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Design of a Continuous Stirred Tank Reactor for the Production of 500,000,000 tons per Year of Titanium Dioxide from the Hydrolysis of Titanium Tetrachloride

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Abstract
The intrinsic urge of this research is predicated on the economic importance of titanium dioxide (T_iO_2) in industrial applications and the zeal to meet the ever-growing demand of titanium dioxide in the world. The research considered the design of a continuous stirred tank reactor (CSTR) for the production of titanium dioxide from the hydrolysis of titanium tetrachloride. The CSTR was operated isothermally at a steady state process condition during the production of 500,000,000 tons of titanium dioxide. The reactor design or size specification models were developed through the application of the first principle of mass and energy balance and simulated in MATLAB at initial feed and operating temperature of1190.395k and 1200k and fractional conversion within the range of $X_A \geq 0 \leq 0.95$. At maximum conversion of 95%, the optimum value of the CSTR functional parameters such as its volume, height, diameter, space time, space velocity, quantity of heat generated as well as the quantity of heat generated per unit volume of the reactor were 112.685m^3, 8.310m, 4.155m, 17.320sec., 0.058sec^{-1}, 851.580j/s and 7.557j/sm^3 respectively. The height and diameter of the CSTR stirrer specifications were 7.8102m and 3.1551m with allowance or clearance of 0.5m and 1m respectively. The CSTR design is validated based on the fact that the relationship between the operating temperature, fractional conversion and the reactor functional parameters were in agreement with the trend and mathematical relationship of CSTR production processes at steady operating condition.

Keywords: *Titanium dioxide, Titanium tetrachloride, Hydrolysis, CSTR, Design, MATLAB simulation*

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1. Introduction

One of the much-anticipated metal oxides is titanium dioxide (T_iO_2) because of its characteristics as an inert, safe, less expensive, strong chemical corrosion resistant with a distinguished optical characteristic (Khan *et al*., 2015; Fares *et al*., 2022). Titanium itself is the seventh most common metal on earth usually found in rocks, sediments, organic matter and natural waters (Knittel, 1983). It is the ninth most abundant element in the earth crust that makes up about 0.6% of the planets crust (Rudnick and Gao, 2003). Titanium dioxide is widely applied in the ceramic, pigment, polymer, pulp, and metallurgical industries for the production of glass, ceramics, paints, coating materials, inks, fillers, plastics, rubber, paper, metals, food and cosmetics (Zhang *et al*., 2011; Agustina *et al*., 2024). It can also be used in biological treatment and in air purification for the removal of pollutants in the air as well as volatile organic compounds, nitrogen oxide and sulphur oxide as a photo-catalyst (Prasetya *et al*., 2021; Agustina *et al*., 2021).

For the purpose of economics and sustainability of utilizing titanium dioxide, this research delves into the design of a continuous stirred tank reactor for the production of 500,000,000 tons per year of titanium dioxide from the hydrolysis of titanium tetrachloride. The CSTR design is an integral aspect of chemical engineering that utilizes knowledge or experience from varieties of areas such as chemical reaction engineering and reaction kinetics, thermodynamics, transport phenomenon sciences, economics as well as the application of the principle of mass and energy balance. The CSTR design involves the determination of the reactor volume, height, diameter, space time, space velocity, quantity of heat generated as well as the quantity of heat generated per unit volume of the reactor (Wosu and Ezeh, 2024; Ojong *et al*., 2024; Wosu *et al*., 2024; Wosu *et al*., 2023; Wordu and Wosu, 2019). The design of the CSTR stirrer which is responsible

for ensuring uniform mixing of the reactant species (titanium tetrachloride and water) is also considered in this article. The choice of CSTR over other reactor types like the plug flow reactor (PFR), packed bed reactor (PR), batch reactor (BR) is based on the nature of the reactant species and the type of reaction occurring (liquid phase hydrolysis) during the process.

Considerable research has been carried out on the applications, extraction or production of titanium dioxide and thusAgustina *et al*. (2024) stated that green titanium dioxide photo-catalysts is synthesized by using lactobacillus bulgaricus for processing palm oil mill effluent by investigating the molarity and temperature of the photo-catalyst which was characterized using a particle size analyzer and the result showed that the produced photo-catalyst have nanoparticle size range of 1-100 nanometer.

Gazquez*et al*. (2014) stated that titanium ore is utilized as starting material by TiO_2pigment and titanium metal producers. Commercial titanium ores occur naturally as ilmenite (usually, $F_eO.T_iO_2$ or $T_iF_eO_3$) with 40% - 65% of T_iO_2 composition, others are ferrous and ferric iron oxides as well as other oxide impurities of chromium, manganese, vanadium, magnesium, aluminum, calcium, silicon, etc. depending on their geological formation (Barksdale, 1966). Globally, Gambogi (2011) reported that as at 2009, the leading producing regions of ilmenite were South Africa, Australia, Canada, China, India, Vietnam, Norway, and Ukranie with production rate in millions of 1.05Mt, 1.02Mt, 0.65Mt, 0.5Mt, 0.42Mt, 0.412Mt, 0.30Mt and 0.30Mt respectively while the total production stood at 5.3Mt. While the major rutile producers were Australia, South Africa and Sierra Leona with production rate of 0.266Mt, 0.127Mt and 0.06Mt respectively with a total production of 0.55Mt. Presently, ilmenite and rutile reserves are projected to be about 650,000,000 and 42,000,000 metric tons respectively and ilmenite is said to supply about 91% of the global demand for titanium minerals production of about 530,000,000 metric tons in 2009. In the next decade, world demand for T_iO_2 is projected to rise at an average rate of about 3% yearly (Gambogi, 2009; Gamboji, 2010). Based on the projection above, this research article becomes highly imperative and necessary to ensure continuous production and sustainability of titanium dioxide to meet the ever-growing demand of the economic production globally.

2. Materials and methods

The methodology adopted in this research is quantitative and the data used were obtained from thermodynamic properties of the reactant species and products, literature and calculated/derived data. The procedures adopted included the development of the reaction kinetic models, development of design or sizing models for reactor volume, height, diameter, space time, space velocity, quantity of heat generated as well as quantity of heat generated per unit volume of the reactor, development of energy balance model of the process and the design of the CSTR stirrer.

2.1.1 Development of the reaction kinetic models

The reaction kinetic scheme for the liquid phase hydrolysis of titanium tetrachloride is given as:

$$TiCl_4 + 2H_2O \xrightarrow{k_1} TiO_2 + 4HCl \quad (1)$$

The reaction can be expressed symbolically as:

$$A + 2B \xrightarrow{k_1} C + 4D \quad (2)$$

The reaction rate is 1st-order and zero-order with respect to water and thus, the rate of feed depletion can be expressed as:

$$-r_A = k_o e^{-E/RT} C_{Ao}(1 - x_A) \quad (3)$$

2.1.2 Development of CSTR design/sizing models

Consider the schematic representation of a continuous stirred tank reactor with feed stream, product stream and heat effects.

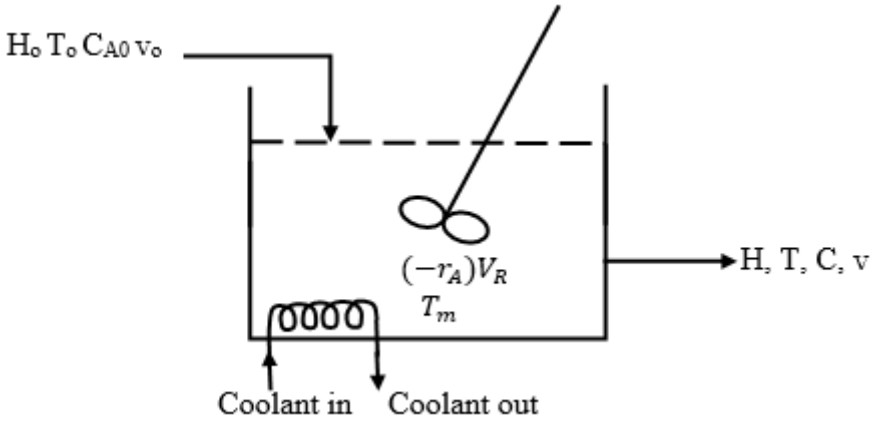

Fig. 1: CSTR with heat effects for titanium dioxide production

For the CSTR, the following assumptions were made.

i. The feed assumes a uniform composition throughout the reactor
ii. The reacting mixture is well stirred
iii. The composition of the exit stream is the same as that within the reactor
iv. Shaft work by the impeller or stirrer is negligible
v. The temperature within the reactor is kept at a constant value by the heat exchange medium.

The CSTR design parameters can be obtained by applying the principle of material balance stated as follows:

$$\begin{bmatrix}\text{Rate of}\\ \text{accumulation}\\ \text{of material}\\ \text{within the}\\ \text{volume}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{input of}\\ \text{feed into}\\ \text{the volume}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{outflow of}\\ \text{feed from}\\ \text{the voume}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{depletion of}\\ \text{feed due to}\\ \text{chemical}\\ \text{reaction}\end{bmatrix} \quad (4)$$

The terms in Equation (4) can be defined, substituted, simplified at steady state to give the CSTR functional parameters thus:

$$V_R = \frac{F_{Ao}x_A}{k_o e^{-E/RT}C_{Ao}(1-x_A)} \quad (5)$$

$$H_R = \left[\frac{16F_{Ao}x_A}{\pi K_o e^{-E/RT}C_{Ao}{}^3(1-x_A)(m-2x_A)^2}\right]^{\frac{1}{3}} \quad (6)$$

$$D_R = \frac{\left[\frac{16F_{Ao}x_A}{\pi k_o e^{-E/RT}C_{Ao}(1-x_A)}\right]^{\frac{1}{3}}}{2} \quad (7)$$

But, $F_{Ao} = C_{Ao}v_o$

$$\tau_{CSTR} = \frac{x_A}{k_o e^{-E/RT}C_{Ao}(1-x_A)} \quad (8)$$

$$S_V = \frac{k_o e^{-E/RT}C_{Ao}(1-x_A)}{x_A} \quad (9)$$

$$Q = \Delta H_R F_{Ao} x_A \quad (10)$$

$$q = \frac{\Delta H_R F_{Ao} x_A}{V_R} \quad (11)$$

The energy balance of the CSTR in Figure 1 can be obtained by applying the principles of conservation of energy and the resultant model is the temperature effect model of the alkylation process.

$$\begin{bmatrix}\text{Rate of}\\ \text{accumulation}\\ \text{of heat}\\ \text{within the}\\ \text{volume}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{Input of}\\ \text{heat to}\\ \text{the volume}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{Output of}\\ \text{heat from}\\ \text{the volume}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{depletion}\\ \text{of heat due}\\ \text{to chemical}\\ \text{reaction}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{heat}\\ \text{removal}\\ \text{to the}\\ \text{surrounding}\end{bmatrix} + \begin{bmatrix}\text{Shaft}\\ \text{work}\\ \text{done by}\\ \text{the stirrer}\end{bmatrix} \quad (11)$$

The terms in Equation (11) can be defined, substituted, simplified at steady state to give the temperature effect model thus:

$$T = \frac{\tau\Delta H_R r_i v_o + UA_c T_c + \rho v_o c_p T_o}{\rho v_o C_p + UA_c} \quad (12)$$

The CSTR stirrer design is done by allowing a clearance C between the stirrer height (H_{ST}) and diameter (D_{ST}) (Perry *et al*., 2008).

$$H_{st} = H_R - C \quad (13)$$

$$D_{st} = D_R - 2C \quad (14)$$

2.1.3 Data for evaluation

The data for evaluation in this research are the properties/thermodynamic data, calculated/derived data and data obtained from literatures as presented in Table 1.

Table 1: Data obtained from literatures

Data	Values	Description	References
T	1200K	Operating temperature of the reactor	Mark & Robert, 2003
k_o	$8.0 \times 10^4 s^{-1}$	Pre-exponential factor	Mark & Robert, 2003
k_i	$1.182 \times 10^1 s^{-1}$	Rate constant	Mark & Robert, 2003
E	88000J/mol	Activation energy	Mark & Robert, 2003

3. Results and discussion

3.1 MATLAB Simulation of Titanium dioxide from the hydrolysis of titanium tetrachloride

The results obtained from the simulation of the Titanium dioxide from the hydrolysis of titanium tetrachloride using MATLAB R2023a software are presented in Table 2. Table 2 shows the design of the CSTR in terms of volume of reactor (m^3), height of the reactor (m), diameter of the reactor (m), residence time (s), space velocity (1/s), quantity of heat generated (J/s) and quantity of heat generated per unit volume of reactor (J/sm^3) dependent on fractional conversion and temperature. From Table 2 it can be observed that the value of fractional conversion ranges from 0 to 0.95 at intervals of 0.05. The temperature of the reactor remained constant because the reactor was operated isothermally at 1190.395K. The volume of the reactor is seen to be increasing with fractional conversions of reactants due to the fact that as more reactants are been consumed to form products so does the volume increases. The volume of reactor is directly proportional to the diameter and height of the reactor. So, as the volume increases so also the diameter and height also increases. The residence time of the reactor increases with fractional conversion because the volume of reactor is directly proportional to the residence time. On the other hand, the space velocity of reactor which is the inverse of residence time is decreasing with fractional conversion of reactor, the reason for this decrease is because volume of reactor is inversely proportional to the space velocity of reactor and if volume is increasing then we expect the space velocity of reactor to decreases as depicted in Table 2. The quantity of heat generated also known as the heat load is increasing with fractional conversion because when the energy barrier known as activation energy has been overcome, product formation proceeds, hence this requires energy to break the activation energy, so it is expected to increase with fractional conversion. Lastly, the quantity of heat generated per unit volume of reactor is seen to be decreasing with fractional conversion.

Table 2: Model results for different CSTR parameters

X_A	T(K)	V_R (m3)	H_R (m)	D_R(m)	tau_CSTR(s)	S_V(1/s)	Q(J/s)	q(J/sm3)
0.05	1190.395	0.016	0.437	0.219	0.003	396.014	44.820	2728.152
0.15	1190.395	0.062	0.679	0.340	0.010	105.677	134.460	2184.033
0.25	1190.395	0.132	0.876	0.438	0.020	49.365	224.100	1700.372
0.35	1190.395	0.246	1.078	0.539	0.038	26.486	313.740	1277.168
0.45	1190.395	0.441	1.310	0.655	0.068	14.748	403.380	914.422
0.55	1190.395	0.805	1.601	0.800	0.124	8.078	493.020	612.134
0.65	1190.395	1.574	2.001	1.001	0.242	4.135	582.660	370.303
0.75	1190.395	3.559	2.627	1.313	0.547	1.828	672.300	188.930
0.85	1190.395	11.203	3.850	1.925	1.722	0.581	761.940	68.0149
0.95	1190.395	112.685	8.310	4.155	17.320	0.058	851.580	7.557

3.2 Effect of fractional conversion on process parameters

The effect of fractional conversion on process parameters such as: volume of reactor, temperature of reactor, diameter, height, residence time, space velocity, quantity of heat generated, quantity of heat generated and quantity of heat generated per unit volume of reactor is presented in Fig. 2 to 9.

3.2.1 Effect of fractional conversion on volume of reactor

Fig. 2 shows the effect of varying fractional conversion on the volume of the reactor. Fractional conversion of the reactor was varied from 0 to 0.95 at intervals of 0.05 and this caused a corresponding increase in the volume of the reactor from 0 m^3 to 112.685 m^3. This indicates that as more reactant is converted into products, the reactor needs to accommodate a larger volume of reaction mixture to maintain the desired conditions. The relationship between fractional conversion and reactor volume is influenced by factors such as reaction kinetics, desired product yield, and the need to maintain optimal conditions for the reaction to proceed efficiently. For example, as the reaction progresses and more reactants are consumed, the reactant concentration decreases, which might require a larger reactor volume to achieve the same level of conversion. In summary, the graph of fractional conversion versus reactor volume provides valuable insights into the relationship between these two variables in a reaction system. By understanding how fractional conversion affects reactor volume, engineers can optimize reactor design and operation to achieve the optimum desired conversion levels.

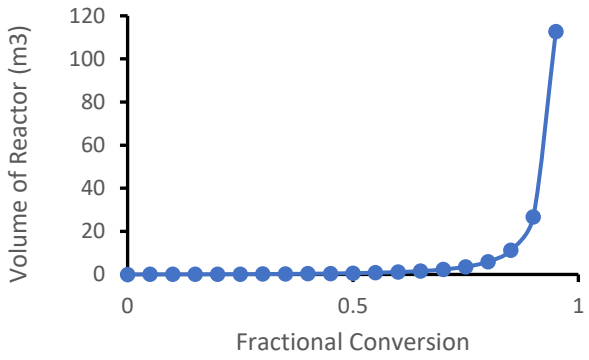

Fig. 2: Profile of the CSTR volume and fractional conversion

3.2.2 Effect of fractional conversion on height of reactor

Fig. 3 shows the effect of varying fractional conversion on the height of the reactor. Fractional conversion of the reactor was varied from 0 to 0.95 at intervals of 0.05 and this caused a corresponding increase in the height of the reactor from 0 m to 8.310 m. This suggests that as more reactant is converted into products, a greater height of the reactor is required to accommodate the reaction mixture. The relationship between fractional conversion and reactor height is influenced by factors such as reaction kinetics, mass transfer limitations, and the need to maintain optimal conditions for the reaction to proceed efficiently. As the reaction progresses and more reactants are consumed, the reactant concentration decreases, which might require a greater height of the reactor to achieve the same level of conversion. The plotted graph can provide insights into optimizing the height of the reactor for a given reaction system.

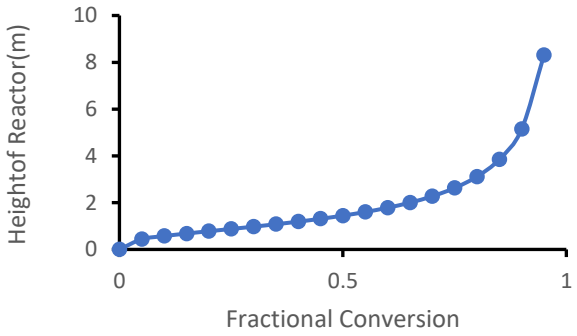

Fig. 3: Profile of the CSTR height and fractional conversion

3.2.3 Effect of fractional conversion on diameter of reactor

Fig. 4 shows the effect of varying fractional conversion on the diameter of the reactor. Fractional conversion of the reactor was varied from 0 to 0.95 at intervals of 0.05 and this caused a corresponding increase in the diameter of the reactor from 0 m to 4.155 m. This suggests that the diameter of the reactor does not significantly change with increasing conversion in the plotted range. The lack of significant variation in reactor diameter with increasing conversion could indicate that the reaction system does not require adjustments in reactor diameter to accommodate changes in conversion. Alternatively, it may suggest that other factors, such as reactor height or volume, play a more significant role in accommodating the reaction mixture as conversion progresses. The plotted graph may provide insights into the optimal diameter of the reactor for a given reaction system within the plotted range of conversion.

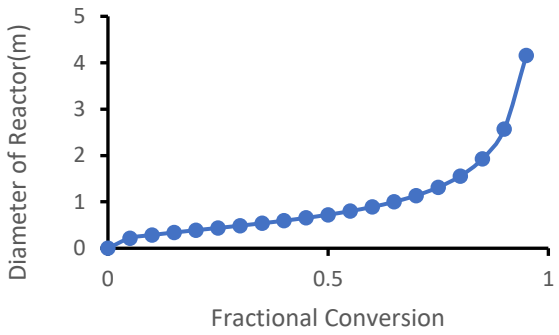

Fig. 4: Profile of the CSTR diameter and fractional conversion

3.2.4 Effect of fractional conversion on residence time of reactor

Fig. 5 shows the effect of varying fractional conversion on the diameter of the reactor. Fractional conversion of the reactor was varied from 0 to 0.95 at intervals of 0.05 and this caused a corresponding increase in the residence time of the reactor from 0 seconds to 17.320 seconds. This suggests that as more reactant is converted into products, less time is required for the reaction to achieve the desired conversion level. The relationship between fractional conversion and reactor residence time reflects the kinetics of the reaction and the efficiency of the reactor design. As the reaction progresses and more reactants are consumed, the reaction rate might increase, requiring less time for the reactants to achieve the same level of conversion. The plotted graph provides insights into optimizing the residence time of the reactor for a given reaction system.

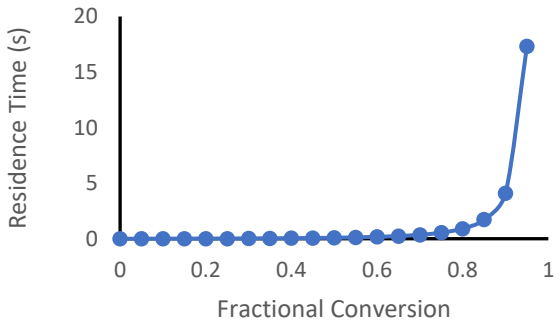

Fig. 5: Profile of the CSTR residence time and fractional conversion

3.2.5 Effect of fractional conversion on space velocity of reactor

The space velocity represents the flow rate of reactants through the reactor per unit volume of the catalyst. It is measured in reciprocal seconds (1/s) and indicates how quickly the reactants are being processed. The space velocity is calculated as the ratio of the volumetric flow rate of the reactants to the volume of the catalyst in the reactor. Figure 6 shows the effect of varying fractional conversion on the space velocity of the reactor. Fractional conversion of the reactor was varied from 0 to 0.95 at intervals of 0.05 and this caused a corresponding decrease in the residence time of the reactor from 0.30 per second to 0.058 per second. This suggests that as more reactant is converted into products, the rate at which reactants flow through the reactor per unit volume of catalyst decreases. The relationship between fractional conversion and space velocity reflects the dynamics of the reaction and the performance of the reactor. As the reaction progresses and more reactants are consumed, the reactant concentration decreases, leading to a decrease in the rate at which reactants flow through the reactor to achieve the same level of conversion. The plotted graph provides insights into optimizing the space velocity of the reactor for a given reaction system.

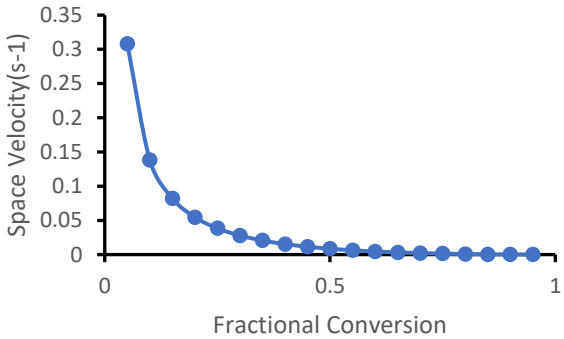

Fig. 6: Profile of the CSTR space velocity and fractional conversion

3.1.6 Effect of fractional conversion on quantity of heat of reactor

The quantity of heat (Q) represents the rate of heat generation or consumption in the reaction system. It is measured in Joules per second (J/s) and indicates the amount of heat either released or absorbed by the reaction per unit time. Fig. 7 shows the effect of varying fractional conversion on the quantity of heat. The fractional conversion of the reactor was varied from 0 to 0.95 at intervals of 0.05 and this caused a corresponding increase in the quantity of heat of the reactor from 0 to 851.580 kilo Joules per second. This suggests that as more reactant is converted into products, less heat is being generated or consumed by the reaction per unit time. The relationship between fractional

conversion and quantity of heat reflects the thermodynamics of the reaction and the energy balance within the reactor. As the reaction progresses and more reactants are consumed, the rate of heat generation or consumption may decrease due to changes in reactant concentrations, reaction kinetics, and heat transfer effects. The plotted graph provides insights into optimizing the quantity of heat for a given reaction system.

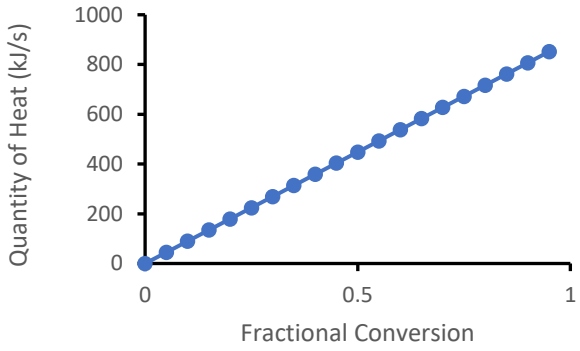

Fig. 7: Profile of the CSTR quantity of heat generated and fractional conversion

3.2.7 Effect of fractional conversion on quantity of heat per unit volume of reactor

The quantity of heat generated per unit volume (q) represents the rate of heat generation or consumption per unit volume of the reactor. It is measured in Joules per second per cubic meter (J/sm^3) and indicates the amount of heat either released or absorbed by the reaction per unit volume of the reactor per unit time. Fig. 8 shows the effect of varying fractional conversion on the space velocity of the reactor. Fractional conversion of the reactor was varied from 0 to 0.95 at intervals of 0.05 and this caused a corresponding decrease in the quantity of heat per unit volume of the reactor from 2728.152 J/m^3s to 7.557 J/m^3s. This suggests that as more reactant is converted into products, less heat is being generated or consumed per unit volume of the reactor per unit time. The relationship between fractional conversion and quantity of heat per unit volume reflects the thermodynamics and kinetics of the reaction, as well as the heat transfer characteristics within the reactor. As the reaction progresses and more reactant is consumed, the rate of heat generation or consumption per unit volume may decrease due to changes in reactant concentrations, reaction kinetics, and heat transfer effects. The plotted graph provides insights into optimizing the quantity of heat per unit volume for a given reaction system.

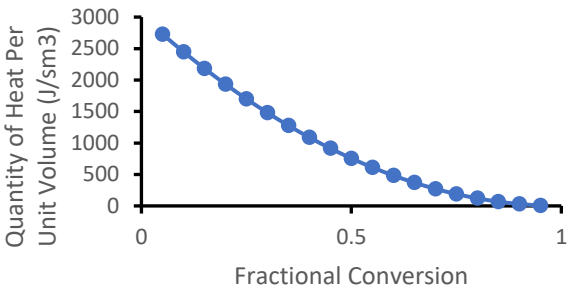

Fig. 8: Profile of the CSTR quantity of heat generated per unit volume of reactor and fractional conversion

3.2.8 Effect of fractional conversion on temperature of reactor

The reactor temperature is the thermal energy present in the reactor and can significantly influence reaction kinetics and equilibrium. Fig. 9 shows the effect of varying fractional conversion on the temperature of the reactor. Fractional conversion of the reactor was varied from 0 to 0.95 at intervals of 0.05 and this neither caused an increase nor a decrease in temperature because the reactor was operated isothermally. The lack of significant variation in reactor temperature with increasing conversion could imply that the reaction is conducted isothermally or that the heat generated or absorbed by the reaction is effectively managed and controlled within the reactor. It's also possible that the temperature is actively controlled or regulated to maintain optimal reaction conditions.

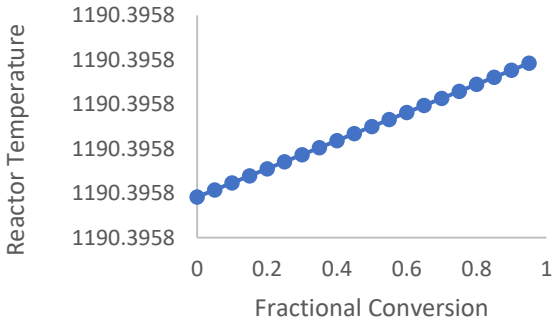

Fig. 9: Profile of the CSTR temperature and fractional conversion

4. Conclusion

This work considered the design of a continuous stirred tank reactor for the production of 500,000,000 tons per year of titanium dioxide from hydrolysis of titanium tetrachloride. The design equations were formulated to compute process

parameters such as the volume, temperature, residence time, space velocity, quantity of heat generated, quantity of heat generated per unit volume of reactor by varying the fractional conversion of the reactor from 0 to 0.95 at intervals of 0.05. After the formulation of the model equations, they were then solved through the application of MATLAB R2023a software to compute the desired design parameters of the reactor. Finally, the effect of varying fractional conversion on volume, temperature, residence time, space velocity, quantity of heat generated, quantity of heat generated per unit volume of reactor were studied after which the effect of varying the volume of reactor on residence time and temperature of reactor was also carried out.

Competing interest

The author declare that they have no known competing financial interest or personal relationship that could have appeared to influence the work reported in this paper.

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Nomenclature

Symbol	Definition	Unit
ΔH_R	Change in enthalpy of reactants	J/mol
A	Titanium Tetrachloride	-
B	Process water	-
C	Titanium dioxide	-
C_i	Initial concentration of species	mol/m^3
C_P	Specific heat capacity	J/mol
D	Hydrochloric acid	-
D_R	Diameter of the reactor	M
E	Activation Energy	J/mol
F_A	Initial molar flow rate	mol/S
H_i	Enthalpy of species	J/mol
H_R	Height of the Reactor	M
K_o	Pre-exponential factor	S^{-1}
Q	Quantity of Heat generated	J/S
Q	Quantity of heat generated per reactor volume	J/Sm^3
R	Gas constant	$Nmmol^{-1}k^{-1}$
r_A	Reaction rate of species	$mol/m^3/s$
S_V	Space velocity	Sec^{-1}
T	Operating Temperature	Kelvin
T_c	Temperature of coolant	K
T_o	Initial or fed temperature	K
UAc	Heat transfer coefficient	Kg/m^2SK
V_i	Fractional conversion	Dimensionless
V_o	Volumetric flow rate	m^3/S
V_R	Volume of the Reactor	m^3
ρ_i	Density of species	Kg/m^3
τ	Space time	Seconds

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