

**Isothermal Continuous Stirred Adsorption Tower (CSAT) for Vanadium Catalyst Based
Sulphur Trioxide Hydration Process**
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Abstracts

Catalytic hydration of sulphur trioxide results to production of sulphuric acid and it is industrially very important chemical specie due to the associated uses. Hence the continuous search for the development of suitable design model to optimize its production capacity for reactor types is eminent. Therefore presented in this paper is development of design models for performance evaluation of continuous stirred adsorption tower (CSAT) for sulphur trioxide hydration process using vanadium catalyst at isothermal condition. The design models were stochastically appraised and found to be capable of simulating performance dimensions as a function of kinetic parameters. These performance dimensions include tower volume, height, space time, space velocity, and rate of heat generation per unit volume. The developed performance models were generalized to accommodate any CSAT plant capacity design basis as a function of fractional conversion. The proposed performance dimensions design models could also be used to develop the heat exchanger functional parameters aimed at achieving the isothermal condition of the hydration process. The model equations were further simulated to evaluate the stipulated performance dimensions using Matlab R2007B within the operational limits of conversion degree at constant temperature. The results of the performance dimensions showed a dependable relationship with fractional conversion.

Keywords: Isothermal, CSAT, Design, Sulphur trioxide, hydration, Performance.

Introduction

The continue search for the most suitable reactor models to optimize sulphuric acid production is increasing globally (Austein ,1984, Duecker and West, 1975 and Faith, 1965). This is due to the numerous industrial and domestic applications of sulphuric acid. Sulphuric acid otherwise called oil of vitrol and king of chemicals is a diprotic acid with structural formula presented in figure 1.

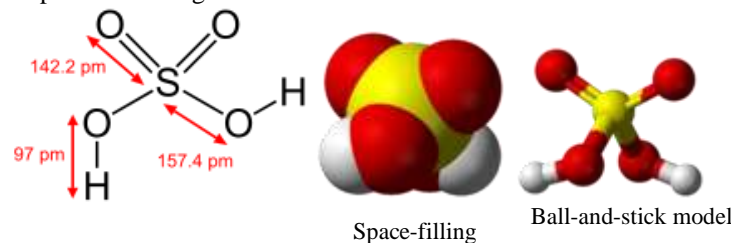


Figure 1: Structural formula of Sulphuric acid

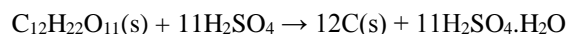
Sulphuric acid possesses high ionization and dissociation capacities that influence its reactivity with other chemicals resulting to useful finished industrial products. Such sulphuric acid reactivity finished products includes;

- Sulphuric acid ionises in water in two stages: $\text{H}_2\text{SO}_4(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HSO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 $\text{HSO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- Sulphuric acid is a strong acid (complete dissociation in water, K_a approaches infinity)
- Sulphuric acid reactions:
 - sulphuric acid + metal \rightarrow metal sulfate + hydrogen gas
 - sulphuric acid + carbonate \rightarrow metal sulfate + carbon dioxide gas + water
 - sulphuric acid + base \rightarrow salt + water
 - sulphuric acid + ammonia \rightarrow ammonium sulfate

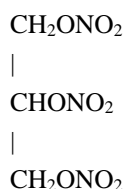
- Sulfuric acid can take part in redox reactions.
- Other Uses of Sulfuric Acid (H_2SO_4) that attract global attention are;
- Sulfuric acid is the electrolyte used in lead-acid batteries (accumulators)
 - Sulfuric acid is important in the production of fertilizers such as ammonium sulfate (sulfate of ammonia), $(NH_4)_2SO_4$, and superphosphate, $Ca(H_2PO_4)_2$, which is formed when rock phosphate is treated with sulfuric acid.
 - Sulfuric acid is used to remove oxides from iron and steel before galvanising or electroplating
 - Concentrated sulfuric acid (18M) is used as a dehydrating agent, that is, to remove water, since it has a tendency to form hydrates such as $H_2SO_4 \cdot H_2O$, $H_2SO_4 \cdot 2H_2O$, etc.

Sulfuric acid is often used to dry neutral and acidic gases such as N_2 , O_2 , CO_2 and SO_2

Sulfuric acid will "suck" water out of carbohydrates and some other organic compounds which contain oxygen and hydrogen. For example, sulfuric acid will "suck" water out of sucrose, $C_{12}H_{22}O_{11}(s)$, (cane sugar) to produce a spongy mass of carbon:



- Sulfuric acid is used in the production of nitroglycerine, an inorganic ester & organic nitrate, which is used as an explosive but can also be used as a *vasodilator*, a substance that dilates blood vessels and can be used in the treatment of certain types of heart disease:

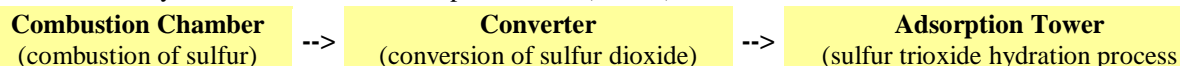


Although the production of sulphuric acid is eminent and known globally, related literatures have shown that numerous treaties have been written and published on it Corma et al(2005), York Fair (1968) The purpose of this research is to investigate into past works on the development of performance models for reactor types for the production of sulphuric acid, and to specifically identify and develop appropriate performance models for the areas that are deficient in past work.

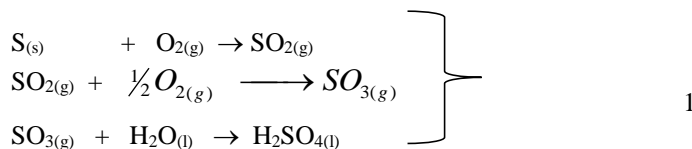
However, little or no known published work had been recorded for the development of performance models for the production of the acid using batch, continuous stirred tank reactor, and plug flow reactors. Recently works of Goodhed and Abowei (2014) focused on development of design models for H_2SO_4 production based on semi batch, isothermal plug flow (IPF) non-isothermal plug flow (NIPF) and non- isothermal continuous adsorption tower. Therefore, in this present paper we considered development of design equations for the simulation of isothermal continuous stirred adsorption tower (CSAT) primarily to evaluate the performance as a function of kinetic parameters which seemly not appraised.

2.0 KINETIC EVALUATION

The stoichiometry in the manufacture of Sulphuric Acid (H_2SO_4) is summarized as follows;



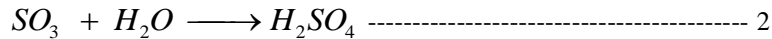
The *Contact Process* is a process involving the catalytic oxidation of sulfur dioxide, SO_2 , to sulphur trioxide, SO_3 . A vanadium catalyst (vanadium (V) oxide) is also used in this reaction in order to speed up the rate of the reaction. The current work looked at the development of performance evaluation models for vanadium catalyst based isothermal continuous stirred adsorption tower sulphur trioxide hydration process in the production of sulphuric acid. The stoichiometric chemistry is given as,



Substantial works had been done and documented on the kinetics of sulphuric acid production (Chrstenson et al (1999). Literatures have shown that direct dissolution of sulphur trioxide in water to produce the acid is not done due to very high heat of reaction occasioned in the process. Instead sulphur trioxide is absorbed in concentrated sulphuric acid to form oleum, and subsequently diluted with water to form sulphuric acid of 98%-100% concentration.

The reaction mechanism as presented in equation (3) showed chain reaction characteristics [Austin, 1984]. Gibney and ferracid (1994) reported on the photo-catalysed oxidation of SO_3^{2-} by (dimethyl-glyoximato) $(SO_3)_2^{3-}$ and its (Co(dimethyl-glyoximato) $(SO_3)_3^2$.

The work showed that the reaction



is described as irreversible bimolecular chain reaction. Further research into the works of Erikson, [1974] and Gibney, (1994) established the reaction as second order reaction with rate constant $K_2 = 0.3$ mole/sec. Blinding (1953) performed abinitio calculation and determined the energetic barrier and established conclusively that the irreversible bimolecular nature of the reaction have $\Delta H_f = -25$ kcal/mol at 25°C.

Following the outcome of the work of Chenier (1987), Charles (1977) and Ancheya (1997) as cited above, the rate expression for the formation and production of sulphuric acid is summarized as in equation 2.

$$-R_A = K_2 [SO_3] [H_2O] \text{ 3}$$

Hence from equation 3 the amount of SO₃ and H₂O that have reacted at any time t can be presented as;

$$-R_A = K_2 [C_{A0} - C_{A0} X_A] [C_{B0} - C_{A0} X_A] \text{ 4}$$

Where

- C_{A0} = Initial concentration of SO₃ (moles/Vol)
- C_{B0} = Initial concentration of H₂O (moles/Vol)
- X_A = Fractional conversion of SO₃ (%)
- $-R_A$ = Rate of disappearance of SO₃ (mole/ Vol/t)

In this work, the rate expression (-R_A) as in equation 4 will be used to develops the hypothetical continuous stirred tank reactor tower design equations with inculcation of the absorption coefficient factor as recommended in the works of Van-Krevelen and Hoftyger cited in Austein (1984) and Danner,(1983). This is achieved by modifying equation 4 as illustrated below. The hypothetical concentration profile of the absorption of sulphur trioxide by steam (H₂O) is represented in fig.2

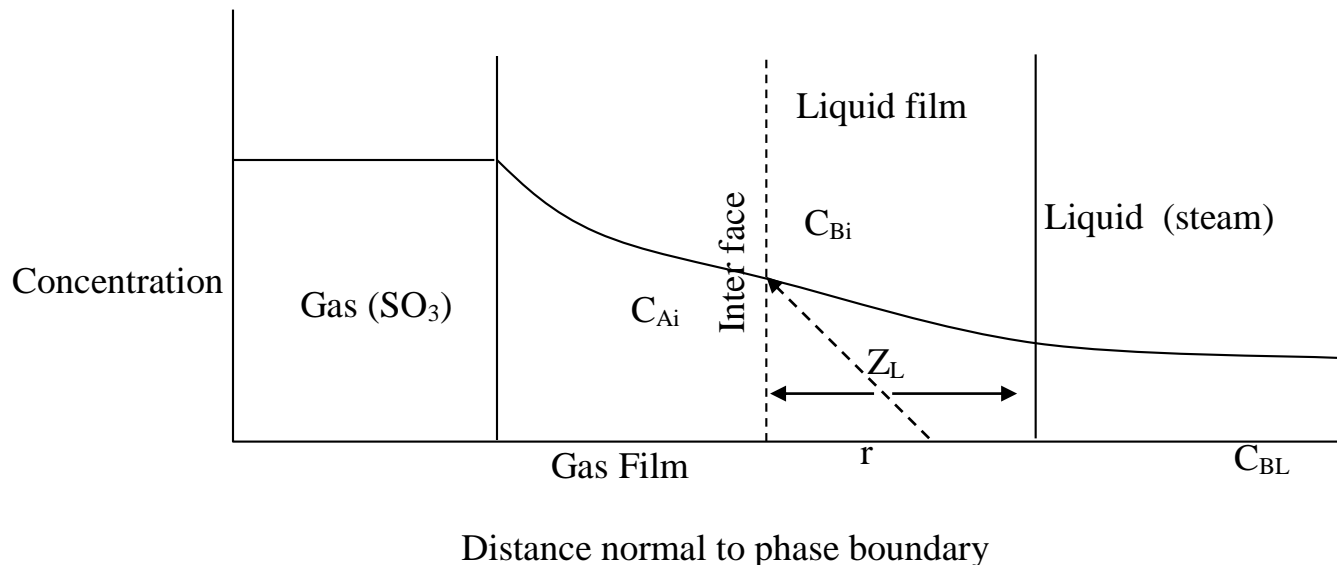


Figure 2: Absorption with chemical Reaction

Sulphur trioxide (A) is absorbed into the steam (B) by diffusion. Therefore the effective rate of reaction by absorption is defined by

$$-R_A = \frac{rD_L}{Z_L} (C_{Ai} - C_{AL}) = rK_L (C_{Ai} - C_{AL}) \text{ 5}$$

Invoking the works of Krevelen and Hoftyzer, the factor r is related to CAi, DL and KL to the concentration of steam B in the bulk liquid CBL and to the second order reaction rate constant K₂ for the absorption of SO₃ in steam solution. Thus

$$r = (K_2 D_L C_{BL})^{1/2} / K_L \dots\dots\dots 6$$

Substituting equation 6 into 5 results in

$$-R_A = (C_A) C_{BL}^{1/2} K_2^{1/2} D_L^{1/2} \dots\dots\dots 7$$

Previous reports (Octave levenspiel, 1999, Dewachtere et al, 1999) showed that the amount of SO₃ (C_A) and steam (C_{BL}) that have reacted in a bimolecular type reaction,

With conversion X_A is C_{AO}X_A. Hence equation 7 can be rewritten as

$$-R_A = K_2^{1/2} D_L^{1/2} (C_{BO} - C_{AO} X_A)^{1/2} (C_{AO} - C_{AO} X_A)$$

$$= K_2^{1/2} D_L^{1/2} C_{AO}^{3/2} (m - X_A)^{1/2} (1 - X_A) \dots\dots\dots 8$$

Where

$$m = \frac{C_{BO}}{C_{AO}}$$

- m = The initial molar ratio of reactants
- R_A = Rate of disappearance of SO₃
- K₂ = Absorption reaction rate constant
- D_L = Liquid phase diffusivity of SO₃.
- K_L = Overall liquid phase mass transfer coefficient
- r = Ratio of effective film thickness for absorption with chemical reaction

Materials and method

Development of performance model

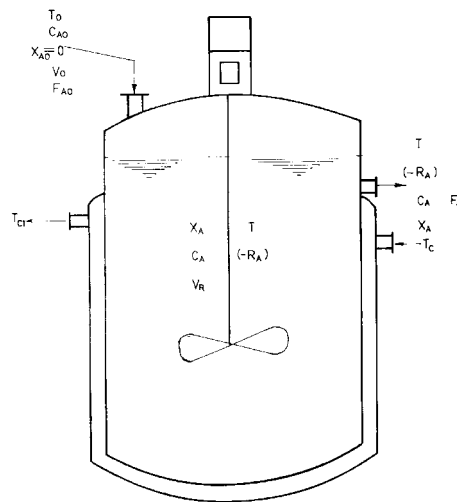


Fig. 3. Hypothetical model of a Jacketed CSAT

Reactor Volume

The performance equation for isothermal mixed flow reactor makes an accounting of a given component within an element of volume of the system. But since the composition is uniform throughout, the accounting may be made about the reactor as a whole. Octave Levenspel (1986) and Coulson & Richardson (1979, and 1979; Forglar, 1994 and Forment, 2001). Thus,

$$\text{Input} = \text{Output} + \text{disappearance by reaction} + \text{accumulation} \dots\dots\dots 9$$

Where

Accumulation = 0 for steady state process.

If $F_{A0} = V_0 C_{A0}$ is the molar feed rate of SO_3 to the reactor, then considering the reactor as a whole we have

$$\text{Input of } SO_3, \text{ moles/time} = F_{A0} (1 - X_A) = F_{A0} \quad 10$$

$$\text{Output of } SO_3, \text{ moles/time} = F_A = F_{A0} (1 - X_A) \quad 11$$

$$\text{Disappearance of } SO_3 \text{ by reaction, moles/time} = (-R_A) V_R \quad 12$$

Introducing the three terms in the material balance

Equation 9 yields.

$$F_{A0} X_A = (-R_A) V_R \quad 13$$

Which on re-arranging becomes

$$V_R = \frac{F_{A0} X_A}{(-R_A)} \quad 14$$

$$\text{But, } -R_A = \frac{dC_A}{dt} = K_2^{1/2} D_L^{1/2} C_{A0}^{3/2} (m - X_A)^{1/2} (1 - X_A)$$

Substitution in equation 14 results in

$$V_R = \frac{F_{A0} X_A}{K_2^{1/2} D_L^{1/2} C_{A0}^{3/2} (m - X_A)^{1/2} (1 - X_A)} \quad 15$$

F_{A0} = Molar feed rate of SO_3 , (mole/sec)

X_A = Conversion degree

C_{A0} = Initial concentration of SO_3 , (mole/m³)

K_2 = Absorption reaction rate constant, (1/sec)

D_L = Liquid phase diffusivity of SO_3 , (m²/sec)

M = Initial molar ratio of reactants.

Space Time

The space time T_s is mathematically defined as,

$$T_s = \frac{\text{Volume of reactor}}{\text{Volumetric flowrate}} = \frac{V_R}{V_0} \quad 16$$

Putting equation 15 into 16 results in

$$T_s = \frac{X_A}{K_2^{1/2} D_L^{1/2} C_{A0}^{1/2} (m - X_A)^{1/2} (1 - X_A)} \quad 17$$

3.1.3 Space Velocity

This is the reciprocal of the space time T_s and expressed mathematically as

$$V_s = \frac{1}{T_s} = \frac{V_0}{V_R} \quad 18$$

Then from equation 17 it is possible that

$$V_s = \frac{K^{1/2}_2 D^{1/2}_L C^{1/2}_{A0} (m - X_A)^{1/2} (1 - X_A)}{X_A} \quad 19$$

Reactor Height

Considering a reactor with cylindrical shape we have

$$V_R = \pi r^2 h$$

$$h = \frac{V_R}{\pi r^2} \quad 20$$

$$= \frac{F_{A0} X_A}{\pi r^2 K^{1/2}_2 D^{1/2}_L C^{3/2}_{A0} (m - X_A)^{1/2} (1 - X_A)} \quad 21$$

For 0.1m ≤ r ≤ 1.0m

Heat Generation Per Reactor Volume

Heat flow rate of CSAT is a function of heat of reaction for SO₃ addition to water, molar feed rate and the conversion degree. It is mathematically expressed (Abowei,1989) as;

$$Q = (-\Delta H_R) F_{A0} X_A \quad 22$$

The heat generation per reactor volume is obtained by dividing both sides of equation 22 by the reactor volume and substituting equation 15 accordingly gives,

$$R_q = \frac{Q}{V_R} = (-\Delta H_R) K^{1/2}_2 D^{1/2}_L C^{3/2}_{A0} (m - X_A)^{1/2} (1 - X_A) \quad 23$$

3.2 COMPUTATIONAL PROCEDURE

The developed models as presented in section 3 .1 were programmed using MATLAB and the flow chart describing the computational procedure is given in Fig 4. Performance dimensions such as CAST volume, length, space time, space velocity, heat generation per unit volume, and functional parameters capable of maintaining isothermal conditions were cleverly inculcated into the computer algorithm. The equations of these performance measures were expressed as a function of fractional conversions and other kinetic parameters at constant operational temperature. The computational algorithm exploited for the evaluation of performance parameters as a function of kinetic data is presented in figure

Algorithm flow chart for isothermal cast

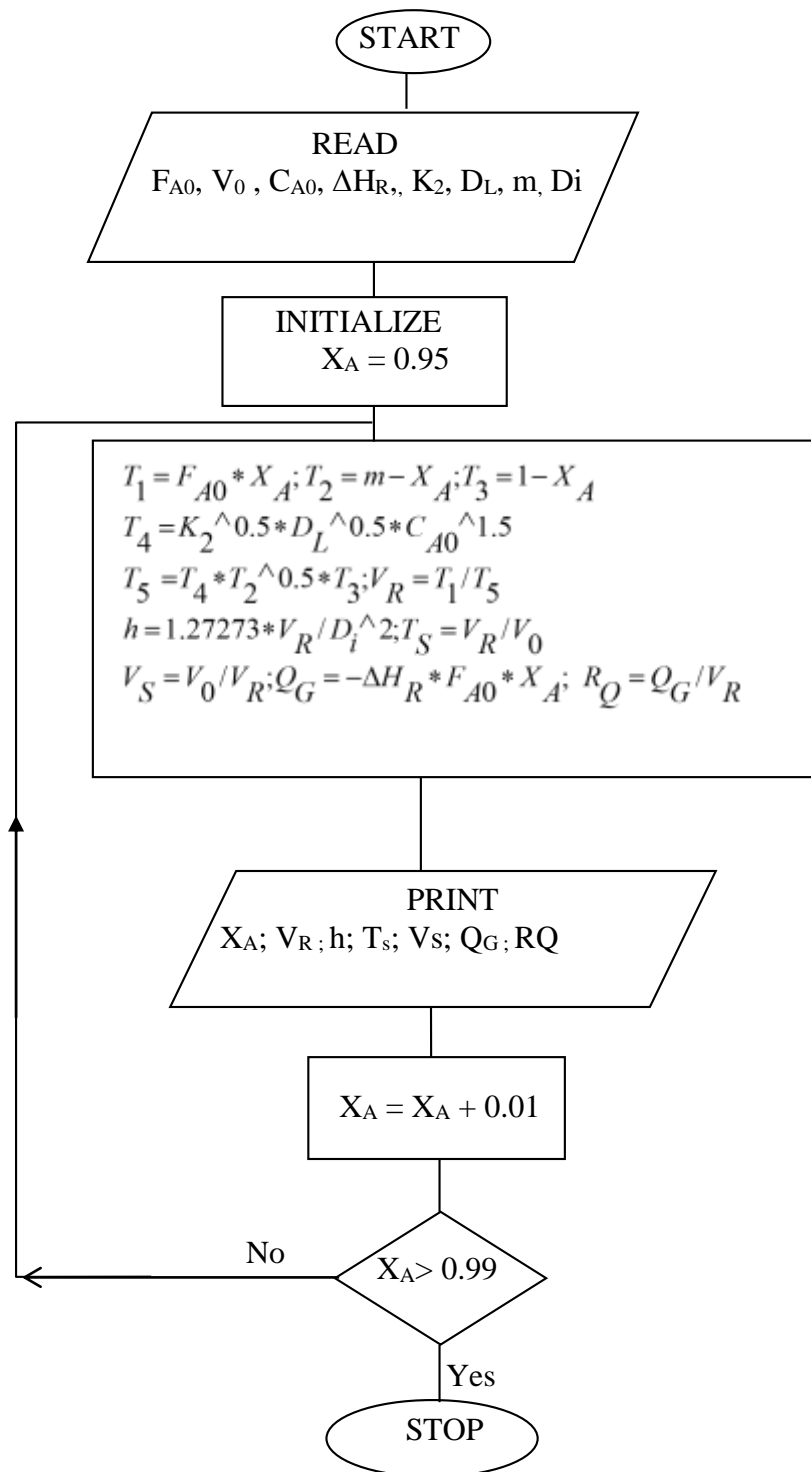


Figure 4: Flow chart describing the computation of isothermal CSAT functional Parameters.

Input parameters evaluation

The CSAT performance models developed in section 3 contain unknown parameters such as the molar flow rate, concentration, volumetric flow rate etc. These parameters have to be determined before equations 15 - 23 can be evaluated.

Table 1 Design data sheet.

Quantity	Symbol	Value	Unit
Initial concentration of SO ₂	C _{A0}	16,759	mol/m ³
Heat of reaction	ΔH _R	-88	Kj/mol
Product Density (H ₂ SO ₄)	ρ _p	1.64x10 ³	Kg/m ³
Absorption reaction rate constant	K ₂	0.3	1/sec
Conversion degree	X _A	0.95 - 0.99	%
Reactant molar flow rate	F _{A0}	3.937	mol/sec
Molar ratio of reactants	m	1.0 - 1.5	
Radius of CSTR	R	0.025 - 0.5	m
Liquid phase diffusivity of SO ₃	D _L	17	m ² /Sec
Volumetric flow rate of reactants	V ₀	2.352 x10 ⁻⁴	m ³ /Sec

Results and discussion

Industrial reactors for the production of sulphuric acid over a range of degree of conversion $X_A = 0.95$ to 0.99 have been investigated and designed. The reactor have a capacity of 1.389×10^3 Kg/hr of sulphuric acid. This reactor was designed with hastelloy because it has excellent corrosion and sulphuric acid resistance properties. The reactor performance models were simulated with the aid of MATLAB R2007b. The results provided information for the functional reactor parameters. These parameters include reactor volume, reactor height, space time, space velocity, and rate of heat generation per reactor volume. It is the purpose of this section to present and discuss the results of the reactor. The functional parameters of the reactor are tabulated in appendices A and B. The results showed that the reactor volume is dependent on degree of conversion X_A . The volume of the reactor would tend to infinity at 100% conversion. The variation of the reactor volume, space time, space velocity, heat generation per reactor volume, and reactor height as a result of sulphur trioxide addition to water with conversion degree is illustrated in figures 4, 5, 6, 7, and 8.

From the results it was observed that the reactor volume, space time, and reactor height increases with increasing degree of conversion, while the space velocity, and heat generation per reactor volume decreases with increasing degree of conversion.

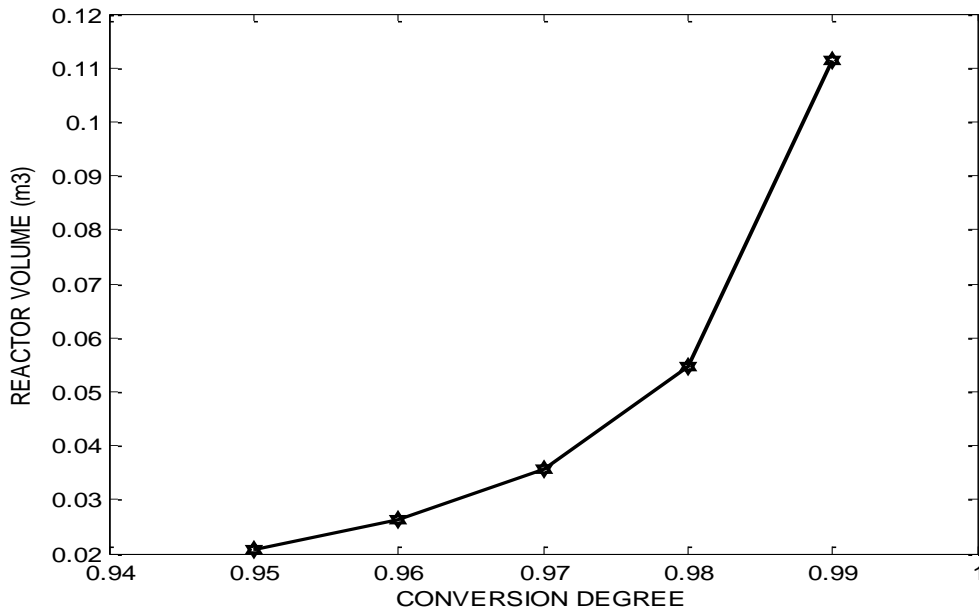


Figure 5: Plot of Reactor Volume against Conversion Degree for Isothermal CSTR

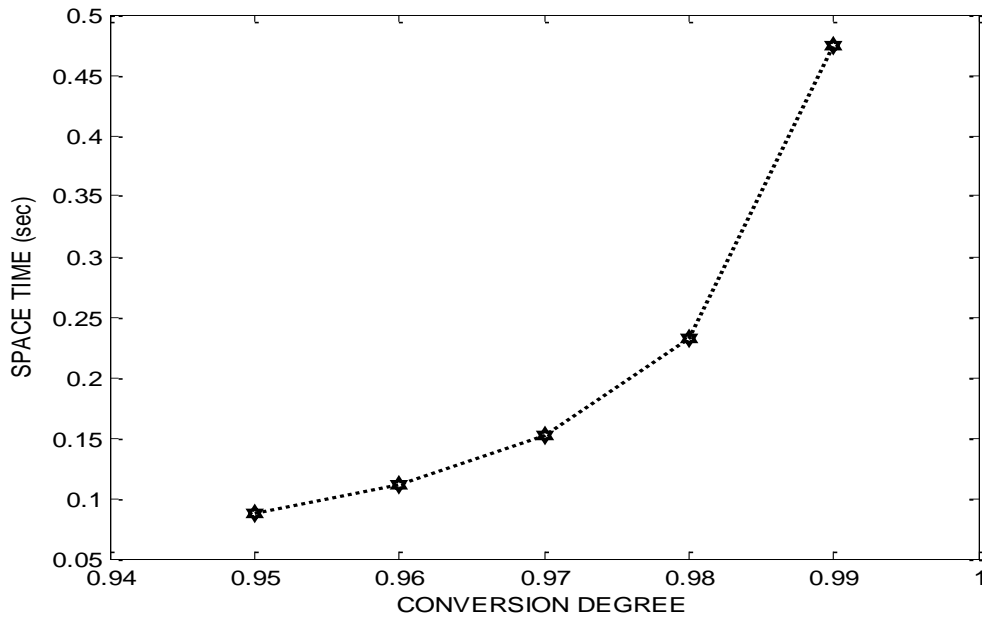


Figure 6: Plot of Space Time against Conversion Degree for Isothermal CSTR

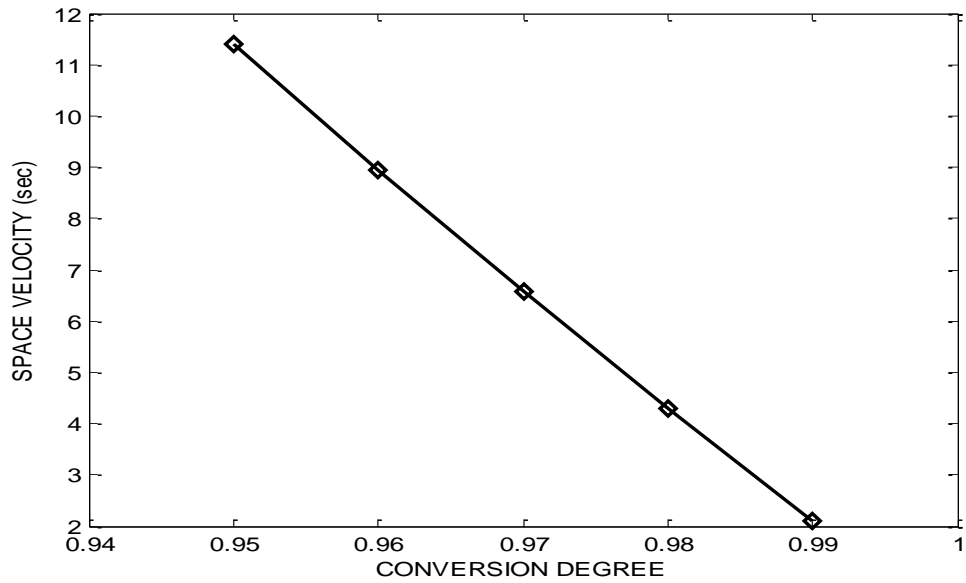


Figure 7: Plot of Space Velocity against Conversion Degree for Isothermal CSTR

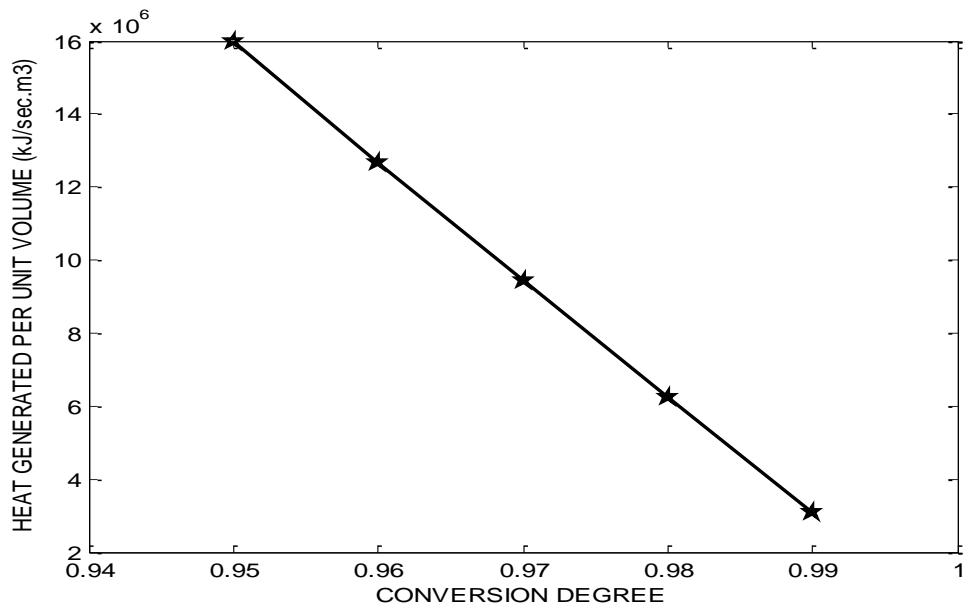


Figure 8: Plot of Heat Generated per unit Volume against Conversion Degree for Isothermal CSTR

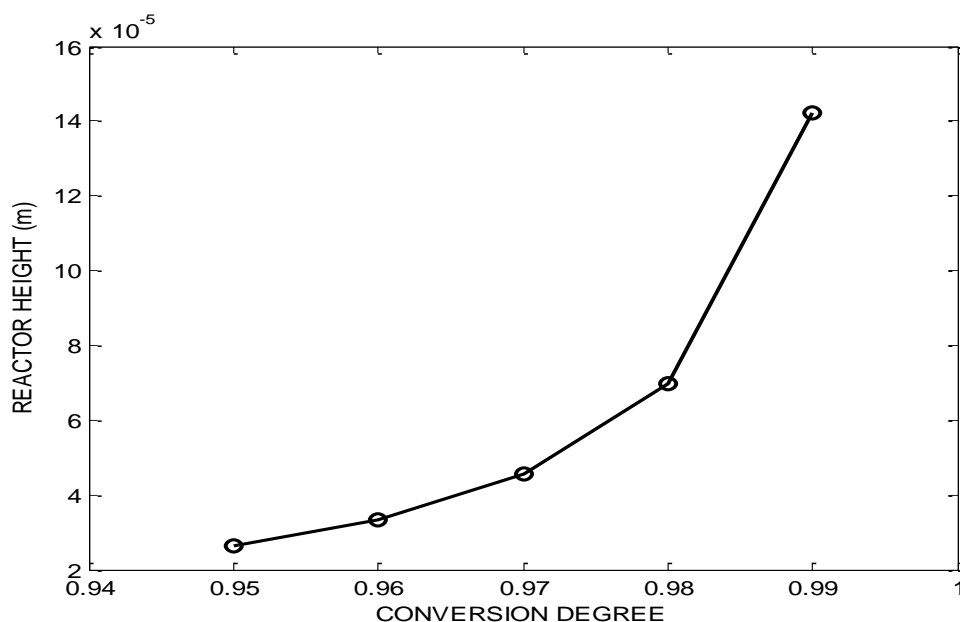


Figure 9: Plot of Reactor Height against Conversion Degree for Isothermal CSTR

From the results of the computation for the isothermal CSAT it was found that, if the degree of conversion, X_A was 0.95, the reactor volume, V_R were $6.84E-05m^3$ and $2.06E-05m^3$ when the reactant molar ratio, $m=1.0$ and 1.5 respectively but increase of X_A resulted in increase of the reactor volume up to $7.965E-04m^3$ to $1.115E-04m^3$ when $X_A=0.99$ and $m=1.0$ to 1.5 .

Conclusion and recommendation

An isothermal continuous stirred adsorption tower for vanadium catalyst based sulphur trioxide hydration process in the production of sulphuric acid have been designed. Computer program was developed and utilized to simulate the tower performance models over a range of conversion degree aimed at studying the performance functional dimensions behaviour. From the results of computation, it is clearly established that:

When the degree of conversion, $X_A=0.95$, the reactor volume, V_R are $6.84E-05m^3$ and $2.06E-05m^3$, the space time, T_S are $0.2906sec$ and $8.76E-02sec$, the reactor height h are $8.71E-05m$ and $2.62E-052m$, and the rate of heat generation per reactor volume, R_Q are $4.8205E06KJ/sec.m^3$ and $1.5988E07KJ/sec.m^3$ for the reactant molar ratio, $m=1.0$ and 1.5 respectively.

When the degree of conversion, $X_A=0.99$, the reactor volume, V_R are $7.965E-04m^3$ and $1.115E-04m^3$, the space time, T_S are $3.3863sec$ and $0.4742sec$, the reactor height, h are $1.0137E-03m$ and $1.42E-04m$, and the rate of heat generation per reactor volume, R_Q are $4.312E05KJ/sec.m^3$ and $3.079E06KJ/sec.m^3$ for the reactant molar ratio, $m=1.0$ and 1.5 respectively.

From (a) – (b) above, the reactor volume, the reactor height and the space time were greater at the upper limit of conversion degree, while the space velocity and the rate of heat generation per unit reactor volume decreases as conversion degree increases. Further work should critically concentrate on the aspects of process optimization and comparison analysis of all the sulphur trioxide hydration towers.

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