The equilibrium constants reported in the publications are high which would essentially put the value of equilibrium conversion close to completion. Zeng *et al.*⁸ have reported about the reversible nature of this reaction. Authors have calculated and estimated thermodynamic properties of methyl carbamate and have determined the equilibrium constant experimentally. Their reported values of equilibrium constant are close to 7 at the temperature of 433.15 K. Authors have used Benson's method to estimate the missing properties of Methyl carbamate such as enthalpy and entropy of formation. Contributions of the carbamate group are not originally covered in Benson method⁹, therefore authors have used a contribution of the closest possible group. The method of calculation of activity of ammonia in liquid phase from experimental data is also inaccurate. Marochkin and Dorofeeva¹⁰ have commented on the suitability of using these contributions in estimation of properties and have suggested changes in the value of heat of formation and entropy based on their own molecular simulations. Appropriate thermodynamic properties for MC, EC and their eutectic have been reported by Bernard *et al.*¹¹.

Overall there is substantial degree of ambiguity for the nature of this reaction and contradictory data is reported in the literature. The reaction needs to be understood adequately to proceed to the reaction engineering and reactor design. In this work we have presented an analysis of this reaction and we have begun this by investigation of its reversibility. The equilibrium constant and its dependence on temperature have been calculated from first principles. Based on these values we have found the equilibrium conversion of this reaction at various mole ratios of methanol to urea for different values of equilibrium constants. Based on these results, it was decided to build an experimental setup containing a tubular reactor followed by a separator for removing ammonia. Experiments were carried out for the Urea to alkyl carbamate reactions to obtain conversion vs. residence time data at different temperatures. Kinetic data and established values of kinetic parameters are not reported here for honouring the confidentiality obligations. The values however used to estimate relevant ranges of Damköhler numbers for urea alcoholysis reaction. Systematic reaction engineering

analysis over the relevant range of Damköhler numbers is presented here. The approach and results presented here will be useful to establish optimal reactor configuration and design for urea alcoholysis reactions.

Estimation of equilibrium constant and conversion

Urea alcoholysis is a reversible reaction generating alkyl carbamate and ammonia as shown below in Scheme 1. It can be performed in the presence of catalysts as given in Sowa¹², Joseph *et al.*¹³, Robeson¹⁴ and Deng *et al.*¹⁵ or performed non-catalytically e.g. Sun *et al.*⁶ and Zenget *al.*⁸.



Scheme 1 — General reaction for urea alcoholysis to alkyl carbamate

The equilibrium constants for the urea alcoholysis were estimated from first principles and the methodology is depicted in Fig. 1. A thermodynamic cycle was built whereby the Gibbs free energy change of the reaction was calculated for the reaction at various temperatures. Properties required for the calculation are given in Tables 1, 2 and 3. The calculation was performed in following steps¹⁶:

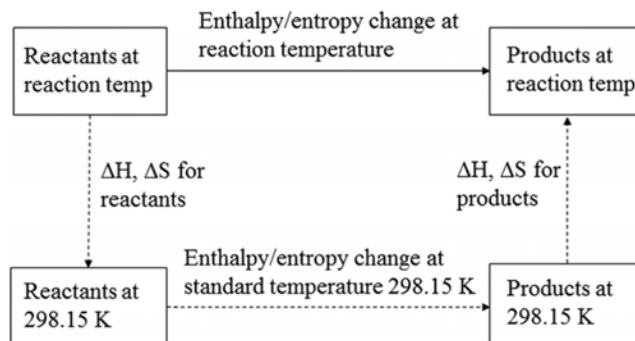


Fig. 1 — Calculation of the Gibbs free energy change of the reaction at reaction temperature

Table 1 — Data used to calculate Gibbs free energy change at standard temperature

Compound and source	State	Heat of formation [kJmol ⁻¹]	Entropy [Jmol ⁻¹ K ⁻¹]
Urea	Solid	-333.1	104.3
Methanol	Liquid	-238.4	127.2
Ethanol	Liquid	-276	159.9
Methyl carbamate	Solid	-489.4	100.3
Ethyl carbamate	Solid	-518.2	152.4
Ammonia	Gas	-45.9	192.8

Table 2 — Heat capacity correlation parameters for compounds involved for urea and methyl carbamate

Compound and source	State	Correlation parameters ($C_{p,i,s} - [Jg^{-1}K^{-1}]$)		
		a,0	a,1 $\times 10^3$	a,3 $\times 10^6$
Urea	Solid	-0.1825	7.28	-4.9825
Urea	Liquid	2.9786	-6.29	11.973
Methyl carbamate	Solid	12.321	-77.46	133.24
Methyl carbamate	Liquid	2.0135	-1.1	3.6528
		Correlation parameters ($C_{p,i,s} - [Calmol^{-1}K^{-1}]$)		
Ethyl carbamate	Solid	32.9281	0.1505	0.0006
Ethyl carbamate	Liquid	46.908	0.0476	0

Table 3 — Heat capacity correlation parameters for compounds involved for methanol and ammonia

Compound and source	State	Correlation parameters ($C_{p,i,s} - [Jmol^{-1}K^{-1}]$)				
		a,0	a,1 $\times 10^2$	a,3 $\times 10^4$	a,4 $\times 10^6$	a,5 $\times 10^1$
Methanol	Liquid	632.828	-7.969	0.409	-9.09	0.756
Ethanol	Liquid	55.2744	62.78	-0.46	1.6	-0.107
Ammonia	Gas	35.235	-3.504	1.697	-0.176	0.633

1. Estimation of properties such as heat of formation and entropy of compounds at standard temperature (298.15 K here) and standard states. The standard state for urea and Alkyl carbamate is solid whereas for methanol it is liquid and for ammonia it is gas.
2. Calculation of Gibbs free energy change of reaction at standard temperature (Eq 1) and standard states.
3. Estimation of enthalpy and entropy change to bring reactants to the standard temperature from reaction temperature and to bring products from standard temperatures from standard temperature to the reaction temperature as depicted in Fig. 1 and Eqs 2, 3, 4 and 5.
4. Enthalpy and entropy change for individual compounds were calculated from Eqs 4 and 5. Here the standard values of enthalpies of phase change and temperature of phase change were used to calculate the enthalpy and entropy change.
5. Enthalpies and entropies of compounds were added e.g. Alkyl carbamate and ammonia for products and Urea and methanol for reactants.
6. Gibbs free energy at reaction temperature was calculated from Eq 3.
7. The equilibrium constant at respective temperature was calculated from Eq 6.

$$\Delta_r G^\circ = \Delta_r H^\circ - T^\circ \Delta_r S^\circ \quad \dots (1)$$

$$\Delta_r G(T) = \Delta_r H(T) - T\Delta_r S(T) \quad \dots (2)$$

$$\Delta_r G(T) = [\Delta_r H^\circ + \Delta H_{prod} - \Delta H_{react}] - T[\Delta_r S^\circ + \Delta S_{prod} - \Delta S_{react}] \quad \dots (3)$$

$$\Delta_r H(i) = \int_{T^\circ}^{T_{PC}} C_{p,i,s} dT + \Delta H_{PC} + \int_{T_{PC}}^T C_{p,i,s} dT \quad \dots (4)$$

$$\Delta_r S(i) = \int_{T^\circ}^{T_{PC}} \frac{C_{p,i,s} dT}{T} + \frac{\Delta H_{PC}}{T_{PC}} + \int_{T_{PC}}^T \frac{C_{p,i,s} dT}{T} \quad \dots (5)$$

$$K_{eq} = \exp\left(\frac{-\Delta G_r(T)}{RT}\right) \quad \dots (6)$$

Experimental data on thermodynamic properties of alkyl carbamates is scarcely available in literature. We have therefore used Group contribution methods to estimate properties whenever experimental data was not available. Estimation of equilibrium constant at standard conditions requires information on heat capacity of respective phases which is not readily available. Here we restrict the scope of discussion to Methyl and Ethyl carbamate. Heat of formation for Methyl carbamate was taken from Marochkin and Dorofeeva¹⁰ and other properties such as data for phase change and entropy were taken from Bernard *et al.*¹¹. Heat capacity data for urea and Methyl carbamate in crystalline state was taken from Zeng *et al.*⁸. Authors have generated these values by using standard DSC (Differential Scanning Calorimetry). Properties of Ethyl carbamate were estimated with the help of Benson group contribution method and the heat capacity data was generated by using NIST's Thermodynamic Data Engine (ThermoML polynomial) through Aspen Properties. Values of heat capacity of liquid alcohols for a broad range of temperatures were taken from Zabransky *et al.*¹⁷ and heat capacity parameters were regressed. All required data for calculation of equilibrium constant at reaction conditions is given in Tables 1, 2 and 3.

The reaction is mildly endothermic in nature and therefore the value of equilibrium constant increases with temperature effectively shifting the equilibrium to the side of products. The values obtained are given in Table 4. These values clearly indicate that the reaction is indeed reversible and the analysis henceforth is based upon this assessment.

The equilibrium conversion was calculated based on these estimated values of equilibrium constant assuming the law of mass action as given in Eq (7).

Table 4 — Equilibrium constant from theory for urea alcoholysis

Temperature [K]	Equilibrium constant for reaction	
	Methyl carbamate	Ethyl carbamate
423	0.12	0.08
448	0.19	0.21
473	0.28	0.46

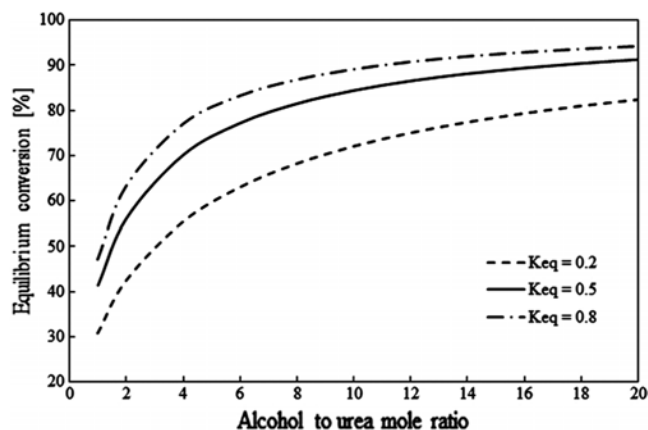


Fig. 2 — Equilibrium conversion as a function of methanol to urea mole ratio for different equilibrium constants

$$K_{eq} = \prod_{i=1}^n a_i^{v_i} \quad \dots (7)$$

Figure 2 shows the values of equilibrium conversion achieved as a function of alcohol to urea mole feed ratio for different values of equilibrium constants. We can see that the equilibrium conversion achieved is higher as the ratio of alcohol to urea increases. While calculating the equilibrium conversion, a simplification was done by assuming the values of activity coefficients of all components to be 1. For more realistic calculations, activities of components must be involved to calculate equilibrium conversion¹⁶. After looking at Fig. 2 one can see that there is sharp increase in the slope as the mole ratio increases and the slope diminishes continuously as the mole ratio increases. The advantages of having large amount of methanol towards getting higher conversion is not pronounced after the molar ratio of 12. Taking a very high ratio of methanol to urea would certainly increase the equilibrium conversion but will dilute the product to a great extent and make the separation more difficult. Theoretically if ammonia is stripped out from the reaction zone we may overcome the limitation posed by the reaction equilibrium and drive reaction forward. The separation can be performed in situ or in the separate equipment. Considering that reasonably high conversion can be

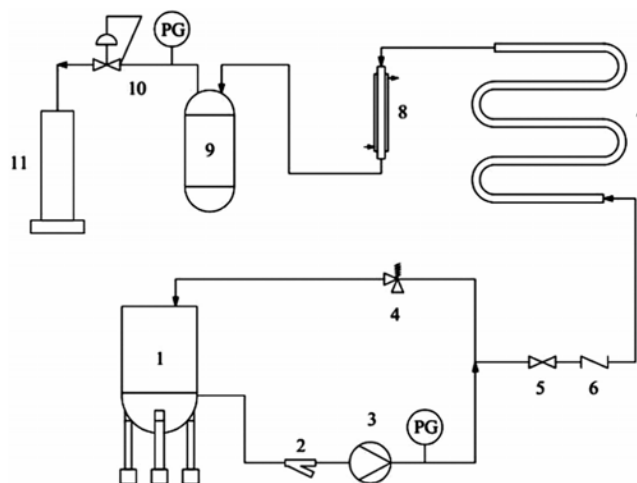


Fig. 3 — Schematic of the tubular reactor setup: 1- Urea-methanol solution storage, 2- Strainer, 3- Piston pump, 4- Pressure safety valve, 5- Needle valve, 6- Non-return valve, 7- Tubular reactor, 8- Cooler, 9- Product storage, 10- Back pressure regulator, 11- Scrubber

obtained without simultaneous removal of ammonia, experiments were planned to obtain reaction kinetics. These are discussed in the following.

Experimental Section

Tubular reactor setup for urea alcoholysis

A tubular reactor setup was designed and developed for urea alcoholysis. Schematic of the setup is shown in Fig. 3. The tubular reactor is essentially an empty SS tube. Urea-methanol solution is stored in vessel (1). This solution is continuously pumped against reactor pressure with help of a Piston pump (3). Since this is a reciprocating type of pump, safety features such as Pressure safety valve (4) etc. were provided. In order to ensure a smooth and safe operation of the pump a Non-return valve (6) is fitted on the downstream of the pump. The setup consists of a Tubular reactor (7), Pump (3), Heaters, Product cooler (8) and product collection vessel (9). The reactor was heated from outside (heated outer wall) to a suitable temperature so that desired temperature is achieved inside the tube where the reaction is taking place. Heater was tuned to maintain a steady outer wall temperature so that the temperature on the inside was also stable throughout the experiment. A back pressure regulator (BPR) was installed at the downstream of the tubular reactor. A pre-set desired value was given as a reference pressure to the BPR so that, that exact pressure was maintained on the upstream of BPR i.e. in the reactor. The reaction mixture exiting from the reactor is still close to reaction temperature which is cooled to room temperature in an

after-cooler (8). Cooled reaction products then are collected into product collection vessel (9).

Preliminary experiments were carried out to estimate the required residence time. The flow in the reactor falls under laminar flow regime at such residence time values. In laminar flow reactors there is significant axial dispersion which may deteriorate the reactor performance. This problem has been addressed in literature with sufficient rigour and the impact of having coiled reactor configuration to enhance mixing has been studied. The extent of axial dispersion in tubular reactor has been expressed in literature in the form of dimensionless Péclet number. It is shown that there is at least three fold decrease in axial dispersion in a laminar flow coiled reactor compared to a straight tube with same flow rates. This has been attributed to the secondary flows getting generated due to the curvature of the flow geometry which promotes mixing thereby reducing the axial dispersion. Such coiled reactor can achieve performance level close to a PFR. More information is found in literature such as Janssen¹⁸, Saxena and Nigam¹⁹ etc. Therefore we have designed the tubular reactor in the form of a helical coil. This reactor was followed by a stripper (not shown in Figure 3) where ammonia concentration was reduced to almost nil with the help of inert gas sparging.

Experimental procedure

Experiments were performed as per the procedure given here in order to achieve consistent performance and smooth operation. At first urea+methanol mixture was charged into the storage/feed vessel (1) as shown in Fig. 3. Then desired pressure was taken inside reactor (downstream of BPR (10) and upstream of pump (3)). The pressure of reaction was chosen such that all the reactants remain in the liquid phase at the reaction temperature. Pump (3) was started with desired flow rate and the material was allowed to pass through the reactor. Once the reactor was full i.e. after passage of time equal to the residence time of reactor, the heaters installed on the reactor wall were fired to attain appropriate temperature. The material inside the reactor took some time to reach to the desired temperature and once that temperature was achieved the time was noted as the starting point of the reaction. Throughout the experiment steady flow and temperature profile was maintained inside the reactor. The temperature profile was monitored through thermocouples mounted along the length of reactor at specific intervals.

The experiment was continued till a definitive steady state was achieved which usually was time equivalent to 4 residence times. Cumulative samples were collected after experiments and were analyzed using GC and HPLC to quantify raw materials and products. Analysis of urea was conducted by HPLC whereas alkyl carbamate concentration was quantified by GC. When synthetic mixtures in the expected range were analysed for raw materials as well as products, less than 3% error was observed in estimation.

Estimation of kinetic parameters

Experiments were performed with the tubular reactor configuration for different flow rates and temperatures. For each temperature above mentioned procedure was carried out for one flow rate and then the flow rate was changed to obtain the next steady state. Urea conversion obtained as a function of residence time for different temperatures is shown Fig. 5. The error in analysis of samples reflected into conversion was about 0.8%. Experiments were performed at various temperatures. Different flowrates are represented in the form of residence times. We have performed kinetic analysis based on the data obtained. Since the reaction is reversible the kinetic data obtained was fitted against the kinetic expression given in Equation (8). Concentration of all components were expressed as a function of initial concentration of urea (see Eq (9)).

$$r_U = k_f \left(C_U C_{ME} - \frac{1}{K_{eq}} C_{MC} C_N \right) \quad \dots (8)$$

$$C_U = C_{U,L}^{in} (1 - X); C_{ME} = C_{U,L}^{in} (\alpha - X); \\ C_{MC} = C_N = C_{U,L}^{in} X \quad \dots (9)$$

The equilibrium constants estimated earlier were taken and regression was carried out to estimate the rate constant of reaction. The result of this fitting procedure is shown in Fig. 4 for the temperature of T1. On the X-axis of Figs 4 and 5, the residence time is given in arbitrary units [au] due to restriction posed by confidentiality of the work. The experimental data is represented by points and the fitted trend is shown as line. It is clear that the fit obtained is poor. The trend of fitted curve is more flat than the experimental data indicating the possibility of inaccurate estimation of the reaction equilibrium. Therefore a two parameter fit i.e. taking equilibrium constant and forward reaction rate constant as adjustable parameters was attempted.

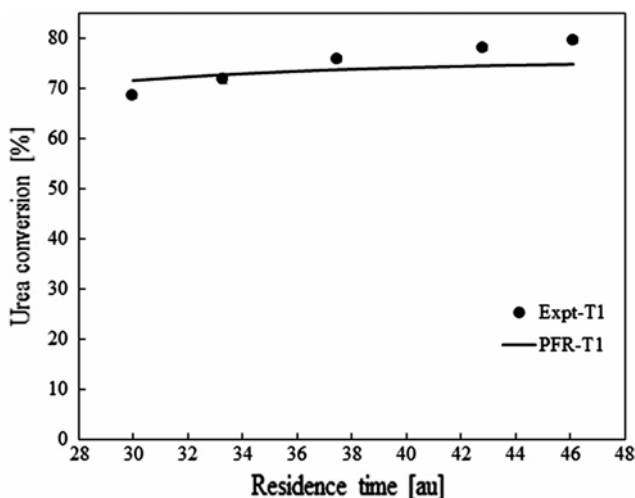


Fig. 4 — Result of fitting to kinetic data by adjusting reaction rate constant at T1 with equilibrium constant taken from theoretical calculation

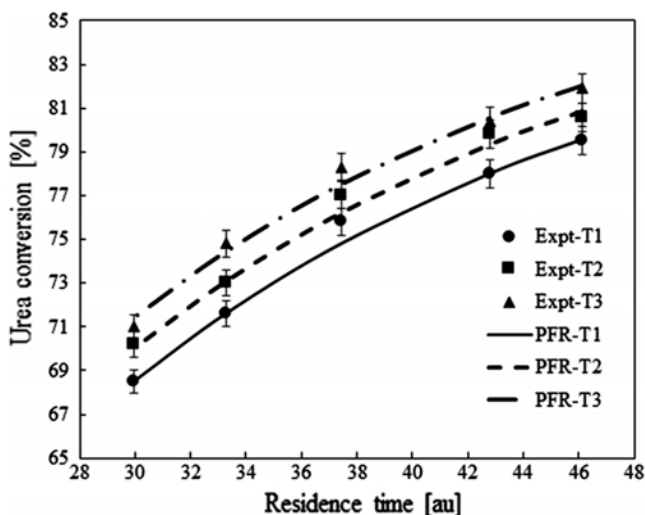


Fig. 5 — Data fits for kinetic data for with reaction rate constant and equilibrium constant as adjustable parameters

This data was regressed and parameters were estimated. These rate equations were inserted into a standard steady-state PFR model. A non-linear least square estimation was performed and as given in the objective function described in Eq (10) the summation of difference between experimental and calculated values of urea conversion was minimized.

$$\min_{K_{eq}, k_f} f(K_{eq}, k_f) = \sum_{j=1}^m (X_{exp} - X_{calc})^2 \quad \dots (10)$$

Since this was a multi-parametric optimization problem, the 'fminsearch' function in MATLAB was used with appropriate tolerances. The data fits along with the experimental data in the form of points and

the fitted trend-lines are shown in Fig. 5. The quality of fit obtained is good. There was significant difference between calculated value of equilibrium constants and experimentally fitted values of equilibrium constants. This can be attributed to unavailability of reliable thermodynamic data for carbamates. We found that slight error in estimation of properties such as enthalpy of formation and entropies can result in significant difference in the value of equilibrium constant completely changing the characteristic of reversibility of the reaction. The estimated values of rate constant of formation of alkyl carbamate reactions were in the range of Damköhler number 1 to 100 and the equilibrium constant for the reactions were in the range of 0.2 to 0.8. Systematic reaction engineering analysis for selecting appropriate reactor configuration for reversible reaction of alkyl carbamate using the range of kinetic and equilibrium constants in this work is discussed in the following.

Selection of reactor configuration

Equilibrium limited reactions often require reactive separations because in situ removal of one or more products from reaction zone pushes the equilibrium towards the products side. The case of alkyl carbamates in which ammonia may have to be removed is considered here. In situ removal of ammonia by stripping would accomplish higher conversion than equilibrium conversion values in shown Fig. 2. Unlike the cases with very small equilibrium constant (where simultaneous removal of one of the products is essential) or very large equilibrium constant (where simultaneous removal is not necessary), the choice of reactor configuration for the cases of alkyl carbamates is not obvious because of intermediate value of equilibrium constants (0.2 to 0.8) and reaction rates (Damköhler number 1 to 100). In order to arrive at appropriate reactor configuration of alkyl carbamates, systematic reaction engineering analysis was carried out.

Classical reaction engineering models were developed to simulate different configurations of alkyl carbamates based on simultaneous or sequential operations of reaction and separation in single or multistage reactors. The schematic for the arrangement of reactors in sequential and simultaneous stripping are shown in Fig. 6. In sequential mode the stripping operation is discrete. Here we assumed that all of the ammonia generated in the previous reactor is removed in stripper and then the material without ammonia passes on to the next

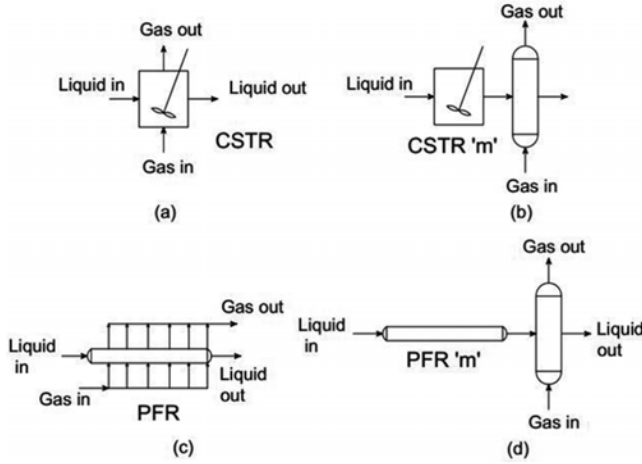


Fig. 6 — Reactors with Simultaneous and Sequential stripping modes (a) CSTR with simultaneous stripping; (b) CSTR with sequential stripping ('m' CSTRs and strippers); (c) PFR with simultaneous stripping; (d) PFR with sequential stripping ('m' PFRs and strippers)

reactor. This analysis was carried out for the limiting cases of back-mixing in reaction phase i.e. CSTR and PFR.

Model equations

Simple mathematical models were developed and simulations were performed to evaluate different configurations shown in Fig. 6 for a range of equilibrium constants and Damköhler numbers. In order to retain the simplicity, stripping was assumed to be complete in the sequential mode and stripping was assumed to be controlled by liquid phase mass transfer. These assumptions allow us to ignore gas phase mass balances. The dimensionless forms for overall liquid phase mass balances (see Eqs (11) and (13) for CSTR and PFR respectively) and component balances (Eqs (12) and (14) for CSTR and PFR respectively) are as follows:

CSTR with stripping

Overall mass balance

$$1 - \bar{q}_L^o \bar{\rho}_L - \frac{Da'' \sum_{i=1}^n (\bar{C}_{iL} - \bar{C}_i^*)}{\sum_{i=1}^n \bar{C}_{iL}} = 0 \quad \dots (11)$$

Component balance

$$\bar{C}_{iL}^i - \bar{q}_L^o \bar{\rho}_L \bar{C}_{iL} + Da' \varepsilon_L V_i \left(\bar{C}_U \bar{C}_{ME} - \frac{1}{K_c} \bar{C}_{MC} \bar{C}_N \right) - Da'' (\bar{C}_{iL} - \bar{C}_i^*) = 0 \quad \dots (12)$$

PFR with stripping

Overall mass balance

$$\frac{d\bar{q}_L}{d\bar{v}} = \frac{-Da'' \sum_{i=1}^n (\bar{C}_{iL} - \bar{C}_i^*)}{\sum_{i=1}^n \bar{C}_{iL}} \quad \dots (13)$$

Component balance

$$\frac{d\bar{F}_{iL}}{d\bar{v}} = Da' \varepsilon_L V_i \left(\bar{C}_U \bar{C}_{ME} - \frac{1}{K_c} \bar{C}_{MC} \bar{C}_N \right) - Da'' (\bar{C}_{iL} - \bar{C}_i^*) \quad \dots (14)$$

Definition of included dimensionless parameters are given in Equation (15) and (16). Da^I is the Damköhler number defined for the rate of second order reaction and Da^{II} is the Damköhler number for rate of mass transfer as defined in Equation (16). For sequential stripping the Da^{II} was set to 0 and complete removal of ammonia was assumed in a separation stage after the reactor. Dimensionless quantities defined are:

$$\bar{q}_L^{in} = \frac{q_L^{in}}{q_L^{in}}; \bar{q}_L^o = \frac{q_L^o}{q_L^{in}}; \bar{C}_{i,L}^{in} = \frac{C_{i,L}^{in}}{C_{U,L}^{in}}; \bar{C}_{i,L} = \frac{C_{i,L}}{C_{U,L}^{in}}; \bar{C}_{i,L} = \frac{C_{i,L}}{C_{U,L}^{in}}; \bar{C}_i^* = \frac{C_i^*}{C_{U,L}^{in}} \quad \dots (15)$$

$$\bar{\rho}_L = \frac{\rho_L}{\rho_L^{in}}; \tau = \frac{V_R}{q_L^{in}}; Da^I = k_f \tau C_{U,L}^{in};$$

$$Da^{II} = k_L a \tau \quad \dots (16)$$

These model equations of overall and component mass balance were solved simultaneously using MATLAB. For CSTR model the equations are non-linear algebraic equations and inbuilt 'fsolve' function was used to solve them. PFR model consists of first order ordinary differential equations for which 'ODE 45' function of MATLAB was used.

Results and Discussion

Reaction engineering analysis and discussion

Though the range of Damköhler number relevant to alkyl carbamate systems is from 1 to 100, here we present results over much wider range of Damköhler number for the sake of completeness. For the sake of brevity, only sample of results are presented here (at values of $K_{eq} = 0.5$ and number of stages, $m=4$). The

ratio $Da^{\text{II}}/Da^{\text{I}}$ describes the ratio of dimensionless mass transfer rate to that of the dimensionless reaction rate. In the classical literature of gas-liquid reactions where a fast reaction taking place in film assists mass transfer, the corresponding enhancement factor is defined as the ratio of mass transfer with chemical reaction to that of without chemical reaction²⁰. In this work we have developed our analysis which is analogous to the earlier described more common phenomenon where we are describing the enhancement factor as improvement in reaction because of mass transfer defined as the ratio of $Da^{\text{II}}/Da^{\text{I}}$. Typical simulated results are shown in Figs 7 and 8.

It can be seen from Fig. 7 that the conversion profile of the reactor exhibits distinct zones or

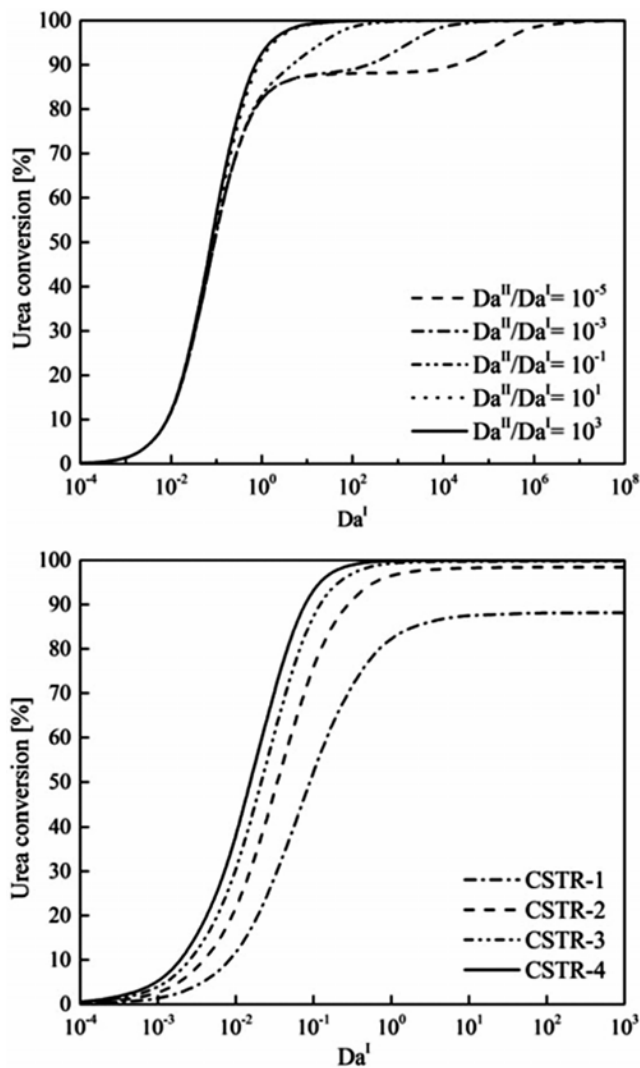


Fig. 7 — CSTR performance for simultaneous stripping (left) and sequential stripping with $m = 4$ (right) $K_{\text{eq}} = 0.5$

regimes. There is sharp increase in the conversion with respect to Da^{I} initially which flattens eventually as the value approaches equilibrium conversion value for the equilibrium constant value of 0.5. The slope of the curve remains flat and this regime is dominated by limitations posed by chemical equilibrium as the mass transfer rate is not high enough to effectively remove ammonia from the reaction zone. It is noteworthy that for CSTR operating for the same value of dimensionless reaction rate and at a certain value of dimensionless mass transfer rate where the chemical equilibrium prevails the reactor will not be able to achieve conversion beyond the value at equilibrium. At these values of Da^{I} and Da^{II} the liquid phase in reactor is saturated with ammonia. The saturation of ammonia inferred here is from viewpoint of the

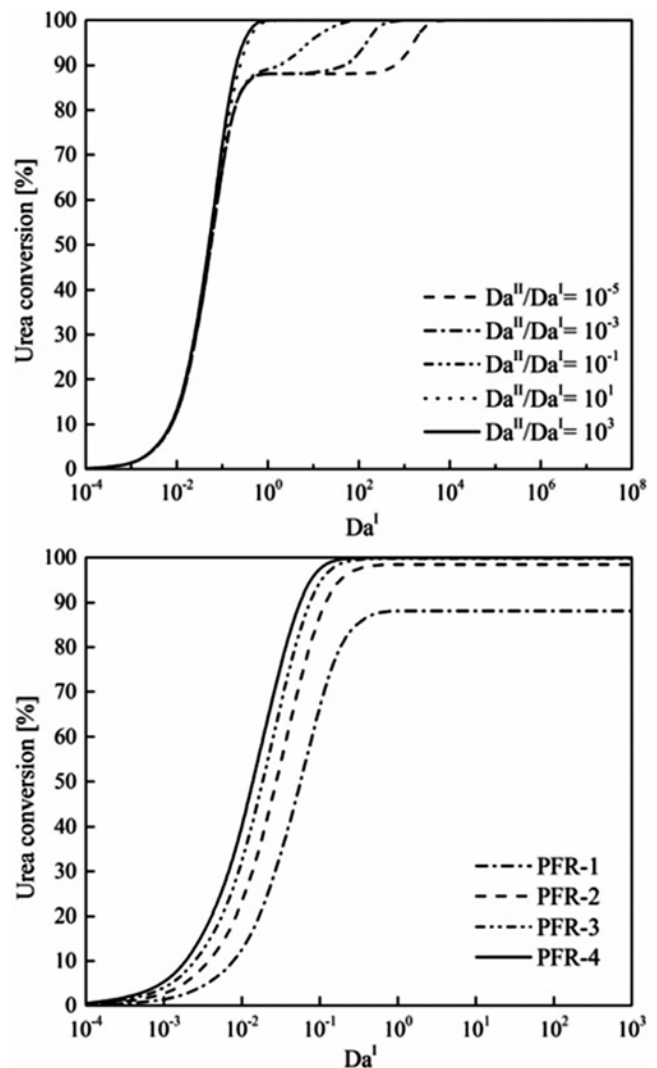


Fig. 8—PFR performance for simultaneous stripping (left) and sequential stripping with $m=4$ (right) $K_{\text{eq}} = 0.5$

reaction (chemical) and not the physical (solubility). In the right part of Fig. 7 we can clearly see that the value of urea conversion stops at the corresponding equilibrium value same as depicted in the equilibrium dominated region of simultaneous stripping. In the case of simultaneous stripping, as the value of Da^I increases beyond a threshold the reactor overcomes the equilibrium barrier and complete conversion is achieved mainly because the value of Da^{II} also increases for the fixed ratio of Da^{II}/Da^I .

For higher ratios of Da^{II} to Da^I , the mass transfer rates are sufficiently high so that the conversion in reactor never realizes the region dominated by the chemical equilibrium. In simultaneous stripping plot (e.g. see left part of Figs. 7 and 8) the trend for enhancement factor for effect of fast reaction on mass transfer rate is included. The simulations of simultaneous and sequential stripping were performed for same reactor volume. For sequential mode of stripping, once the equilibrium conversion is achieved in one reactor, it passes through following stripper where ammonia is removed. In this work we have not performed simulation of stripping but simply removed ammonia from the mixture and rest of the components (Urea, methanol and MC) were transferred to the next reactor. Due to removal of ammonia the reaction would go forward and attain a next step of ammonia saturation in the next reactor. This process was repeated 'm' times and the conversion trends are shown as reactants progress through reactors-separators in series for $m=4$. If the equilibrium constant of the reaction is sufficiently high, number of subsequent reactors required to achieve substantial conversion would decrease. For example to achieve a conversion of more than 90%, two reactors are sufficient for the value of equilibrium constant of 0.5 (see Fig. 8).

If we compare the performance of CSTR to that of PFR (Figs 7 and 8), as expected the same performance can be achieved much faster in PFR. Since ammonia dissolved in the liquid phase in CSTR is more diluted than in PFR the conversion in CSTR requires higher residence time. In PFR the ammonia is removed more effectively along the length as it forms and therefore the conversion is faster. In simultaneous stripping mode the complete conversion is achieved in two orders of magnitude faster in PFR than in CSTR for the lowest value of Da^I . In the case of sequential stripping there is a difference of one order of magnitude between PFR and CSTR.

Practical implementation of simultaneous stripping in PFR would be possible by having small CSTR's in series with continuous removal of ammonia or ideally in membrane type of reactor where reaction products are removed through wall. It is also noteworthy that in the initial regime of urea conversion, the performance of sequential and simultaneous stripping is similar. Afterwards the performance mainly depends upon the mass transfer rate. In sequential mode we can stop the reaction at the end of region 1 and take advantage of the fast initial response of reaction. In simultaneous reaction-separation the reactor performance would depend on the effectiveness of mass transfer. If the products remain at reaction temperature for extended periods of time the selectivity of alkyl carbamates may decrease due to probable side reactions. In sequential stripping we avoid this because the separation is carried out at lower temperature and pressure, significantly lowering the likelihood of undesired reactions. Analysis shows that for this reaction sequential reactor-separation is sufficient to get substantial conversion of urea even for $Da^I = 1$. Based on this analysis a tubular reactor and a sequential reactor-separator configuration is recommended.

Conclusion

Reaction engineering analysis of urea alcoholysis has been carried out based on experiments as well as simplified mathematical models. It is observed that values of equilibrium constants obtained from fitting the experimental data of tubular reactors with kinetic models are higher than those estimated theoretically. Considering the uncertainties in estimation of key thermodynamic properties required for calculation of equilibrium constants, experimental estimation is recommended. The obtained values of equilibrium constants are in the range of 0.2 to 0.8 indicating that in-situ removal of ammonia may not be essential. Experimental data from tubular reactors is also used to obtain key kinetic parameters. The range of Damköhler number values for alkyl carbamates is found to be 1 to 100. Systematic reaction engineering analysis was carried out to evaluate simultaneous and sequential removal of ammonia from reacting mass using multi-stage reactors (either CSTR or PFR). It is observed that in the simultaneous stripping mode a threshold of mass transfer is required to overcome for the reaction to get out of equilibrium controlled region. The analysis shows that for the alkyl carbamate system, sequential reactor-separation is adequate to achieve substantial conversion of urea

even for $Da^I = 1$. Based on this analysis two reactors in series with a separator in between with tubular reactor as the reactor of choice is recommended for the urea alcoholysis to carbamates reaction.

Nomenclature

Symbol	Details
a_i	Liquid phase activity of component 'i'
C_i	Concentration of component 'i' [$\text{kmol}/(\text{m}^3)^{-1}$]
C_i^*	Concentration of component 'i' in gas phase [$\text{kmol}/(\text{m}^3)^{-1}$]
$C_{i,L}^{in}$	Inlet concentration of component 'i' [$\text{kmol}/(\text{m}^3)^{-1}$]
$\bar{C}_{i,L}$	Dimensionless concentration of component 'i'
$\bar{C}_{i,L}^{in}$	Dimensionless concentration of component 'i' coming in
$Cp_{i,s}$	Heat capacity of component 'i' for state 's' [$\text{kJ kmol}^{-1} \text{K}^{-1}$]
Da^I	Damköhler number for reaction
Da^{II}	Damköhler number for mass transfer
$F_{i,L}^{in}$	Molar flow rate of component 'i' arriving in reactor [kmol s^{-1}]
$\bar{F}_{i,L}$	Molar flow rate of component 'i' in reactor, Dimensionless
f_i^G	Fugacity of component 'i' in gas phase [kPa]
$f_{i,Pure}^L$	Pure liquid phase fugacity of component 'i' [kPa]
$\Delta_r G^o$	Gibbs free energy change for reaction at standard conditions [kJ kmol^{-1}]
$\Delta_r G(T)$	Gibbs free energy change for reaction at reaction temperature [kJ kmol^{-1}]
$\Delta_r H^o$	Enthalpy change for reaction at standard conditions [kJ kmol^{-1}]
$\Delta_r H(T)$	Enthalpy change for reaction at reaction temperature [kJ kmol^{-1}]
$\Delta H(i)$	Enthalpy change required to bring component 'i' from one temperature to another [kJ kmol^{-1}]
ΔH_{Prod}	Enthalpy change required to bring products from one temperature to another [kJ kmol^{-1}]
ΔH_{React}	Enthalpy change required to bring reactants from one temperature to another [kJ kmol^{-1}]
i	Component i involved in the reaction
K_{eq}	Equilibrium constant
k_f	Forward reaction rate constant, second order [$\text{m}^3 \text{kmol}^{-1} \text{s}^{-1}$]
$k_L a$	Volumetric mass transfer coefficient [s^{-1}]
K_x	Mole fraction ratio
K_γ	Activity coefficient ratio
MW_i	Molecular weight of component 'i' [kg kmol^{-1}]

n	Number of components
q_L^{in}	Inlet flow rate of liquid [m^3/s]
q_L^o	Outlet flow rate of liquid [m^3/s]
\bar{q}_L	Dimensionless liquid flow rate
R	Universal gas constant [$\text{kPa m}^3 \text{kmol}^{-1} \text{T}^{-1}$]
$\Delta_r S^o$	Entropy change for reaction at standard conditions [$\text{kJ kmol}^{-1} \text{K}^{-1}$]
$\Delta_r S(T)$	Entropy change for reaction at reaction temperature [$\text{kJ kmol}^{-1} \text{K}^{-1}$]
$\Delta S(i)$	Entropy change required to bring component 'i' from one temperature to another [$\text{kJ kmol}^{-1} \text{K}^{-1}$]
ΔS_{Prod}	Entropy change required to bring products from one temperature to another [$\text{kJ kmol}^{-1} \text{K}^{-1}$]
ΔS_{React}	Entropy change required to bring reactants from one temperature to another [$\text{kJ kmol}^{-1} \text{K}^{-1}$]
T	Reaction temperature [K]
V_R	Volume of reactor [m^3]
v	Differential element of reactor volume under consideration in plug flow reactor [m^3]
\bar{v}	Differential element of reactor volume, Dimensionless
X	Conversion of urea
x_i	Mole fraction of component 'i'

Greek symbols

ρ_L	Liquid density [$\text{kg} (\text{m}^3)^{-1}$]
ρ_L^{in}	Liquid density [$\text{kg} (\text{m}^3)^{-1}$]
$\bar{\rho}_L$	Liquid density dimensionless
τ	Residence time [s]
ν_i	Stoichiometric coefficient

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