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OJONG, O.E., AKPA, J.G., DAGDE, K.K. and AMADI, D.

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Rate expression model from thermodynamics application and optimal kinetic parameters determination for urea synthesis and production process

O.E. Ojong^{a,*}, J.G. Akpa^b, K.K. Dagde^b, D. Amadi^c

^a Department of Chemical Engineering, Faculty of Engineering and Technology, University of Calabar, Calabar, Cross River State, Nigeria

^b Department of Chemical/Petrochemical Engineering, Faculty of Engineering, Rivers State University, Nkpulu Oroworukwo Port Harcourt, Rivers State, Nigeria

^c School of Engineering, Robert Gordon University, Garth Dee Rd, Garth Dee, Aberdeen, AB10 7G, United Kingdom

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ABSTRACT

Urea, an essential organic fertilizer, enhances soil fertility by providing 0.466 nitrogen for maximum crop yield. In this study, urea is synthesized from NH_3 and CO_2 in an equilibrium reaction process adhering to Le Chatelier's principle, maintained under process conditions: flow rate of 63.5 kg/s, temperature of 184 °C, and pressure of 160 kg/cm². A new rate expression model, formulated in terms of extent of reaction and mole fraction, was developed based on mass action relations and thermodynamic models. Two industrial reactors were considered: a plug flow reactor (PFR) at Notore and a continuous stirred tank reactor (CSTR) at Indorama plants. Transient reactor models, based on material and energy balance conservation principles, were numerically resolved using MATLAB version 2020 with specified input conditions. A non-linear regression statistical optimization model was employed to refine kinetic parameter values, ensuring optimal and high-quality urea yield. Model validations were conducted using literature data, revealing higher urea yields of 0.726 and 0.7032 for the CSTR and PFR, respectively. Deviations (0.134, 0.10 to 1.135 and 0.635, 0.326 to 0.850) and root mean square errors (RMSE) (0.043, 0.033 to 0.193 and 0.137, 0.087 to 0.162) were observed when validated against plant and literature values for the CSTR and PFR respectively. The refined kinetic parameters (activation energies, Arrhenius constants, and rate constants) exhibited negligible deviations (0.0004–0.0466 and 0.0004 to 0.0491) and RMSE (0.0228, 0.0055, and 0.0256 and 0.0241, 0.0096, and 0.0269) when validated against plant data, significantly enhancing urea yield in CSTR and PFR reactors respectively.

1. Introduction

Urea is an essential nitrogenous fertilizer whose utilization has steadily increased, making it a preferred nitrogen fertilizer worldwide due to its composition containing 0.466 N₂ as a chemical element that enriches soil [1]. Urea is a white, colorless, hygroscopic solid and non-corrosive substance with a molecular weight of 60.05 g/mol, a relative humidity of 0.6, a specific gravity of 1.335, and a heat of fusion of 60 cal/g. Its heat of solution in H₂O is 58 cal/g, and it has a bulk density of 0.74 g/cc [1,2].

In the agricultural industry, urea is widely used as an organic fertilizer, with approximately 0.56 and 0.31 fractions used as solid and liquid fertilizers, respectively. Additionally, about 0.13 fraction is used in urea and melamine formaldehyde resins and adhesives [2–4]. Urea

accounts for more than half of the nitrogen fertilizer market, with global demand increasing significantly over recent decades. In terms of energy, urea is considered a hydrogen-storage compound (6.71 wt%) and ammonia-storage compound (56.7 wt%), giving it fuel potential. Its crystalline structure allows for safe storage and transportation, meeting the US Department of Energy's requirements for hydrogen-storage substances [2].

Urea is also utilized in photocatalytic processes, where approximately 0.66 fraction combines with TiO₂-CeO₂ for the photodegradation of paracetamol [5].

In pursuit of Sustainable Development Goal 2, Nigeria, as a developing country, focuses on the agricultural sector for food security, particularly by providing farmers with sufficient organic fertilizers to enhance crop yields. The country has established urea manufacturing

* Corresponding author.

E-mail addresses: ojong.ojong@unical.edu.ng (O.E. Ojong), akpa.jackson@ust.edu.ng (J.G. Akpa), dagde.kenneth@ust.edu.ng (K.K. Dagde), d.amadi@rgu.ac.uk (D. Amadi).

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companies such as Indorama and Notore plants through collaborations with foreign groups and individuals, aimed at producing adequate urea for Nigeria, Africa, and parts of Asia [6–8].

Urea is synthesized from various feed materials depending on the production route, CO₂ emissions released as pollutants, and the quantity and quality of the product. For example, urea is manufactured from natural gas, where ammonia and CO₂ are significant secondary feed materials [9,10]. It is also synthesized from biogas obtained from cow dung [11] on a pilot scale, urine from animals in small amounts [4], and via biomass gasification processes for green urea on a pilot scale [12]. Environmentally friendly methods include using CO₂ in amine-based adsorbents [13], and processes using NaOH and fly ash [14] that minimize pollutants. Additionally, urea can be synthesized via simultaneous photocatalyzed reduction of CO₂ and nitrogen compounds using TiO₂-based materials [2], which is cost-effective but typically on a small scale.

Various rate expression models for urea synthesis from different feed materials and routes have been reviewed. For instance Ref. [15], developed a first-order rate model based on the partial pressure of CO₂, considering ammonia as the limiting reactant. Their process conditions in the carbamate reactor were at 190 °C and 140 bar, yielding 0.46 compared to the plant's simulated value of 0.43 using a steady-state mole fraction reactor model [16]. [17] applied the Soave Redlich-Kwong equation of state thermodynamic model as the fluid package to simulate high-pressure and temperature carbamate reactions. They operated at 188 °C and 155 bar, achieving a urea yield of 0.6 by weight without defining a specific rate expression or reactor model [18]. [17] studied the reaction rate, focusing on the slow step i.e. the dissociation of carbamate to urea and water, an endothermic stage with a heat of reaction of 32 kJ/mol. They obtained a urea yield of 0.53 from NH₃-CO₂ feed materials under process conditions of 155 °C and 60–90 min [19]. experimentally synthesized urea from NH₃ and CO₂, yielding between 0.198 and 0.34 depending on temperatures ranging from 140 °C to 150 °C over 4 h. Optimal synthesis temperature of around 184 °C were recommended [20]. achieved an overall urea yield of 0.23 from a 0.60 conversion of CO₂ and excess NH₃, without developing a specific rate expression model, using feed materials derived from methane or biogas steam reforming processes. They applied unsteady-state material and energy balance principles to develop transient concentration and temperature models for urea synthesis reactor with a biogas ratio of 14.8, simulated numerically to determine yields [16].

Notably [10], demonstrated urea production from natural gas with zero CO₂ emissions using UNISIM software to simulate an entire proposed plant. Their process comprised four subsections: steam methane reforming, gaseous separation, ammonia synthesis, and urea synthesis. Section one, producing urea and H₂ with a molar feed flow rate of O₂ > 0.383, was more profitable than section two, which produced urea and power with a molar feed flow rate of 0 < O₂ < 0.383. Industrial examples include Indorama and Notore plants, where urea is produced from natural gas and NH₃-CO₂ as primary feed materials, achieving yields of 0.64 and 0.53, respectively [21,22]. Following concentration in absorbers and evaporators, purity levels of up to 0.98 are attained [23]. conducted a techno-economic analysis of ammonia and urea production processes, revealing that the overall expenditure on feed materials comprised 0.45 shaft work, 0.39 hot fluid, 0.003 coolant, and 0.13 refrigerant for the process plant [24]. emphasized urea as a reliable, biodegradable nitrogenous organic fertilizer, providing optimal plant growth due to its high N₂ content (45 %–60 %) as a macro-nutrient compared to non-renewable fertilizers, which pose greater environmental impacts due to their weaker sustainability [25]. proposed the Bosch-Meiser technology for small-scale urea synthesis, aiming to reduce greenhouse gas emissions to 0.021. This electrochemical process involves urea production from nitrates and CO₂.

[26] Studied the kinetics of ammonia-urea synthesis via model development and computer software simulation with plant data [27,28]. successfully optimized the activation energies, Arrhenius constants, and

rate constants (with minimal deviation values ranging from 0.0002 to 0.18) of the forward and reversible reaction processes when paraffinic hydrocarbon was cracked in a furnace reactor to naphthene, aromatics, and gas (C1-C3) compounds using non-linear statistical search regression models.

Over the years (from 1999 to 2018), urea production capacity was about 5.8 million tons [6], insufficient to meet global demand by 2023 due to the increasing world population [7] (<https://www.ifastat.org>). Nowadays, global urea production reaches 229 million tons per year; however, urea consumption is projected to increase significantly, from 8.9 million hectares in 2007 to 46.6 million hectares in 2024, equating to over 89.3 million tons per year. This demand is driven by its extensive use in fertilizers for the agricultural industry, polymers as adhesives, and chemicals for resins and catalytic activities (<https://www.statista.com>). Consequently, there is a pressing need to increase urea production to meet global demand as the world's population continues to grow daily (<https://www.spglobal.com>).

Due to high demand in sustaining Nigeria's agricultural sector for food security and other functions, there is a necessity to significantly increase urea production owing to the rising population [7]. From the literature reviewed, it is deduced that the most effective method to produce urea in large quantities involves using NH₃ - CO₂ feed materials obtained from the natural gas steam reforming process, due to the relatively small and controllable amount of greenhouse gases emitted. A well-defined rate expression model for the synthesis reaction process is crucial in optimizing the kinetic parameters to enhance urea quality and yield within the reactor.

This study focuses on utilizing ammonia and CO₂ as feed materials for urea synthesis within reactors on a large scale. A case study will examine continuous stirred tank reactors (CSTRs) in series and tubular or plug flow reactor (PFR) as implemented industrially in plants like Indorama and Notore, respectively. The rate expression model will be developed based on the extent of reaction or reaction coordinate and the application of thermodynamic models. Optimizing the kinetic parameters of the synthesis reaction using suitable statistical optimization tools will determine optimal yields for both reactor types, essential for reactor design and optimization purposes.

2. Materials and method

2.1. Materials

The materials used for this article are laptops, reference books (text-books and journals), physiochemical data of the raw materials (carbon dioxide gas and ammonia liquid charts), products (urea and water data), thermodynamic data, F-distribution table, and plant data.

2.1.1. Urea process description

The urea production process is based on two different reactors: the CSTR and PFR, observed and implemented at two distinct plants in Nigeria, particularly in the Niger Delta Region, specifically in the Eleme Local Government Area of Rivers State [29]. These plants, namely Indorama Eleme Fertilizer and Chemical Limited (IEF&CL) and Notore urea plants, are situated in Rivers State and are dedicated to producing significant quantities of nitrogenous fertilizer for both local and international consumption [21,22]. The production processes for both plants are similar, with nearly identical process conditions and feed materials, except that the IEF&CL urea reactor comprises a system of CSTRs in series, while the Notore urea reactor is a PFR known as a carbamate reactor.

2.1.2. Process conditions for urea production

The Indorama urea plant utilizes a series of Continuous Stirred Tank Reactors (CSTRs) housed within a Vertically Submerged Carbamate Condenser (VSCC) where urea is produced. The VSCC operates at an ammonia-carbon dioxide ratio (N/C) of 2.8–3.0, at a high temperature

range of 180 °C–182 °C, and a high pressure of 155 kg/cm²G. The primary two-stage reactor operates at an N/C ratio of 3.7, with a residence time of 2.5 min. Inert gas is fed into the reactor at only one-fifth of the amount used in conventional CO₂ stripping processes, achieving a high CO₂ conversion rate of 63–64 % at temperatures ranging from 182 °C to 184 °C and a pressure of 155 kg/cm²G.

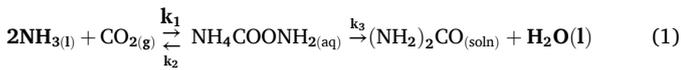
The Notore plant features a High-Pressure Carbonate Converter (HPCC), functioning as a Plug Flow Reactor (PFR) where a portion of the raw materials' conversion to urea occurs. Liquid NH₃ is pumped from the NH₃ Surge Drum through the NH₃ booster pump to the NH₃ heater (operating at a temperature of 131.4 °C), and also from the NH₃ heater into the HPCC [16; 18b]. The optimal operating conditions include a temperature of 183 °C, a residence time of 3.7 min, CO₂ conversion efficiency of 53 %, a pressure of 160 kg/cm²G, and an N/C ratio of 3.3.

2.2. Method

The method is theoretical, qualitative, and analytical. Procedures include developing the rate expression for the equilibrium reaction process of urea synthesis based on reaction coordinates or extent of reaction, mole fraction of components, and applying thermodynamic models, especially the van't Hoff equation [30]. Determination and optimization of kinetic parameters for optimal yield from reactor design and modeling of the urea production process are based on the application of nonlinear regression models [28].

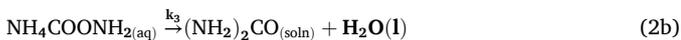
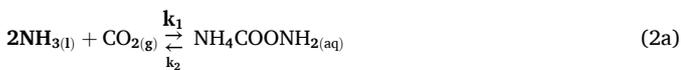
2.2.1. Development of the rate expression model for urea production from extent of reaction

Urea synthesis involves an equilibrium reaction process where NH₃ and CO₂ react to form an intermediate compound called ammonium carbamate. This compound slowly dissociates to produce urea and water in solution. The rate model is expressed as a function of the extent of the reaction (reaction coordinates), based on the mass action relationship and thermodynamic models involving the van't Hoff equation [30] and fugacity functions applied to express individual component rates for urea synthesis. The synthesis reaction follows an equilibrium process (see equation (1)):



where, k_1 is the rate constant for the forward reaction, k_2 is the rate constant for the backward reaction, and k_3 is the rate of reaction for the dissociation of ammonium carbamate to yield urea and water.

Equation (1) is a consecutive reaction divided into exothermic [21] and endothermic parts [31], as shown in equations (2a) and (2b), respectively.



The overall reaction rate was investigated through stage II, where the total change in heat of reaction equalled -33 kcal/mol, derived from the individual heat of reactions of $\Delta H_R = -38.5$ kcal/mol and $\Delta H_R = +5$ kcal/mol in equations (2a) and (2b), respectively. The algorithm for the development of the rate expression are as follows:

- (i) The rates of formation of carbamate and urea (2a and 2b) are expressed as terms of the relative reaction rates based on the principle of mass action [32,33], as explained mathematically in equations (3a) and (3b), respectively as

$$\frac{(-r_1)}{-2} = \frac{(-r_2)}{-1} = \frac{(-r_3)}{1} \quad (3a)$$

where, $(-r_1)$ is the rate of depletion of ammonia, $(-r_2)$ is the rate of depletion of CO₂, and $(-r_3)$ is the rate of formation of ammonium carbamate.

$$\frac{(-r_3)}{-1} = \frac{(-r_4)}{1} = \frac{(-r_5)}{1} \quad (3b)$$

where $(-r_3)$ is the rate of dissociation of ammonium carbamate, $(-r_4)$ is the rate of formation of urea, and $(-r_5)$ is the rate of formation of water. Equations (3a) and (3b) are combined to obtain the overall rate of urea formation as follows:

$$(-r_4) = -(-r_3)_t = -\{(-r_3)_1 + (-r_3)_2\} \quad (3c)$$

where $(-r_3)_t$ is the overall rate of ammonium carbamate formation, $(-r_3)_1$ is the rate of formation of ammonium carbamate from the exothermic equilibrium reaction (2a), and $(-r_3)_2$ is the rate of dissociation of ammonium carbamate from the endothermic reaction (2b).

- (ii) CO₂ is the limiting reactant as the reaction stops immediately its amount is finished within the reactor and expresses the rate of formation of ammonium carbamate and urea in terms of concentrations of the reactants gives equations (4a) to (4d) as:

$$(-r_3)_1 = (k_1 - k_2)C_1^2C_2 \quad (4a)$$

where C_1 is the concentration of ammonia in the equilibrium reaction [mol/m³], and C_2 is the concentration of carbon dioxide in the equilibrium reaction [mol/m³].

$$(-r_3)_2 = k_3C_3 \quad (4b)$$

where C_3 is the concentration of ammonium carbamate concentration in the reactor. Equations (4a) and (4b) are combined to give the overall rate of ammonium carbamate in the reactor as:

$$(-r_3)_t = (k_1 - k_2)C_1^2C_2 + k_3C_3 \quad (4c)$$

Applying equation (4c) to equation (3c) gives the rate of urea formation in the reactor as follows:

$$(-r_4) = (k_2 - k_1)C_1^2C_2 - k_3C_3 \quad (5)$$

Expressing equation (5) in-terms of Dalton's law of partial pressure [22] and the mole fraction gives

$$(-r_4) = (k_2 - k_1)P_T^3y_1^2y_2 - k_3P_Ty_3 \quad (6)$$

where y_1 is the mole fraction of ammonia in the equilibrium reaction, y_2 is the mole fraction of carbon dioxide in the equilibrium reaction process, y_3 is the mole fraction of ammonium carbamate in the reaction process, and P_T is the total pressure of the system [atm]. The partial pressure of the gas is related to the mole fraction and total pressure of the system as follows:

$$P_i = y_iP_T \quad (7)$$

where P_i is the partial pressure of species i , y_i is the mole fraction of species i .

- (iii) The rate equation for urea formation is expressed as extent of the reaction or the reaction coordinates.

This is possible by designating ξ_1 and ξ_2 as the two reaction coordinates used for equations (2a) and (2b), respectively, which clearly shows the progress of the reaction from reactants to products with various intermediate and transition states in between and also shows the progress of bond breaking and bond formation [34]. The extent of the reaction is the quantity that measures the extent to which the reaction has proceeded or often refers to the extent of the reaction when

Table 1
Mole Fraction of Components in terms of Extent of Reaction.

Component	Initial Amount	Amount Reacted	Exit Amount	Mole Fraction
NH ₃ (1)	n _{1,0}	-2ξ ₁	n _{1,0} - 2ξ ₁	$y_1 = \frac{n_{1,0} - 2\xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1}$
CO ₂ (2)	n _{2,0}	-ξ ₁	n _{2,0} - ξ ₁	$y_2 = \frac{n_{2,0} - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1}$
NH ₄ COONH ₂ (3)	0	ξ ₁ - ξ ₂	ξ ₂ - ξ ₁	$y_3 = \frac{\xi_2 - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1}$
(NH ₂)CO (4)	0	ξ ₂	ξ ₂	$y_4 = \frac{\xi_2}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1}$
H ₂ O (5)	0	ξ ₂	ξ ₂	$y_5 = \frac{\xi_2}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1}$
Total ($\sum n_i$)				$n_{1,0} + n_{2,0} + \xi_2 - \xi_1$

equilibrium has been reached [35,36], defined mathematically as

$$dn_i = \sum v_{i,j} d\xi_j \quad (8)$$

where dn_i is the change in the amount of i-component [mol], v_{i,j} is the stoichiometric coefficient of the i-components in the j-coordinate, and ξ_j is the extent of the reaction in the j-coordinate [mol].

Interms of the reaction co-ordinates ξ₁ and ξ₂, the components are assigned digits as, 1(NH₃), 2(CO₂), 3 (carbamate), 4 (urea), and 5 (water), and the rate expression stoichiometrically in-terms of the extent of reaction or reaction coordinates is expressed mathematically as

$$\frac{dn_1}{-2} = \frac{dn_2}{-1} = \frac{dn_3}{1} = d\xi_1 \quad (9a)$$

$$\frac{dn_3}{-1} = \frac{dn_4}{-1} = \frac{dn_5}{1} = d\xi_2 \quad (9b)$$

Assuming that the reaction started with n_{1,0} moles of NH₃ and n_{2,0} moles of CO₂, the mathematical expressions for v_{i,s} and y_{i,s} as a function of ξ₁ and ξ₂ give the mole fractions of the different species in the equilibrium reaction process summarized in Table 1, and the rate of urea formation interms of the extent of reaction is stated in equation (10), respectively, as

$$\begin{aligned} (-r_4) &= (k_2 - k_1)P_T^3 \left(\frac{n_{1,0} - 2\xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right)^2 \left(\frac{n_{2,0} - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right) \\ &\quad - k_3 P_T \left(\frac{\xi_2 - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right) \end{aligned} \quad (10)$$

2.2.2. Determination of rate constants and equilibrium constants

The following steps were used to study the rate constants and equilibrium constants of the synthesis process.

- (i) The equilibrium constant K_C is defined as the ratio of the rate constant for the forward reaction k₁ to that of the backward reaction k₂ for the equilibrium reaction process in equation (2b), which is defined mathematically as

$$K_P = K_C = \frac{k_1}{k_2} \quad (11)$$

- (ii) The thermodynamic equilibrium constant interms of the change in Gibbs free energy ΔG⁰.

The equilibrium constant K_C or K_P for the concentration of species or partial pressure of gases, as shown in equation (1), relates the ratio of the forward reaction constant to the backward reaction constant. The van't Hoff equation [30] relates the equilibrium constant to the Gibbs free energy to determine the equilibrium constant for the reaction process with the relation given as

$$\Delta G^0 = -RT \ln K_P \quad (12)$$

Equation (13) gives an expression for the equilibrium constant after manipulation (12) as,

$$K_P = \exp \left(-\frac{\Delta G^0}{RT} \right) \quad (13)$$

where ΔG⁰ is the change in Gibbs free energy [kJ/mol] and, R is the gas constant for an ideal gas [J/mol. K] and T is the absolute temperature of the mixture [K].

- (iii) Express the equilibrium constant interms of fugacity, fugacity coefficient, partial pressure, and extent of reaction of the reacting species.

Thermodynamically, the equilibrium rate constant is derived from fugacity, f, and extent of reaction ξ [37]. Because the process is a gas-phase reaction at high pressures and temperatures, fugacity is used as the parameter defined as high pressure values in the reacting system, and the equilibrium constant is defined in-terms of fugacity with unit [atm] as

$$K_P = \prod f^{-v_{ij}} \quad (14)$$

where ∏f^{-v_{ij}} is an operator based on the quotient of fugacity product raised to the respective coefficients v of the j-component to the fugacity of the reactants to the exponent of coefficient v of the i-component defined clearly as

$$\prod f^{-v_{ij}} = \frac{f^{v_j}}{f^{v_i}} \quad (15)$$

where f^{v_j} is the fugacity of the products raised to the power of their stoichiometry and f^{v_i} is the fugacity of the reactants, raising their respective stoichiometric coefficients.

Applying equations (14) and (15) gives,

$$K_P = \frac{f_3}{f_1^2 f_2} \quad (16)$$

where f₁ is the fugacity of ammonia, f₂ is the fugacity of CO₂, and f₃ is the fugacity of ammonium carbamate. The unit of fugacity is the atmosphere, or the unit of pressure. The fugacity coefficient φ is defined in relation to the ratio of the fugacity to the pressure of the k component as follows:

$$\phi = \frac{f_k}{P_k} \quad (17)$$

where φ is the fugacity coefficient, f_k is the fugacity of component k, P_k is the partial pressure of component k, and k is 1, 2, 3, or n defined as component in the reaction process.

$$f_k = \varnothing P_k \quad (18)$$

Applying equation (18) into equation (17) gives,

$$K_p = \left(\frac{P_3}{P_1^2 P_2} \right) \frac{\varnothing}{\varnothing^3} = \left(\frac{P_3}{P_1^2 P_2} \right) \varnothing^{-2} \quad (19)$$

Substituting (7) into equation (19) and further simplification gives,

$$K_p = \frac{k_1}{k_2} = \prod \varnothing (P y_k)^{-v_{ij}} = \frac{y_3}{y_1^2 y_2} \varnothing^{-2} P^{-2} \quad (20)$$

Substituting mole fractions in Table 1 into equation (20) gives,

$$K_p = \frac{\left(\frac{\xi_1 - \xi_2}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right)}{\left(\frac{n_{1,0} + 2\xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right)^2 \left(\frac{n_{2,0} - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right)} \varnothing^{-2} P^{-\xi} \quad (21)$$

Knowing that in the high-pressure system decreases to a lower value because of the aqueous solution of the product formed, the fugacity coefficient becomes unity and equation (21) is transformed to give

$$K_p = \frac{(n_{1,0} + n_{2,0} + \xi_2 - \xi_1)^2 (\xi_1 - \xi_2)}{(n_{1,0} - 2\xi_1)^2 (n_{2,0} - \xi_1) P^2} \quad (22)$$

(iv) The Rate Constants, Equilibrium Constant and Extent of Reaction are related to obtain an expression of the reaction coordinate or extent of reaction.

The extent of the reaction is obtained based on the relationship between the equilibrium constant terms of Gibbs free energy and algorithm "ii" by combining equations (12) and (22) as

$$\exp\left(-\frac{\Delta G^\circ}{RT}\right) = \frac{(n_{1,0} + n_{2,0} + \xi)^2 (-\xi)}{P (n_{1,0} + 2\xi)^2 (n_{2,0} - \xi)} \quad (23)$$

where $\xi_2 = 2\xi_1 = \xi$, $P = P_T$ is the pressure of the system [atm].

Equation (23) is solved using the quadratic formula method or by completing the square method to obtain the extent of reaction ξ . Knowing the extent of the reaction value and the equilibrium constant, the rate constants were determined using equations (11), (12) and (23) with the relation shown in equations (24) and (25).

$$\exp\left(-\frac{\Delta G^\circ}{RT}\right) = \frac{k_1}{k_2} \quad (24)$$

$$\frac{(n_{1,0} + n_{2,0} + \xi)^2 (-\xi)}{P (n_{1,0} + 2\xi)^2 (n_{2,0} - \xi)} = \frac{k_1}{k_2} \quad (25)$$

2.2.3. Determination of the optimal kinetic parameters from the application of optimization model

The non-linear statistical search regression approach is an optimization method used to obtain a more refined values of Arrhenius constants, activation energies, and rate constants. This model was developed by Ref. [28], and applied by many scholars [27] and others for optimal kinetic parameter determination. The optimization model is applied to the transient reactors' models developed in this study to obtain the best kinetic parameters for better description of the urea synthesis process and improved urea yields in both reactors.

The rate constant, k_i to be optimized for non-isothermal process is defined mathematically as

$$k_i = k_{i,0} \exp(E_i / RT), \quad (26)$$

where $k_{i,0}$ is the pre-exponential or Arrhenius constant for species i , E_i is the activation energies for the species i , and $i = 1, 2, 3$ represent the

forward and backward rate constants for the equilibrium reaction process shown in equation (2a) and the dissociation rate constant for the endothermic reaction shown in equation (2b), respectively [31].

Numerically, the optimization of kinetic parameters is based on the analysis of variance (ANOVA) using the F-distribution tables and agrees with convergence set: that If $F_{cal} > F_{tab}$, then, the criterion for convergence is met and the kinetic parameters are calculated at 5 % confidence interval for optimal values [31]. The algorithm for this searched method follows the defined equations:

$$F_{cal} = \frac{MSE}{MSM} \quad (27)$$

where MSE is the mean square error and MSM is the mean of the square mean defined mathematically as

$$MSE = \frac{SSM}{p} \quad (28a)$$

$$MSM = \frac{SSE}{n - p} \quad (28b)$$

where SSM is the sum of the square means, SSE is the sum of the square means, n is the number of iterations performed and p is the number of parameters considered.

The SSM and SSE are defined mathematically from the mole fraction and temperature models of the reactors as,

$$SSM = \sum_p^n \left\{ (y_{i,cal} - \bar{y}_i)^2 + (T_{j,cal} - \bar{T}_j)^2 \right\} \quad (29a)$$

$$SSE = \sum_p^n \left\{ (y_{i,cal} - y_{i,plant})^2 + (T_{j,cal} - T_{0,plant})^2 \right\} \quad (29b)$$

where $y_{i,cal}$ are the mole fraction values computed from the simulation of the mole fraction models of species i , \bar{y}_i is the mean value of the mole fraction obtained from the simulation of the i -components, $T_{j,cal}$ are the temperature values obtained from the simulation of the j -iterations, \bar{T}_j is the mean value of the computed temperature for the j -iterations performed, $y_{i,plant}$ is the mole fraction of the plant for the i -components involved, and $T_{0,plant}$ is the temperature value of the reactor initially at the start of the production process. The mean values of the mole fraction and temperature were computed as

$$\bar{y}_i = \frac{\sum_{j=1}^n y_i}{n} \quad (30)$$

$$\bar{T}_j = \frac{\sum_{j=1}^n T_j}{n} \quad (31)$$

Therefore, if the criterion stated earlier is met, then the kinetic parameters are computed as

$$E_i^{(j+1)} = E_i^j + \alpha \Delta \quad (32a)$$

$$A_i^{(j+1)} = A_i^j + \alpha \Delta \quad (32b)$$

where $E_i^{(j+1)}$ and $A_i^{(j+1)}$ are the optimal activation energies and Arrhenius constants of i -components in the equilibrium reaction process based on the convergence criterion set, E_i^j and A_i^j are the current or input values of the activation energies and Arrhenius constants, α is a scalar constant ranged from $0.35 \leq \alpha \leq 0.95$ [31], and Δ is the incremental change defined mathematically as,

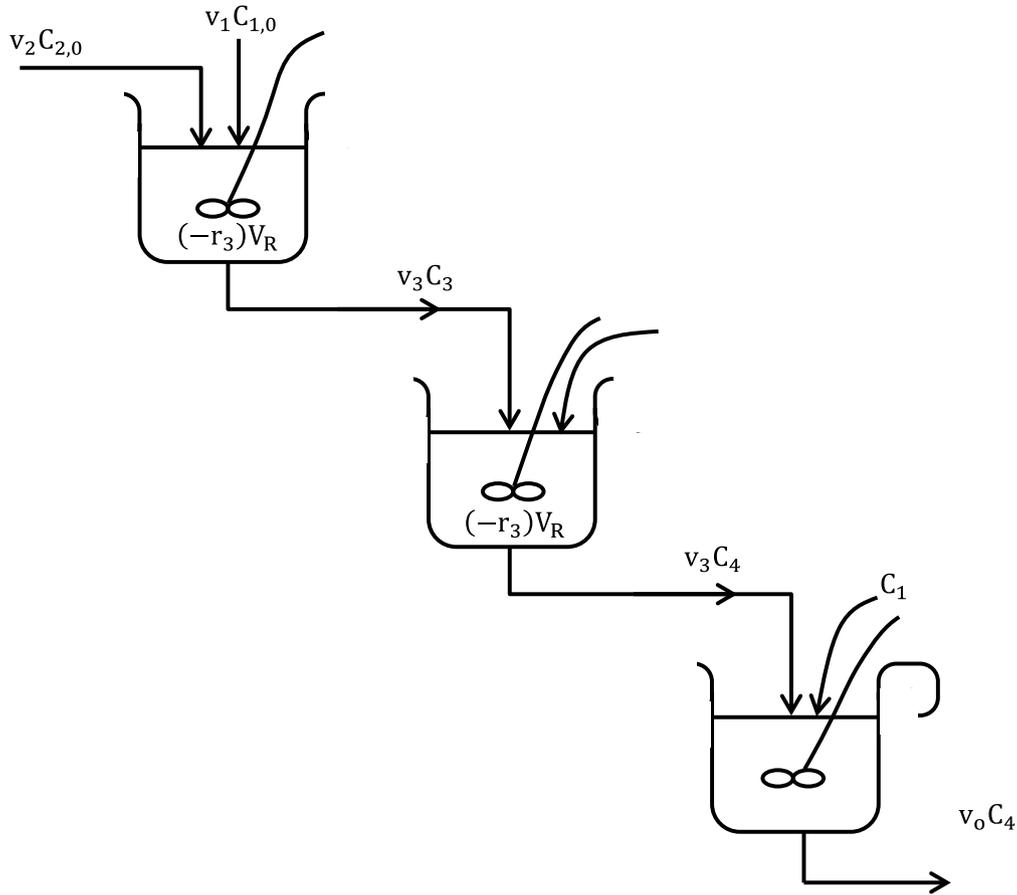


Fig. 1. Materials flow in the indorama urea reactor (CSTR in series) for urea production from CO₂ and NH₃.

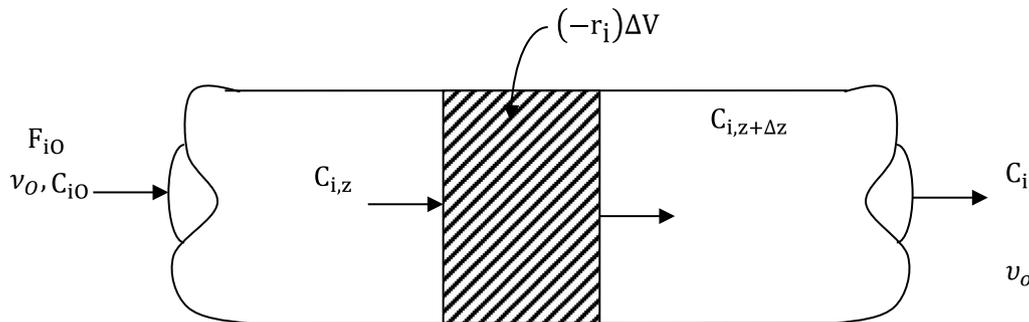


Fig. 2. Schematic diagram of a notore urea reactor (PFR) indicating material flow into and out of the reactor for the Process.

$$\Delta = -\text{inv}(\mathbf{J}\mathbf{J}^T) \cdot \mathbf{J} \tag{33}$$

where, $\text{inv}(\mathbf{J}\mathbf{J}^T)$ is the inverse of the product of matrix \mathbf{J} and its transpose, and \mathbf{J} is an $n \times p$ matrix. Then, the optimized rate constant is calculated as

$$\mathbf{k}_j = \mathbf{A}_i^{(j+1)} \exp\left\{-\frac{\mathbf{E}_i^{(j+1)}}{RT}\right\} \tag{34}$$

2.2.4. Development of the transient mole fraction and temperature models of the urea reactors

The essence of modeling is to predict and describe the production process within reactors under various initial and boundary conditions, based on mathematical expressions developed from material and energy balance principles applied to the reactors. The reliability and

acceptability of these models depend on their performance and error analysis.

Reactor modeling involves determining a more reliable rate expression, optimizing the reactor’s operation, and predicting the entire process within the reactor. In this study, urea reactors are considered: the Indorama reactor modeled as a CSTR and the Notore reactor as a PFR. Models for their mole and temperature profiles were derived using unsteady-state material and energy balance equations, applying the principles of conservation of mass and energy to these urea reactors.

The plants’ reactors for the industrial production of urea are the CSTR for Indorama Environmental and Chemicals Limited (IEF&CL) and the PFR for Notore, where large quantities of the product are manufactured.

I Mole Fraction Models for the Reactors

The general material balance equation applied to generate the mole fraction models for the reactors is stated as

$$\left\{ \begin{array}{l} \text{Rate of accumulation} \\ \text{of materials within} \\ \text{the urea reactors} \end{array} \right\} = \left\{ \begin{array}{l} \text{Rate of inflow of} \\ \text{materials into the urea reactors} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of outflow of} \\ \text{materials from} \\ \text{the urea reactor} \end{array} \right\} + \left\{ \begin{array}{l} \text{Rate of production} \\ \text{of Carbamate due} \\ \text{to Chemical Reaction} \end{array} \right\} \quad (35)$$

Applying equation (35) to the CSTR and PFR shown in Figs. 1 and 2 respectively, gives the ordinary and partial differential equations (ODE and PDE) interms of mole fractions for the reactors as.

For 1 mol of reactants entering the reactor to produce urea, equation (35) is applied on Fig. 1. At unsteady state to describe the urea process interms of mole fraction and incorporating the rate expression model as shown in equation (36):

$$\frac{dy_{ij}}{d\tau} = \frac{1}{\tau_1} y_{1,0} + \frac{1}{\tau_2} y_{2,0} + \left\{ \begin{array}{l} -k_3 P_T \left(\frac{\xi_2 - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right) - \\ (k_1 - k_2) P_T^3 \left(\frac{n_{1,0} - 2\xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right)^2 \left(\frac{n_{2,0} - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right) \end{array} \right\} \quad (36)$$

where y_{ij} denotes the mole fraction of the i -component in the j -reactor (i.e., $i = \text{NH}_3, \text{CO}_2, \text{Carbamate}, \text{urea}, \text{or water}$, and $j = 1, 2, \text{ or } 3$).

Similarly to the material balance on the CSTR, the material balance on the PFR is shown in Fig. 2 as.

For one (1) mole of reactants to the reactor, the material balance equation (35) is applied to give PDE interms of mole fraction and extent of reaction as

$$\frac{\partial y_i}{\partial \tau} = -v \frac{\partial y_i}{\partial z} + (k_2 - k_1) P_T^3 \left(\frac{n_{1,0} - 2\xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right)^2 \left(\frac{n_{2,0} - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right) - k_3 P_T \left(\frac{\xi_2 - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right) \quad (37)$$

where y_i denotes the mole fraction of the i -component, and v is the superficial velocity [m/s].

II Temperature Models Developed for the Urea Reactors

Similarly to the material balance model, the general energy balance equation used to develop the temperature unsteady state models for the CSTR and PFR, is stated as shown in equation (38), which is used to obtain temperature models (ODE and PDE for the Indorama and Notore urea reactors respectively) as

$$\left\{ \begin{array}{l} \text{Rate of accumulation} \\ \text{of energy within} \\ \text{the reactors} \end{array} \right\} = \left\{ \begin{array}{l} \text{Rate of inflow of} \\ \text{energy into the reactors} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of outflow of} \\ \text{energy from} \\ \text{the reactors} \end{array} \right\} + \left\{ \begin{array}{l} \text{Rate of production} \\ \text{carbamate due} \\ \text{to Chemical Reaction} \\ \text{within the reactors} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of energy} \\ \text{released from} \\ \text{the reactors} \end{array} \right\} \quad (38)$$

The temperature models (38 and 39) for the CSTR and PFR, respectively, are obtained by applying the energy balance equation (37) together with the rate expression model developed in equation (10) given as

Table 2

Input parameters for the Indorama Plant (CSTR) and Notore Plant (PFR).

S/ N	Parameter	Value	Unit
1.	Temperature, T	184	$^{\circ}\text{C}$
2.	Pressure, P	160	kg/cm^2 . G
3.	Flow rate, F for NH_3, CO_2 & Carbamate	90- 94, 11-13 & 120-125	t/h
4.	Conversion, C	63/53	%
5.	Time, t	3.7/2.5	Min
6.	Equilibrium constant	K_p	115.94
7.	Gibbs Free Energy	ΔG	-197.15
8.	Rate constants	$k_1, k_2, \& k_3$ are 0.691, 0.596, & 1.2212.	hr^{-1}
9.	Activation energy	E_i is 15 for $i = 1 \& 2, E_3 = 17.5$	kJ/mol
10.	Length of reactor	12	m
11.	Pre-exponential constants ($A_1, A_2, \& A_3$)	(0.694, 0.598, & 1.227)	hr^{-1}
12.	Heat of reaction, ΔH_r	131.1	kJ/mol
13.	Capacity	4000	MTPD
14.	Density ρ	1323	kg/m^3
15.	Specific heat C_p	1.339	kJ/kg .

$$\frac{dT_{ij}}{d\tau} = \frac{1}{\tau} (T_0 + T_c - 2T_{ij}) + J \left\{ \begin{array}{l} -k_3 P_T \left(\frac{\xi_2 - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right) - \\ (k_1 - k_2) P_T^3 \left(\frac{n_{1,0} - 2\xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right)^2 \left(\frac{n_{2,0} - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right) \end{array} \right\} \quad (39)$$

where T_{ij} is the output of the i -component in the j -reactor, $J = \frac{(-\Delta H_r)}{\rho C_p} [\text{m}^3 \text{K}]$, T_0 is the input temperature, $\frac{1}{\tau}$ is the space velocity or reciprocal of space time, defined mathematically as $\frac{1}{\tau} = \frac{UA}{\rho C_p V_R} = \frac{v_0}{V_R}$, where T_c is the coolant temperature.

$$\frac{\partial T}{\partial \tau} + v \frac{\partial T}{\partial z} = J \left\{ \begin{array}{l} k_3 P_T \left(\frac{\xi_2 - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right) - \\ (k_1 - k_2) P_T^3 \left(\frac{n_{1,0} - 2\xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right)^2 \left(\frac{n_{2,0} - \xi_1}{n_{1,0} + n_{2,0} + \xi_2 - \xi_1} \right) \end{array} \right\} + \frac{1}{\tau} (T - T_c) \quad (40)$$

where T is the temperature output [K], $J = \frac{(-\Delta H_r)}{\rho C_p}$, and is the ratio of the heat of reaction ($-\Delta H_r$) change to the product of the density (ρ) [kg/m^3] and specific heat capacity (C_p), [$\text{m}^3 \cdot \text{K}/(\text{mol})^{-1}$], $\frac{1}{\tau} = \frac{UA}{\rho C_p V_R}$, is the ratio of the product of the overall heat transfer coefficient (U), [$\text{kW}/\text{m}^2 \cdot \text{K}$] and surface area (A) of the heat exchange [m^2] to the product of the mixture density), specific heat capacity of the mixture, and reactor volume (V_R), and T_c is the coolant temperature [K].

2.3. Input parameters for simulation and validation of results

The input conditions used for the simulation and validation of the models were obtained from Indorama and Notore plants [21,22]. These plants' reactors operated as CSTR and PFR. Hence, the input data were obtained confidentially and with the help of the Head of Chemical/Petrochemical Engineering Department Rivers State University, Nkpolu Oroworukwo Port Harcourt Rivers State Nigeria from the two plants, since the companies are within the state and are accessible for Chemical Engineers and Chemical Engineering students to practice the profession as part of the Institution and Industry collaboration emphasized and

ensured by Council for the Regulation of Engineering in Nigeria (COREN).

2.4. Solution techniques for the simulation of the models

Matrix Laboratory (MATLAB) version 2020 is a numerical programming software used for solving ODEs and PDEs. The initial boundary conditions for the models are a temperature of 184 °C, a pressure of 160 kg/cm².G, and a flow rate of 63.5 kg/s. Additional input data for the simulation are detailed in Table 2. The boundary conditions are defined as $0 < y < 1$ and $0 < t < 3.7$ min for mole fraction and residence time. The simulated results aim to optimize kinetic parameters to enhance the synthesis process, aiming for improved quality and higher yields of urea in both reactors.

The ODEs developed (equations (36) and (39)) are resolved numerically using 4th order Runge-Kutta (R-K) algorithm, written simultaneously for mole fraction and temperature functions in terms of time [27].

Equations (36) and (39) are assigned 1 and 2 respectively for the algorithm as,

$$k_{1m} = hf\left(t_i; y_{ij,p}; T_{ij,p}\right) \quad (i)$$

where, p takes values 0,1, 2, 3, ...n, m stands for 1 and 2.

$$k_{2m} = hf\left(t_i + \frac{1}{2}h_s; y_{ij,p} + \frac{1}{2}k_{11}; T_{ij,p} + \frac{1}{2}k_{12}\right) \quad (ii)$$

where, h_s is the step size for the iteration process.

$$k_{3m} = hf\left(t_i + \frac{1}{2}h_s; y_{ij,p} + \frac{1}{2}k_{21}; T_{ij,p} + \frac{1}{2}k_{22}\right) \quad (iii)$$

$$k_{4j} = hf\left(t_i + h_s; y_{ij,p} + k_{31}; T_{ij,p} + k_{32}\right) \quad (iv)$$

$$y_{ij,p+1} = h_i + \frac{1}{6}(k_{11} + 2k_{21} + 2k_{31} + k_{41}) \quad (v)$$

$$T_{ij,p+1} = T_{ij,p} + \frac{1}{6}(k_{12} + 2k_{22} + 2k_{32} + k_{42}) \quad (vi)$$

$$t_{i+1} = t_i + h_s \quad (vii)$$

The PDEs developed (equations (37) and (40)) are solved numerically using finite difference approximation techniques. Central and forward finite difference approximations are applied for time and space functions to give equations (41) and (42), which are mole fraction and temperature finite difference approximation models as

$$(a + 1)y(\tau, i) = y(\tau + 1, i) + ay(\tau, i + 1) - b \quad (41)$$

where, a is defined as $\frac{\Delta\tau}{\Delta z}$, and b is defined as $(-r_4)\Delta\tau$.

$$(1 - a + a_1)T(\tau, i) = aT(\tau, i + 1) + T(\tau + 1, i) - Jb + b_1 \quad (42)$$

where, b_1 is defined as $\Delta\tau T_C$.

2.5. Validation of the models

The results obtained from simulations of the developed models numerically as explained in section 2.4 are compared with plants and literatures data using root mean square error (RMSE) and deviation models, for the error analysis evaluation as shown in equations (43) and (44) respectively as

$$RMSE = \sqrt{\left(\frac{\text{model} - \text{plant/literature}}{N}\right)^2} \quad (43)$$

where, N is the number of iterations of model results

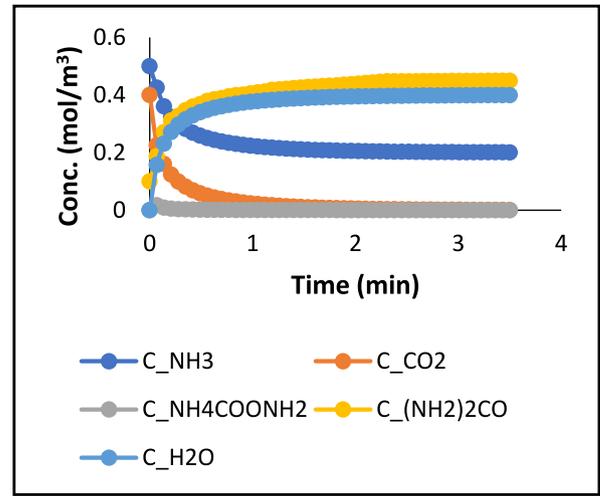


Fig. 3. Variation of concentration vs time.

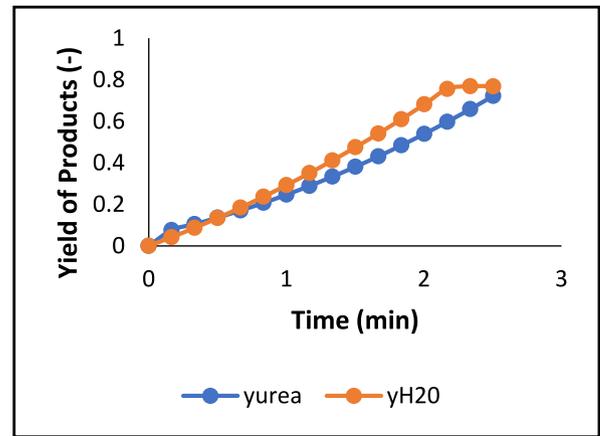


Fig. 4a. Profile of the yield of urea in the Indorama reactor with time.

$$\text{Deviation} = \frac{\left| \text{Model result} - \text{Plant or Lit. data} \right|}{\left| \text{Plant or Literature data} \right|} \quad (44)$$

3. Results and discussion

The rate expression, yield and the optimization results are presented and discuss.

3.1. Rate expression result

The rate expression result is obtained from the simulation of the rate expression model in equation (10) with MATLAB version 2020 using plant data, as presented in Table 2. The profile of the reactant depletion and product formation is shown in Fig. 3.

The concentration profiles over time for components in the urea production process are depicted in Fig. 3. NH₃ and CO₂ are depleted exothermically (with excess heat released) to form carbamate, which subsequently dissociates to yield urea and water endothermically. NH₃ and CO₂ exhibit an exponential decrease in concentration values from 0.5 mol/m³ and 0.4 mol/m³ to 0.20 mol/m³ and 7e-4 mol/m³, respectively, over the time span from the initial value to 3.5 min. This leads to an exponential increase in carbamate concentration from 0 to 0.017 mol/m³, followed by an exponential decrease to 1.09e-5 mol/m³ over the same period. These dynamics correlate with the lowest rate expression result for urea production, as illustrated in Fig. 3,

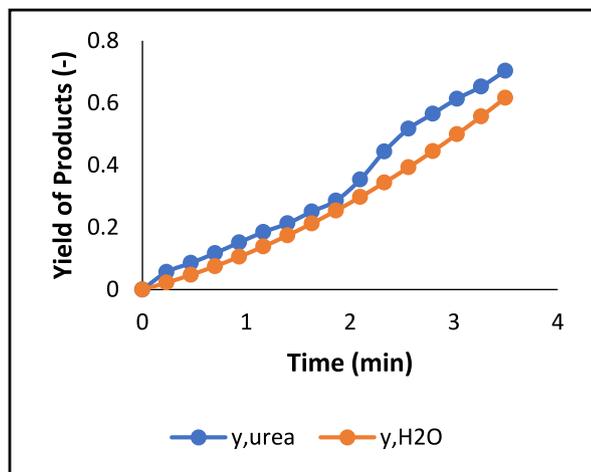


Fig. 4b. Yield of urea in notore reactor with time.

contributing to maximum yields within the reactors. These findings align with values reported in the literature [18,20,38], indicating that the developed rate expression model may be reliable for the urea production process from ammonia and CO₂.

3.2. Yield of urea in the Indorama Reactor

The yield of urea in the Indorama reactor or CSTR is presented and compared with plant and literature values, as shown in Fig. 4a. The yield is due to the performance of the reactor's mole fraction model developed which incorporated the rate expression model.

The yield of urea in the Indorama reactor depends on the rate of urea synthesis, peaking at 0.726 due to the lowest expression of urea rate (refer to Fig. 3 for details). The mole fraction model derived for the Indorama reactor shows the highest yield of 0.726 at a residence time of 2.5 min. However, due to consecutive reactions, the yield decreases thereafter. When compared to yields reported in the literature and at the Indorama plant, the yield surpasses those reported as 0.6 [17] and 0.34 [19] respectively, and matches the reported 0.64 [21] for the Indorama plant (see Fig. 4a).

3.3. Yield of urea in the Notore Reactor

Similarly, the yield of urea in the Notore urea reactor is displayed and compared with literature and plant values in Fig. 4b.

The yield of urea in the Notore reactor over time is depicted in Fig. 4a, showing a yield of 0.7032, significantly higher than the Notore plant's reported yield of 0.43 [16], and literature values of 0.46 [15] and 0.53 [18]. The high yield observed after simulating the rate expression model, illustrated in Fig. 4b, suggests that the developed rate model accurately predicts the equilibrium reaction process. The approach used to develop this model provides more precise information for process description compared to methods found in plant operations and literature. This makes it a recommended tool for researchers and industries, highlighting the need for further studies in this area. Although the Indorama urea reactor shows a slightly better yield than the Notore urea reactor, the yields are closely matched, with an absolute error of 0.032.

3.4. Validation of the yield with plant and literature data for the urea reactors

The yields of the urea reactors were validated using literature values and plant data. Error analysis conducted on the yields from both reactors, as shown in Table 3, indicates RMSE and deviations ranging from 0.033 to 0.162 and 0.100 to 1.135, with higher discrepancies observed. These results suggest that the yields of urea from the reactors, influenced by the newly developed rate expression model, are higher compared to values reported in both plant data [21,22] and literature sources [15,17,18]. Overall, the Notore urea reactor exhibited higher yields than the Indorama urea reactor, as indicated by the model results obtained (see Table 3).

3.5. Optimal kinetic parameters results from the optimization models

The activation energies, pre-exponential factors, and rate constants constitute the kinetic parameters that were determined, optimized, and validated (see Table 4). The kinetic parameter values obtained from the applications of mass action, fugacity coefficient, and thermodynamics models were subsequently optimized using non-linear regression analysis. These results proved instrumental in modeling and optimizing the urea reactors. The kinetic parameter estimation was conducted based on reactor models developed in terms of fractional conversion and

Table 3
Validation of the yield of the simulated models with plant and literatures data for the reactors.

Urea Reactor	Plant Value	Literatures Data			Model Result	Deviation			
	Yield	Yield			Yield	Plant Yield	Literature Yield		
Indorama (CSTR)	0.64 [21]	0.66 [5]	0.34 [19]	0.60 [17]	0.726	0.134	0.10	1.135	0.21
RMSE	0.043	0.033	0.193	0.063	–	–	–	–	–
Notore (PFR)	0.43 [22]	0.38 [10]	0.46 [15]	0.53 [18]	0.703	0.635	0.85	0.529	0.326
RMSE	0.137	0.162	0.122	0.087	–	–	–	–	–

Table 4
Validation of the kinetic parameters with plant values.

S/N	Parameter	Plant Value	CSTR		PFR		Deviation	
			Model	RMSE	Model	RMSE	CSTR	PFR
1	Activation Energy (kJ/mol)	E ₁ 15	15.029185	0.0228	15.0309	0.0241	0.0019	0.0021
		E ₂ 15	15.02566		15.02716		0.0017	0.0018
		E ₃ 17.5	17.506899		17.507305		0.0004	0.0004
2	Arrhenius Constant (m ⁶ mol ⁻¹ s ⁻¹)	A ₁ 0.694	0.68723	0.0055	0.687178	0.0096	0.0098	0.0098
		A ₂ 0.598	0.592155		0.592123		0.0098	0.0098
		A ₃ 1.227	1.23038		1.21296		0.0114	0.0114
3	Rate Constant (m ⁶ mol ⁻¹ s ⁻¹)	k ₁ 0.691	0.723185	0.0256	0.724902	0.0269	0.0466	0.0491
		k ₂ 0.596	0.623655		0.625165		0.0464	0.0489
		k ₃ 1.2212	1.233899		1.234305		0.0104	0.0107

temperature, following material and energy balance principles for both reactors, consistent with findings in the literature [27,28,39].

Table 4 presents refined values of activation energies, Arrhenius constants, and rate constants. Validation of these kinetic parameters with plant data resulted in error values ranging from 0.0004 to 0.0491 for both RMSE and deviations, indicating high accuracy, reliability, and acceptability for control, modeling, and optimization of the reactors to enhance the description of the urea process and performance of the controller. Optimization results from this study were compared with those reported in the literature [27,28,39], revealing very small deviations, which suggests the development of more robust and accurate models for urea reactors, facilitating improved process prediction.

4. Conclusion

The rate of urea formation was found to be lowest in the CSTR and highest in the PFR, with values of 0.726 and 0.7032, respectively, when compared to literature and plant values. This outcome stems from the development of a suitable rate expression and the optimization of kinetic parameters using appropriate tools, resulting in negligible errors ranging from 0.0004 to 0.0491 when compared with literature data. The study of rate expressions and the development of unsteady-state models are recommended for designing and controlling reactors using specific controllers such as PID and Fuzzy Logic Controllers. Simulations of reactor models under various initial and boundary conditions are also recommended to evaluate the performance of the rate expression and the developed models.

CRedit authorship contribution statement

O.E. Ojong: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Conceptualization, Data curation, Investigation, Resources, Validation, Visualization. J.G. Akpa: Visualization, Supervision, Formal analysis. K.K. Dagde: Supervision, Funding acquisition. D. Amadi: Funding acquisition, Resources, Software.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors, Ojong, O.E.; Akpa, J.G.; and Dagde, K.K have not serve in the editorial capacity of Results in Engineering journal and also have no relationship with any of the board member, except that the corresponding author had published his work in this journal 2years ago (see Wordu et al., 2022). If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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