Use of Ozone/Enriched Oxygen for Process Intensification in the Manufacture of Nitric Acid: Modeling, Simulation and Optimization.

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Highlights

- Implications of ozone:Elimination of pollution control and recovery of total reactive nitrogen.
- Increased complexities due to N_2O_5 generation, elimination of formation and desorption of NO due to ozone.
- Sensitivity analysis of the effects of practically all the process parameters.
- Procedures for the estimation of design parameters with R^2 values better than 0.98 and standard deviations within 10%.

1. Introduction

In the manufacture of nitric acid, the absorption column occupies a dominant place. The inlet gases to the absorber (cooled gases from NH_3 oxidiser) consist of NO, NO_2, N_2O_3, N_2O_4, HNO_3, HNO_2, H_2O, O_2, N_2. The principal step which governs the column dimensions is the oxidation of NO. The oxidation rates are low when the NO concentration is less than 5000 ppm and very low when the NO concentration is less than 100 ppm. It was thought desirable to investigate the economic advantage of using enriched oxygen. It was also thought desirable to investigate the use of ozone when NO_x levels are below 5000 ppm. This can result into substantial reduction in column volume and/or the operating pressure. If the latter advantage is realized, the compression cost can considerably be reduced. Further, in practically all the performance models published in the literature the kinetics of oxidation as well as decomposition of HNO_2 have not been considered. Therefore, it was thought desirable to include these steps. The enriched oxidation by ozone is expected to enhance the rate of HNO_2 oxidation (to HNO_3) and hence the HNO_2 available for decomposition reduces. This means that lesser quantities of nitric oxide are desorbed to the gas phase. This feature has crucial implication because the need for the enormous volumes for the gas phase oxidation of NO reduces and hence the absorption columns can become compact. Thus, the use of ozone/ enriched oxygen plays an important role in process intensification. The use of ozone has two more important implications. First is the possible elimination of pollution control system which has been an integral part of classical nitric acid plants. Secondly, ozone is expected to recover all the reactive nitrogen in the form of nitric acid.

2. Mathematical Model

The introduction of ozone in the absorption section incorporates few additional features to the absorption process which already has following complexities: (i) NO_x gases consist of several components NO, NO_2, N_2O_3, N_2O_4, HNO_2, HNO_3, etc. and the liquid phase contains two oxyacids (i.e. nitric acid and nitrous acid), (ii) several reversible and irreversible reactions occur both in gas and liquid phases, (iii) absorption of multiple gases is accompanied by multiple chemical reactions, (iv) desorption of gases occur preceded by chemical reaction, (v) heterogeneous equilibria prevail between the gas and the liquid phase components, (vi) heat effects are associated with absorptions and the chemical reactions. In addition to the above mentioned complexities already present in the conventional absorption column, the newly proposed mathematical model takes into account (a) the enhanced rates of NO oxidation due to ozone/enriched oxygen (b) the presence of ozone also results in the formation of one more NO_X gas (N_2O_5) which incorporates additional gas phase equilibriums and also subsequent absorption N_2O_5 into water (c) it also enhances the rates of liquid phase oxidation as well as decomposition of nitrous acid(d) the use of ozone fully eliminates the formation and desorption of NO thereby reducing the column volume significantly.

3. Results and discussion

The foregoing discussion brings out the substantial advantages of the use of ozone/ enriched oxygen in terms of reduction in column volume (even by a factor of 4), elimination of pollution control system and the recovery of reactive nitrogen into the formation of additional nitric acid which otherwise demands the additional system for pollution abatement . However, the use of ozone/enriched oxygen has cost implications. Therefore, it was thought desirable to understand the cost effectiveness of using ozone/enriched oxygen as an oxidizing agent, to achieve the outlet NO_x (as per statutory standards) in substantially reducing the column volume and hence the capital and the operating costs and also recovering the reactive nitrogen. It is also possible to use ozone/enriched oxygen in ongoing operating plants for increasing the capacity by even a factor of two.

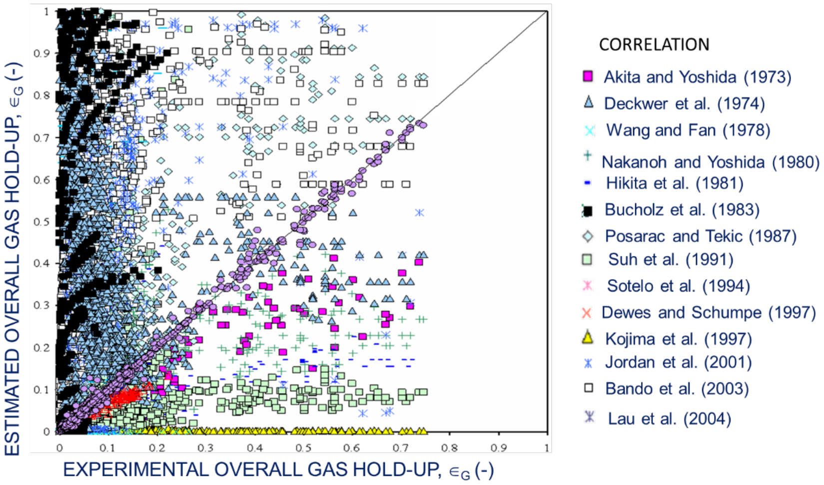

Figure 1. Parity plot for Gas-Hold up in Gas- Liquid Sparged Contactors: Comparision between experimental data and 14 empirical correlations.

4. Conclusions

In addition to providing process intensification with ozone or enriched oxygen; the proposed paper provides one more useful feature of providing reliable estimates of design parameters of plate columns such as gas and liquid side mass transfer coefficients, effective interfacial area, heat transfer coefficient, height of dispersion on plate, etc. This feature is very important because the published empirical correlations give estimates which vary by even 1000% which is shown in Figure 1 for gas hold-up. Such an enormous scatter of data is known to get reduced by the techniques of artificial intelligence such as support vector regression (SVR), genetic algorithm (GA), random forest model (RFM), etc. Using these techniques, procedures will be proposed for the estimation of design parameters with R^2 values better than 0.98 and standard deviations within 10%.

References

[1] V.G.Kankani, I.B. Chatterjee, J.B.Joshi, N.J.Suchak, Chem. Eng. J. 278 (2015) 430-446.

Keywords
"Ozone; Enriched oxygen; NO_x absorption; Process Intensification".

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ADYA ENTERPRISE (2014 - PRESENT) DESIGNATION : CO - FOUNDER

INDUSTRIAL PROJECT HIGHLIGHTS:

- **Improving reactive nitrogen utilization in 90 TPD sodium nitrite plant**

Engineering Challenges:

i. multiple gas phase and liquid phase reactions with heterogeneous equilibria,
ii. measurement of high concentration of NO_x at inlet and outlet of all towers,
iii. rigorous mathematical model development with error bar within 5% for getting NO_x ppm values as per pollution control board norms,
iv. in this wet process NO_x was absorbed in caustic solution leading to the formation of $NaNO_2$,
v. $NaNO_2$ is valued twice that of $NaNO_3$; therefore NO^*/NO_2^* ratio forms a major and critical engineering challenge to achieve 99% selectivity of $NaNO_2$ in the generation of value added products from waste NO_x gases,
vi. improvement in the tower performance by identifying hydrodynamic inefficiency and giving an increased throughput in the same volume.

- **Improving operation efficiency of metal dissolution for a capacity of 1000 kg/month in a noble metal plant from 7 days to 8 hours.**

Engineering Challenges:

i. the entire operation was mass transfer controlled because of lack of surface renewal,
ii. engineering solutions provided ensured enhanced mass transfer with chemical reaction and quicker surface renewal.

- **Treating waste stream of metals for generating value added products**

Engineering Challenges:

i. multiple metal elements including certain heavy metals present in the waste water stream,
ii. the engineering solution provided through electro-chemistry ensured 90 - 95% recovery of metals.

- **100 -125 kg/day high bio-viability proteins green field project**

Engineering Challenges:

i. continuous leaching operation, ± 0.1 pH controlled neutralization,
ii. static mixer design for non-Newtonian fluids for neutralization.

- **10 TPD biomass to ethanol green field project**

Engineering Challenges:

i. dispersion of low density solids in 10 kL reactor with θ_{mix} of 0.95 homogeneity, 30 bar (g) high pressure plug flow reactor design,
ii. vapor-liquid-solid separator design,
iii. NO_x abatement absorber design,
iv. ammonia abatement absorber design.

- **25 kg/day Anisole hydroxylation process with continuous mode of operation**

Engineering Challenges:

i. converting the process from batch mode of operation to continuous mode of operation,
ii. designing plug flow-reactor to ensure 5% conversion in each reactor,
iii. ensuring efficient heat transfer in the packed fixed bed reactors,
iv. continuous distillation system for product separation.

Ph.D. RESEARCH HIGHLIGHTS

DISSERTATION TITLE: *Mathematical Modeling of NO_x Absorption & Optimization of Absorption Systems*
Research Supervisor: *Professor J.B.Joshi*

Designing	*Basket Reactor*	For developing a profound understanding of the intrinsic kinetics of dissolution reactions for variousmetals such as copper, zinc, silver, nickel, uranium oxide in nitric acid.
	Laboratory test facility	Detailed PFD and PID
NO_x Analysis	*Chemiluminescence principle*	NOx analyser
	Reactions	Alkali absorption and peroxide oxidation
	Ion Chromatography	Dionex
Reaction Kinetics and Equilibria	*Reactions*	Multiple, Complex, Multiphase (solid, gas and liquid phase), Absorption, Desorption
	Equilibria	Interface, Heterogeneous
	Kinetics	Decomposition and Oxidation of nitrous acid.
Mathematical Modeling of Packed and Plate Columns	*Model Development for NO_x absorption comprising 23 aspects of the reaction mechanism in the model*	Using air and enriched oxygen for increasing absorption efficiency and miniaturizing
		For liquid phase oxidation of nitrous acid
Parameters quantified	*Kinetic*	Effect of nitric acid concentration on rate of absorption of NO_x gases
	Hydrodynamic	Effects of column diameter, design of internals and the operating parameters
Optimization		Detailed costing and optimization procedure

PUBLICATION & CONFERENCE

- **Kankani, V.G.**, Chatterjee, I.B., Joshi, J.B., Suchak, N.J., "Process Intensification of NOx absorption using enriched oxygen and liquid phase oxidation of nitrous acid". Chem. Eng. J. 278 (2015) 430-446.
- **Poster presentation** at 23rd International Symposium in Chemical Reaction Engineering (ISCRE) and 7th Asia-Pacific Chemical Reaction Engineering Symposium in Bangkok in September 2014

P.G. PROJECTS HIGHLIGHTS

POST GRADUATE DIPLOMA IN CHEMICAL TECHNOLOGY MANAGEMENT (2011-2012)

Project Title: "Improved water purification device",
Project Supervisor: Dr. Ravi Mohan

- Proposal of a comprehensive business plan focusing on the distinctiveness of the business concept
- Conduction of an exhaustive market analysis and survey, literature search on process technology.
- Strategic planning of sales implementation, Financial planning, Project costing and Profitability Calculations

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MASTER'S PROJECT (2006-2007)
Project Title: "Isolation, Characterisation and Quantification of DNA",
Project Supervisor: Dr. Nupur Mehrotra

- Standard protocols used to extract the DNA from following sources: Germinating moong seeds, cauliflower, onion and chicken liver
- Purity Ratios estimated using Absorbance Method
- Quantification of DNA using DPA method and estimation of total Phosphorous content in the DNA

EDUCATION

INSTITUTE OF CHEMICAL TECHNOLOGY, Mumbai, India

- **Ph.D** in Chemical Sciences — April 2008 – February 2015
- **Post-graduate Diploma in Chemical Technology Management** — January 2010- January 2012

MITHIBAI COLLEGE, MUMBAI UNIVERSITY, Mumbai, India

- **Master of Science (Chemistry)**
  Major: Organic Chemistry — June 2005-April 2007
- **Bachelors of Science**
  Major: Chemistry & Applied Chemistry — June 2002-April 2005

SCHOLASTIC ACHIEVEMENTS AND AWARDS

- **Gold** medal by Maheshwari Pragati Mandal, Mumbai for Ph.D. 2015
- **Citation** for **MVPM's Promising Maheshwari Scholar 2014,** Maheshwari Vidya Pracharak Mandal, Pune.
- Recipient of **IGCAR Junior Research fellowship** and **Senior Research Fellowship**
- Recipient of **fellowship** from UPL Trust
- **Second** place in Intercollegiate Kickboxing Tournament in Thane district at Sportsaga in 2013
- **Silver** medal by Maheshwari Pragati Mandal, Mumbai for first class in **B.Sc, 2006**
- Stood **second** in Intra Collegiate Quiz Competition 2005-2006
- Secured **Highest marks in Mathematics (94.66 %)** in **S.S.C 2000** in school

SEMINAR PRESENTATION AND WORKSHOPS

- Training cum workshop on Essential oil, Perfumery and Aromatherapy , Mumbai (May, 2017)
- Presentation on "Isolation, Characterization & Quantification of DNA", S.N.D.T College (February, 2007)
- Participated in 18th Research Scholars Meet, Mithibai College (February 2006)
- "Spectroscopy" & "Organic Chemistry", Chem. Club, Chem. Dept.,Vaze College (September 2005, 2006)
- "Non-Conventional Sources of Energy", Vaze College (September, 2005)
- "Nuclear Chemistry and Application of Radioisotopes" IANCAS,BARC, Mumbai (August, 2004)
- "Experimental Physics", The Department of Physics of R.D.National College & Homi Bhabha Centre for Science Education (January, 2003)

SKILL SET

Experimental	Separation, Analysis and Characterization of Mixtures, Preparations, Thin Layer Chromatography, Distillation, Vacuum Distillation, Volumetric titrations, Gravimetric analysis
Instrumental	Proficient in UV-spectrophotometer, Colorimeter, Flame photometer, pH-meter, Potentiometer
Theoretical	Proficient in Chromatogram Analysis of IR, NMR, Mass Spectroscopy, GC, HPLC
Computational	Fortran , Matlab, Python, Autocad , Mathematical Modeling
Linguistic	English, Hindi, Marwari and Marathi

EXTRA CURRICULAR ACTIVITIES

- Ph.D. mentor for Young Innovator's Choice Competition 2012
- Sponsorship Committee member for Young Innovator's Choice Competition and Young Researcher's Conference 2009
- Volunteered in TEQIP Experimental Workshop 2008-2009
- Exemplary services rendered during 62nd BRNS – IANCAS National Workshop on "Radioisotopes & its' applications to multiple areas" Chem. Dept. Mithibai College and IANCAS (October – November, 2006)

- Active participant in essay and poster competitions at inter and intra- collegiate level from 2003-2006
- Instrumental in making “Kshitij – 2002’’, the first ever College Fest of Mithibai College, a grand success
- Participant in International Assessments for Schools English, an examination for English proficiency conducted by University of New South Wales, Australia (December, 2000)
- Interested in reading, trekking, dancing, swimming, blog writing

REFERENCES

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