**CHEMICAL ENGINEERING**

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Author : **K J N SAI NITESH**

Title of the thesis : **STUDIES ON TORSIONAL BEHAVIOUR OF RECYCLED AGGREGATE BASED STEEL FIBER REINFORCED SELF COMPACTING CONCRETE**

Guide : **Dr. S. VENKATESWARA RAO**

Degree : **Ph. D.**

Student ID No. : **714004**

**ABSTRACT**

Any complex force system can be defined in terms of five basic actions viz. axial compression, tension, bending moment, shear force and a torsional moment. Torsion is one of the basic structural action which is low prioritized though very essential in analyzing the structures subjected to earthquake and wind loads. Torsion failure is mainly due to inherent weakness of concrete in tensile strength. In spite of all the various kinds of failures in concrete, torsional failure is brittle and sudden which occurs abruptly without any prior warning. This failure is magnified if concrete has inherent voids due to improper compaction in members such as columns, beams and slabs due to closer spacing of reinforcement.

Unoccupied voids and macro-pores inside concrete arise from inappropriate vibration and compaction might affect the mechanical strength and durability of the concrete and possible reasons of deterioration in concrete. Self-Compacting Concrete (SCC), originally established by Okamura in 1986 is a well thought-out solution to solve the above stated problems. Self-Compacting Concrete as the name itself indicates, no external effort in compacting the concrete, it compacts itself under its own weight.

Tensile properties of concrete can be significantly improved with addition of various fibers such as glass, steel, polypropylene etc. From literature review, it was found that tensile properties of concrete can be significantly enhanced with the inclusion of steel fibers. The difference between Steel Fiber Reinforced SCC (SFRSCC) and traditional Fiber Reinforced Concrete (FRC) is that the fiber content of FRC is mainly determined by the post-cracking behaviour, whereas the effect of fibers is mainly limited to fresh properties of SCC.

The nature of the construction industry is not environmentally friendly and the need for sustainable methods in construction is very crucial to ensure that natural materials are not depleted for future. The usage of cement and natural aggregate has increased drastically over the past few years in the construction industry. Due to depletion of natural resource such as lime stone and natural aggregates, there is an urgent requirement of replacing the main ingredients in concrete like cement and natural aggregates with locally available waste byproducts like mineral admixtures (flyash, GGBS, silica fume) as substitute to cement and recycled concrete aggregates to natural coarse aggregates. The use of mineral admixtures as partial replacement to cement is a well-established fact that its helps in improving the strength and durability performance of concrete and it is used by many researchers and by construction organizations. Although, the use of recycled concrete aggregate is well recognized as a sustainable material that can replace the natural coarse aggregates and offers solutions to this problem, but it is still considered as inferior to natural aggregate in terms of its structural properties.

There are various softwares available to perform nonlinear analysis on reinforced concrete and to study the behaviour of fiber reinforced concrete (FRC). ATENA Gid is one such software developed exclusively to perform non-liner analysis on reinforced concrete. ATENA is a finite element based software used for nonlinear analysis of reinforced concrete structures**.** By using Atena software, the actual behaviour of reinforced concrete structures, such as concrete crushing, cracking and yielding of reinforcing can be analyzed.

Combining the above and from a detailed literature review, the following points were observed.

* It is evident that use of steel fibers in SCC significantly improve the load carrying capacity and also changes the failure pattern from a brittle behaviour to ductile mode.
* Effect of steel fibers on torsional behaviour of self compacting concrete needs to be investigated.
* Effect of shape and aspect ratio of steel fiber on torsional behaviour of SFRSCC can be studied.
* The performance of SCC need to be evaluated with respect to vibrated concrete under all structural actions and verify the applicability of existing theories of vibrated concrete towards self compacting concrete.
* Effect of aspect ratio of steel fiber and its dosage in self compacting concrete needs to be investigated.
* The torsional behaviour of SCC with use of recycled coarse aggregates as replacement for natural aggregates is to be investigated.
* Analytical modelling using a Finite element based software can be used in studying the torsional behaviour of SCC and VC beams with and without steel fibers.

The scope of the present investigation includes:

* Evaluation of fresh and mechanical properties of steel fiber reinforced self compacting concrete for various dosages of steel fibers for low, medium and high-strength of SCC and thus maximizing the dosage of steel fibers.
* Develop analytical model for predicting torsional strength of steel fiber reinforced self compacting concrete (SFSCC) and Vibrated concrete (SFVC) with natural aggregates.
* Develop analytical model for predicting torsional strength of recycled aggregate based steel fiber reinforced self compacting concrete (RSFSCC) and vibrated concrete (RSFVC).
* Numerical modelling of steel fiber reinforced concrete using a finite element software ATENA for both SCC and VC for 20 MPa, 50 MPa and 80 MPa concrete strength and validate based on experimental results.
* To establish an equation to predict the torsional strength for SCC and VC with and without recycled aggregates.

The following objectives have been formulated to study and validate the use of steel fibers in SCC to evaluate the torsional behaviour.

1. To evaluate the fresh and hardened properties of natural aggregate and recycled aggregate based steel fiber reinforced SCC.
2. To predict the torsional behaviour of natural aggregate based steel fiber reinforced SCC and VC.
3. To propose the torsional behaviour of recycled aggregate based steel fiber reinforced SCC and VC.
4. To validate the experimental results with those obtained from finite element software ATENA.
5. To achieve the above objectives and keeping in view the scope of the research work, a detailed experimental program was planned and the work was divided into four phases.

**Phase: I**

Studies were carried out on fresh and hardened properties of steel fiber reinforced self compacting concrete for various dosages of hooked end steel fibers (0 %, 0.25 %, 0.5 %, 0.75 % and 1 % by volume of concrete) for three strengths i.e. 20 MPa, 50 MPa and 80 MPa. The effect of steel fibers on fresh and mechanical properties are studied with aspect ratio 50, 70 and 100. The various tests were conducted to evaluate the fresh properties of SCC included slump flow test, V-funnel test, V-funnel at T5min and J-ring test .The mechanical properties included compressive strength, split tensile strength and flexural strength.The mix proportions for SCC mixes were designed by using Nansu method of mix design.

**Phase - II:**

Studies on torsional behaviour of natural aggregate based self-compacting concrete for three aspect ratios (l/d= 50, 70 and 100) for 20 MPa, 50 MPa and 80 MPa strengths for both SCC and Vibrated Concrete. To correlate the experimental results with various models available in literature for vibrated concrete.

**Phase - III:**

Studies on torsional behaviour of recycled aggregate based self-compacting concrete for three aspect ratios (l/d= 50, 70 and 100) for 20 MPa, 50 MPa and 80 MPa strengths for both SCC and Vibrated Concrete. To correlate the experimental results with various models available in literature for vibrated concrete.

**Phase -** **IV:**

Analytical modelling of steel fiber reinforced self-competing concrete using both natural and recycled aggregates and to evaluate the effect of aspect ratio of steel fibers and strength of concrete using a finite element software ATENA. Compare the experimental results with results obtained through analytical modelling for 20 MPa, 50 MPa and 80 MPa strength SCC and VC.

The parameters of investigation include

|  |  |  |
| --- | --- | --- |
| Type of concrete | - | Self-Compacting Concrete (SCC) and Vibrated Concrete (VC). |
| Strength of concrete | - | 20 MPa, 50 MPa and 80 MPa. |
| Dosage of steel fibers | - | 0%, 0.25%, 0.5%, 0.75% and 1 % by volume of concrete- for maximizing fiber dosage |
| Aspect ratio of steel fibers | - | 50 (length= 25 mm, diameter = 0.5 mm), 70 (length= 35 mm, diameter = 0.5 mm) and 100 (length= 50 mm, diameter = 0.5 mm). |
| Type of aggregate | - | Natural aggregate (NA) and Recycled Coarse Aggregate (25 % replacement) (RCA ) |
| Dosage of steel fiber | - | 0 % and 0.5 % (maximum dosage of fiber)-adopted for casting of beams. |

From a detailed experimental study on Torsional behaviour of Steel Fiber Reinforced Recycled Aggregate based Self Compacting Concrete, the following conclusions have been drawn.

1. Based on Fresh properties it can be confirmed that 0.5 % dosage of steel fibers by volume of concrete is maximum for all three grades. All the aspect ratios of fibers could not achieve the fresh properties of EFNARC specifications for dosages 0.75 % and 1 %.
2. Based on hardened properties also it can be inferred that 0.5 % dosage of steel fibers by volume of concrete is the maximum dosage for self compacting concrete of three strengths. There is a good increase in the split and flexural strengths due to the fibers bridging the crack propagation and resulted in increased ultimate load carrying capacity of the specimens.
3. It can be concluded that steel fibers with aspect ratio 70 has significant contribution towards increase in mechanical properties of SCC compared to low (50) and high (100) aspect ratios with 0.5 % dosage of steel fibers. It is true for all strengths of SCC.
4. Due to addition of steel fibers, the ultimate torsional strength and angle of twist increased by 18.40 %, 24.77 % in A-VC-70 and 20.77 %, 31.39 % respectively in A-SCC-70 compared to plain beams.
5. In case of B-VC-70 and B-SCC-70, the increase in ultimate torsional strength and angle of twist was 16.22 %, 30.77 % and 17.06 %, 37.31 % respectively.
6. Due to addition of steel fibers, the ultimate torsional strength and angle of twist increased by 14.28 %, 57.75 % in C-VC-70 and 18.38 %, 83.02 % respectively in C-SCC-70 compared to plain beams.
7. The torsional strength of beams using recycled aggregates reduced by 8.59 %, 5.56 % and 8.96 % for plain VC beams of strength 20, 50 and 80 MPa respectively compared to beams with natural aggregates.
8. The torsional strength of beams using recycled aggregates reduced by 7.69 %, 5.28 % and 5.95 % for plain SCC beams of strength 20, 50 and 80 MPa respectively compared to beams with natural aggregates.
9. Similarly, a comparison was made between experimental and existing theories of torsion on vibrated concrete. It can be noticed that the ultimate torsional strength was under estimated by elastic analysis and was over estimated by plastic analysis.

Empirical formula is proposed to estimate the ultimate torsional strength of the member (TSCC) for SCC. This is given by

TSCC = (0.5-0.092(𝑏/𝑑)) (b2dft1) + (𝑙𝑑𝑖𝑎)\*ft2

Similarly, an empirical formula proposed to estimate the ultimate torsional strength of the member (TVC) for VC.

TVC = (0.5-0.118(𝑏/𝑑)) (b2dft1) + (𝑙𝑑𝑖𝑎)\*ft2

1/ ft= (1/ fc) + (1/ fspt)

1. Where, ft1 = Tensile strength of plain concrete; ft2 = Tensile strength of fiber reinforced concrete; fc = Compressive strength of concrete; fspt = Split tensile strength; b = width of beam; d = depth of beam; l = length of steel fiber; dia= diameter of steel fiber.
2. The Numerical results obtained are compared well those with experimental results and maximum values are within 85-90 % level of confidence and with an average error of 9.54 %.

**CHEMICAL ENGINEERING**

Author : **RAJESHKUMAR POLAGANI**

Title of the thesis : **SYNTHESIS, CHARACTERIZATION OF Pt-BASED**

**ELECTROCATALYSTS USING SONOCHEMICAL**

**METHOD: APPLICATION IN PEM FUEL CELLS**

Guide : **Dr. SHIRISH HARI SONAWANE**

Degree : **Ph. D.**

Student ID No. : 715067

**ABSTRACT**

This thesis mainly focused on the development of functional nanomaterials/electrocatalysts using an efficient method is called as **sonochemical (ultrasound) approach** for the polymer electrolyte membrane (PEM) fuel cells. In this present work, platinum (Pt) and Pt-based nanoparticles were synthesized using the sonochemical method. This research work represents the physicochemical, electrochemical characterization and fuel cell performance of Pt-based electrocatalysts. This sonochemical method offers a simple and convenient route to alloy the Pt-based electrocatalysts on support, which is suitable for the further development of high performance fuel cell catalysts. The main objectives of the study is synthesis of Pt-M/C (M = Co, Ni and Cr) and Pt-Co/C-PANI nanoparticles using the sonochemical method. The fabrication of the membrane electrode assemblies (MEA‟s) and their electrochemical and performance studies on PEM fuel cell are the additional objectives. Overall, this research

work deals with five different types of catalytic systems.

The **first system** demonstrates the carbon supported Pt nanoparticles (Pt/C) were

prepared using the sonochemical method and shown the best performance in PEM fuel cell.

The sonochemical method was a responsible technique to provide control over the particle

size of Pt/C nanoparticles. The sonochemical method using reducing agent (U+R) displayed

small particle size (3 nm) and higher distribution profile than the other two approaches

individually. The as-synthesized Pt/C cathode exhibited the higher EASA (8.8 m2/g) than the

commercial Pt/C cathode, which indicates the higher ORR activity. High limiting current

density could be achieved using as-synthesized Pt/C cathode than the commercial Pt/C

cathode. The peak power density produced from the as-synthesized Pt/C cathode was 0.198

W/cm2, which means the mass activity was higher than the commercial Pt/C cathode.

The **second system** demonstrates that the sonochemical method offers better control over the Pt-Co/C nanoparticles exhibits less than 6 nm of particle size. The carbon-supported Pt-Co (Pt-Co/C) nanoparticles with 1:1 molar ration and varying compositions were synthesized by sonochemical method in presence of PVP as a stabilizing agent. X-ray

diffraction (XRD) analysis confirmed the formation of Pt and Co alloys, which was shown by

2θ values increased to higher levels with increasing the Co content. As-synthesized Pt-Co/C

electrocatalysts exhibited the EASA 8.7 m2/g which is an indicative of high ORR activity.

Overall, the EASA and the current density decreased with increase in the Co content of

bimetallic nanoparticles. Different ratios of Pt and Co loadings on carbon support did not

significantly affect the structure of Pt-Co/C nanoparticles, but influenced the particle size, EASA of electrocatalyst and fuel cell performance. The current density decreased with increase in Co content and followed the order as Pt83-Co17/C > Pt75-Co25/C > Pt50-Co50/C. The fabricated PEM fuel cell was given power of 0.176 W/cm2 at 0.436 V with Pt83-Co17/C cathode and 40% Pt/C anode. The fuel cell showed relatively inferior performance when the composition of higher Co content was used in electrodes. The PEM fuel cell performance increases with increasing the cell operation temperature.

The **third system** demonstrates the use of sonochemical method to synthesize the

platinum-cobalt supported on carbon-encapsulated polyaniline (Pt-Co/C-PANI) electrocatalysts for PEM fuel cells. This cavitation technique provides a uniform dispersion of Pt and Co nanoparticles onto the carbon and polyaniline support. The Pt-Co nanoparticles

exhibits the spherical morphology with less than 6 nm of particle size, whereas combined Pt-

Co/C-PANI nanoparticles showed particle size up to 10-30 nm. The use of PANI in catalyst

support provided an additional EASA that promoted the higher electrocatalytic activity. The

ultrasound-assisted method played an important role in synthesis of C-PANI, in which carbon

particles were uniformly distributed in the composite material. The Pt-Co/C-PANI electrode

exhibited open circuit potential (OCP) of 0.91 V and electrochemical active surface area

(EASA) was found to be 5.98 m2/g. The Pt-Co/C-PANI cathode provides a maximum current

density of 120.8 mA/cm2 at 0.29 V and maximum power density of 36.4 mW/cm2 at 0.37 V.

The **fourth system** demonstrates the sonochemical synthesis of 1:1 molar ratio and

different compositions of Pt-Ni/C nanoparticles exhibits the uniform distribution with

spherical shape and the size smaller than 6 nm for PEM fuel cells. The alloy formation was

confirmed by XRD patterns, which shown by shifting of 2θ to higher levels with increasing

the Ni content. The Pt-Ni/C nanoparticles exhibits the monodispersity indicates by the

polydispersity index (PDI) value (0.126). The higher EASA and higher catalytic activity were

observed for the Pt83-Ni17/C electrocatalyst and both were decreased with increasing the Ni

content. The fuel cell performance remained quite low for higher Ni content electrodes. The

performance was high for the Pt83-Ni17/C cathode: 0.162 W/cm2 at 0.45 V tested in a single PEM fuel cell having 100 cm2 active area and the order follows as Pt83-Ni17/C > Pt75-Ni25/C > Pt50-Ni50/C.

The **fifth system** demonstrates the sonochemical method was an effective method to prepare the different compositions of Pt-Cr/C nanoparticles for the cathodes in PEM fuel cell. The sonochemical method provides homogeneous distribution of Pt and Cr nanoparticles on the carbon surface with spherical shape and smaller size (< 6 nm). The shifting of 2θ value in positive direction for the XRD patterns of Pt-Cr/C nanoparticles and the Pt-Cr/C cathodes exhibits the higher oxygen reduction than the Pt/C cathode, which confirms the Pt and Croalloy formation. The Pt83-Cr17/C cathode shows the higher EASA than the other two Pt-Cr/C cathodes, which indicates the high ORR activity. The performance of fuel cell was relatively inferior, if the Cr metal composition was high in Pt-Cr/C cathodes. The Pt83-Cr17/C cathode exhibits the best fuel cell performance as 0.138 W/cm2 power density at 0.38 V among the other two Pt-Cr/C cathodes when tested in 25 cm2 active area of PEM fuel cell with H2-O2 system.

**CHEMICAL ENGINEERING**

Author : **BANAVATH ANIL KUMAR NAIK**

Title of the thesis : **Heat Transfer Enhancement using Non-Newtonian Nanofluids in a Shell and Helical Coil Heat Exchanger**

Guide : **Dr. A VENU VINOD**

Degree : **Ph. D.**

Student ID No. : **715063**

**ABSTRACT**

It has been an established fact that modification of geometry can result in enhancement in heat transfer. Enhancement in heat transfer in a helical coil tube compared to a straight tube is one such example of a passive technique. Nanofluids containing nanoparticles (<100 nm) have been reported to exhibit tremendous potential for enhanced heat transfer. In this work, addition of nanoparticles to a base fluid (a passive technique) was used to study enhancement in heat transfer in a helical coil heat exchanger.

Nanofluids of different concentrations (0.2, 0.4, 0.6, 0.8 and 1.0 wt%) were prepared by dispersing Fe2O3, Al2O3 and CuO nanoparticles in aqueous carboxymethyl cellulose (CMC) solution, (base fluid). Thermo-physical properties viz.; rheological behaviour, thermal conductivity and stability of nanofluid were determined experimentally. The effect of base fluid concentration, nanofluid concentration and temperature on nanofluid viscosity and

thermal conductivity was investigated. Correlations were developed for viscosity and thermal

conductivity of nanofluids. Artificial Neural Network (ANN) modelling of viscosity and thermal conductivity was carried out. Enhancement in heat transfer was determined when nanofluid was used instead of base fluid (aqueous CMC solution) on shell-side, in forced and natural convection.

In this investigation, nanofluid exhibited non-Newtonian (shear thinning) behavior. CMC based nanofluids showed good stability and high effective thermal conductivity. Effective thermal conductivity increases, with the increase in nanofluid concentration and temperature. The developed correlations satisfactorily predicted the effective thermal conductivity of different non-Newtonian nanofluids over a range of concentration (0.2 - 1.0 wt %) and temperature (30-60oC).

Forced convection studies were carried out using nanofluids of three different materials (Fe2O3, Al2O3 and CuO). The effect of (i) nanofluid concentration (0.2, 0.4, 0.6, 0.8 and 1.0 wt%), (ii) temperatures (40, 50 and 60oC), (iii) stirrer speeds (500, 1000 and 1500 rpm) and (iv) Dean number on heat transfer rate (*Q*), overall heat transfer coefficient (*U*), shell-side heat transfer coefficient (*ho*), shell- side Nusselt number (*Nuo*), stirring work, energy savings, and effectiveness of heat exchanger was investigated. The heat transfer rate and overall heat transfer coefficient increase with increase in nanoparticle concentration, temperature, Dean number and stirrer speed. Nanofluid concentration and temperature have more significant effect on heat transfer rate and overall heat transfer coefficient.

Intensification of Natural convection was investigated in the shell and helical coil heat exchanger using CMC based non-Newtonian nanofluids under unsteady state conditions.

Studies have been carried out at different nanofluid concentration, water inlet temperature and coil fluid flow rates (Dean number). Results indicated that the addition of nanofluid has

intensified heat transfer as indicated by the higher temperature of nanofluid when compared to base fluid. A maximum enhancement in heat transfer rate of 23% has been obtained initially. At longer time the enhancement is less due to the lower buoyancy forces prevailing due to lower driving force. Nusselt number and Rayleigh number were found to decrease with time for all the experimental conditions.

The effectiveness of the heat exchanger was evaluated at different experimental conditions. Use of nanofluid resulted in higher values effectiveness of heat exchanger. Further, higher the concentration of nanofluid greater was the effectiveness. Savings in energy when nanofluid was used as a heating medium compared to that of base fluid were determined, at various experimental conditions. Results show that higher shell-side fluid temperature and stirrer speed resulted in more energy savings. CuO nanofluid gave higher percentage of energy savings compared to the other two materials.

**CHEMICAL ENGINEERING**

Author : **D. KISHORE**

Title of the thesis : **IDENTIFICATION AND CONTROL OF A PROCESS USING RELAY FEEDBACK AND SUBSPACE APPROACH**

Guide : **Dr. ANAND KISHORE KOLA**

Degree : **Ph. D.**

Student ID No. : **714146**

**ABSTRACT**

Identification and control plays a crucial role in process control applications. For any process to control and optimize one needs to identify it first either from experimental data or by mathematical modeling through transfer function approach which requires in-depth knowledge of the process which is actually a difficult task. There are various methods available in literature for identification and control of a process. The main limitation of these methods are when the order of the system increases, it is difficult to identify the higher order systems with less information. The investigation carried out in the present research work focuses on developing a novel method to identify and control the processes.

In the present research, four objective works with benchmark case studies namely; Identification of linear SISO process with modified Relay methods, identification and control of non-linear process using Relay feedback approach, identification and control of 2x2 linear multi input and multi output process using Subspace method with Relay and identification and control of 3x3 MIMO process using Subspace method and Relay have been carried out.

A single asymmetric Relay feedback method has been used for identifying a SISO process with sinusoidal excitation to generate sustained oscillations. For effectiveness of the method adapted, it was compared with other existing methods in literature. The identified parameters for SISO system from the adapted test were used to design simple PID controller for different processes and the design method is compared with method proposed by Chidambaram et.al. It has been observed that the results of present work gave better identification accuracy in terms of integral square error (ISE) when compared with Chidambaram’s method. A Relay feedback with subspace method has also been adapted to a SISO system. The relay test was carried out to generate input-output data which can replace experimental data for identification. It can be concluded that the proposed method works well for the identification of a process without any prior knowledge and may be extended for identification and control of higher order systems including unstable systems.

A simple approach is proposed to identify and control the non-linear systems using Relay feedback approach. A relay with hysteresis and combination of the low-pass filter is used to reduce the effect of noise in the process. From the identified model parameters, additional parameters were obtained by solving the set of non-linear equations using MATLAB.

The effectiveness of the proposed method is best illustrated by considering the two non-linear systems such as Hammerstein and Wiener processes.

The identification method adapted for SISO process is also extended for 2X2 MIMO to determine the system transfer function matrix by state space model using N4SID algorithm from system identification toolbox. The proposed identification method neither requires prior knowledge to carry out identification unlike subspace identification method nor involves excessive calculations unlike auto-tuning using relay-feedback method. Examples based on stable transfer functions were considered to observe the efficacy of the proposed method. Identification is followed by control. Subsequently a normalized de-coupler was designed for estimated transfer function matrix of the MIMO system based on RGA-NI-RNGA criterion. The controller parameters were obtained using Skogestad’s IMC (SIMC) with PI/PID tuning rules. It has been observed that the accuracy is much better compared to relay-feedback method even for higher order system. The accuracy for system without disturbance approximates very close to parameters of systems but for systems with disturbance it varies depending on the order of the system & other factors. The closed-loop control scheme also showed that the performance of present control yields faster and stable response compared to other schemes.

The same method was also extended to 3x3 MIMO of Orgunnaike and Ray distillation column with N4SID algorithm. For the identified MIMO process, RGA-RNGA casual, stable and proper decoupler is derived that reduces the interaction and converts 3 × 3 MIMO system to ‘3’ individual SISO systems. Skogestad’s tuning rule was employed to design PI/PID controller parameters. This method is found to be more efficient, less time-consuming and easy for calculations for identification of multivariable systems, since N4SID algorithm is used to carry out matrix operations. Unlike the subspace method that requires pre-designed controller to carry out subspace identification, it doesn’t require predesigned controller, which is replaced by the relay. The fundamental Z–N tuning method was used to determine another set of parameters and the effectiveness of control parameters obtained by both methods were compared. Here, the Skogestad’s tuning rule showed better performance over Z–N PID in terms of minimum IAE.

**CHEMICAL ENGINEERING**

Author : **P. THIRUMALA BAI**

Title of the thesis : **CATALYTIC CONVERSION OF ETHANE TO**

**ETHYLENE BY CARBON DIOXIDE OXIDATIVE**

**DEHYDROGENATION**

Guide : **Dr. S. SRINATH**

Degree : **Ph. D.**

Student ID No. : **714150**

**ABSTRACT**

The consumption of olefins and olefin derived products is increasing year by year. Particularly the demand for ethylene is increasing as it is the preferred raw material for the manufacture of numerous industrially significant products. The global production of ethylene has increased to approximately 160 million tons per year with a growth rate of 4% per year. A majority of industries in the world produce ethylene commercially by dehydrogenation of hydrocarbons feedstock like natural gas and naphtha by steam cracking. This process is energy intensive as it is endothermic in nature. The process operating at high temperatures also has thermodynamic limitations in the paraffin conversions. Besides, it leads to coke formation. To overcome these difficulties Catalytic oxidative dehydrogenation (ODH) using various oxidants especially oxygen has emerged as an extremely attractive alternative for ethylene. This process eliminates thermodynamic limitations in the paraffin conversion and this it can be executed at reasonably low temperatures and it also requires less energy when compared to traditional production routes. Coke formation is also reduced and as a consequence the frequency of catalyst regeneration is diminished. Even though the ODH with oxygen is environmentally friendly, it requires an air separation unit which increases the cost of the process. Due to the exothermic nature the reaction is also associated with some major drawbacks like thermal run-away of reaction and the difficulty in controlling the selectivity of ethylene due to the formation of unwanted oxides of carbon because of over oxidation. Another alternative is the utilization of N2O as the oxidant, wherein high conversions could be realized due to the formation of O- radical species, but the limited

availability of the oxidant and low ethylene selectivity at high conversions make this methodology of ethylene generation less attractive.

Over the past decades, much attention has been paid on limiting the emissions of carbon dioxide into the atmosphere as it is a greenhouse gas and is recognized as a major culprit for global warming. In recent years, carbon dioxide capture and its sequestration has been given immense importance. Instead of looking it as a waste, it is now considered as a cheap raw material in chemical production. It can be used as a non-traditional oxygen source or a mild oxidant for ethylene production in the dehydrogenation of ethane due to its huge advantages in containing the exothermicity of the reaction. It also acts as a diluents to achieve great equilibrium conversion of light alkanes, thus giving way to high selectivity towards ethylene formation. Coke formation on the catalyst can also be reduced and the catalytic activity can be maintained over a longer period of time. An extensive gamut of catalysts with wide variety of supports has been studied for the oxidative dehydrogenation of ethane using different oxidants. Among them supported chromium catalysts are highly active for ODH of ethane and are found to offer superior CO2 conversion. The nature of chromium species formed and their distribution on the support surface play important role in the activity and selectivity of the catalyst. The activity of catalysts and selectivity of supported chromium catalysts are considerably influenced by the type of supports due to their different physico–chemical characteristics like acid-base properties, thermal stability, surface areas, active-phase –support interactions, oxidant (oxygen) storage capacity, reducibility and so on. This observation emphasizes the need for identification of a proper support. It is well known that mixed oxide supports combine good textural and mechanical properties and establish different types of interaction with the active component. It is noticed that sulfation of silica has a positive effect on the catalyst material while strong basic promoters (alkali metal oxides) suppress the catalytic activity. It is required to study the influence of sulfate modification of mesoporous silica supported chromium oxide catalysts in view of their beneficial effects in controlling the aggregation phenomena.

In view of the importance of chromium based catalysts this thesis is proposed to study the preparation, characterization, and evaluation of chromium based catalysts with different support materials i.e. non silica (metal oxides) and silica materials for the Oxidative Dehydrogenation of ethane to ethylene. Carbon dioxide oxidative dehydrogenation of ethane was successfully carried out over the chromium based catalysts. All the chromium based catalysts with different supports were prepared by impregnation technique. The catalysts were characterized by different physico – chemical methods like BET surface area, X-ray diffraction, temperature programmed reduction and X-ray photoelectron spectroscopy for better understanding of their properties and to know the nature of interaction of Cr2O3 with the supports. The characterization results revealed that the chromium can be stabilized on supports with its higher oxidation states along with its highly stable oxidation state (Cr+6, Cr+5 and Cr+3) and also inferred that the redox couples (Cr+6/Cr+5 to Cr+3) are responsible for carbon di oxide oxidative dehydrogenation of ethane. The performance of these catalysts with different supports was evaluated for the Oxidative Dehydrogenation of Ethane in a fixed bed quartz down flow reactor at 550 – 650 °C. The main focus is devoted to deeper insights on nature and type of catalysts and their physico-chemical characteristics in relation to their performance properties.

For metal oxide supported Cr2O3 catalysts with varying Cr2O3 contents ( 5-20 wt%), it has been observed that the performance of catalyst and selectivity are strongly depend on the nature of chromium oxide species formed and the surface enrichment of chromium in the near surface region, The content of chromium in turn strongly influence these two properties. Among all, the 15 wt% chromium loading is necessary to obtain reasonable ethane and carbon dioxide Conversions due to clear enrichment of chromium in the near –surface region and formation of optimum amount of CrOx species. Based on this result 15wt% Cr2O3 has been considered as an optimum loading and it is used for further studies.

It is generally accepted that a mixed oxide support has an edge over its component single oxides as support in combining their good textural and mechanical properties. The performance of mixed i.e Al2O3& ZrO2 supports at different combinations were evaluated for ODH of ethane. Equal compositions of mixed oxide i.e. 15 wt% Cr2O3/Al2O3-ZrO2 (1:1) catalyst showed the best catalytic activity among all the catalysts used in this study. The selectivity of ethylene mainly depends on the oxidizing atmosphere, which can be clearly explained by the C2H4 temperature programmed desorption. The performance of silica supported catalysts was also evaluated with special emphasis to sulfate modifications of the catalysts. The catalytic activity and selectivity over metal oxide and silica material supported chromium based catalysts with varying compositions were found to depend strongly on the nature of support and chromium oxide species formed and the surface enrichment of chromium in the near-surface region. Among all, sulfated SBA-15 supported chromium based catalyst has displayed the superior performance.

In heterogeneous catalytic reactions the heat and mass transfer play a vital role in affecting the rate of a reaction. In the study of intrinsic rates of reaction both the diffusion mechanism should be negligible prior to the kinetic studies. Kinetic parameters were evaluated at different feed conditions. The rate of C2H4 and CO2 formations were measured by varying the total flow rate of the reactants, temperature and Catalyst particle size. The oxidative dehydrogenation of ethane using CO2 is kinetically modeled by various models for mixed supported chromium based catalyst and it is found that the ethane and CO2 decomposition rates are given by LHHW model. The parameters obtained from the model are checked for thermodynamic and statistical consistency. The response surface methodology is formulated for different independent variables and the corresponding surface plots and contour plots are plotted to check for optimum conditions. The optimum results are in good agreement with the experimental values.

**CHEMICAL ENGINEERING**

Author : **PURUSHOTTAMA RAO DASARI**

Title of the thesis : **ANALYTICAL DESIGN OF CONTROL STRATEGIES FOR UNSTABLE TIME DELAY SYSTEMS**

Guide : **Dr. A. SESHAGIRI RAO**

Degree : **Ph. D.**

Student ID No. : **714148**

**ABSTRACT**

For a wider range of stable processes, many analytical PID controller tuning rules are available. However, for unstable processes, the availability of analytical tuning rules is limited. In this thesis, H2 minimization theory in combination with internal model control (IMC) is used to analytically derive PID controller settings which can be used as a ready reference like look-up tables. These analytical settings are developed for a defined range of time delay to time constant ratio. Maximum sensitivity (Ms) is used for evaluating the robustness of the control system. Case studies of unstable systems are considered to evaluate the closed loop performances for set point variations and load disturbance variations. Robustness is evaluated for uncertainties in the process model as well as for the sensor noise. Recently published methods in the literature are considered for the performance comparison with the proposed method. Based on simulation results, it is observed that the current methodology provides significantly enhanced performances when compared with those techniques available in the recent literature. Experimental implementation is carried out on an inverted pendulum for demonstrating the practical applicability of the present method.

Optimal H2 internal model controller (IMC) is designed for control of unstable cascade processes with time delays. The proposed control structure consists of two controllers in which inner loop controller (secondary controller) is designed using IMC principles. The primary controller (master controller) is designed as a proportional-integral-derivative (PID) in series with a lead-lag filter based on IMC scheme using optimal H2 minimization. Selection of tuning parameter is important in any IMC based design and in the present work, maximum sensitivity is used for systematic selection of the primary loop tuning parameter. Simulation studies have been carried out on various unstable cascade systems. The present method provides significant improvement when compared to the recently reported methods in the literature particularly for the disturbance rejection. The present method also provides robust closed loop performances for large uncertainties in the process parameters. Quantitative comparison has been carried out by considering integral of absolute error (IAE) and total variation (TV) as performance indices.

Controller design for unstable processes is relatively difficult when compared to stable processes. The complexity increases further for multivariable unstable processes. In this work, simplified tuning rules are proposed to design PID controller for unstable multivariable processes. Decouplers are applied to make the loops independent and diagonal elements of equivalent transfer function are used to design controllers. Two examples of TITO (two input two outputs) unstable system with time delays are considered for simulation. Comparative analysis has been carried out with the recently reported methods in the literature and observed that the proposed method provides improved closed loop performances. Robustness studies are also carried out with perturbations in the model parameters.

Control of unstable processes with time delays usually result in large overshoots in the closed loop responses. In industry, set-point weighting is one of the recommended methods to minimize the overshoot. In this work, a method is proposed to design the set-point weighting parameters which is relatively simple. Weighting is considered for both proportional (β) and derivative (γ) terms in the PID control law. In the closed loop transfer function for the servo problem, the coefficients of ‘s’ and separately that of ‘s3’ both in the numerator and denominator are set equal in order to find β and γ. The obtained expressions for β and 𝛾 are simple and depends on the controller parameters. The method is carried out first for single input single output (SISO) unstable first order and second order processes with time delays and then for the multi input multi output (MIMO) unstable systems. In control of MIMO systems, decouplers are considered to ensure that the loops have minimum interactions. With the designed values, the closed loop performance is evaluated for different SISO and MIMO unstable systems with time delay. The present method is also compared with the recent methods proposed in the literature and it is observed that enhanced closed loop performances are achieved with the proposed method.

**CHEMICAL ENGINEERING**

Author : **SURESH KUMAR MUDUNURI**

Title of the thesis : **PROCESS INTENSIFICATION USING CAVITATION & MICRO REACTOR: CASE STUDIES ON WATER TREATMENT AND NANOPARTICLE PRODUCTION**

Guide : **Dr. SHIRISH HARI SONAWANE**

Degree : **Ph. D.**

Student ID No. : 701315

**ABSTRACT**

This research work deals with process intensification using cavitation technique as process-intensifying method and microreactor/ advanced flow reactor® as the process-intensifying equipment. In the present work, acoustic caviation has been used for the production of photocatalyst and hydrodynamic cavitation was used as advanced oxidation process for the degradation of organic dye pollutants. It was also investigated that hydrodynamic cavitation (HC) combined with other advanced oxidation processes as well as oxidizing agents for the degradation of organic dye pollutants. In case of process intensifying equipment microreactor and advanced flow reactor®has been used for the production of stable colloidal copper nanoparticles.

The present work mainly deals with four systems,

System I: Production of Bi doped photo catalyst using ultrasound and use of hydrodynamic cavitation for making hybrid system for waste water treatment using photo catalyst for degradation of the dye. Bi-doped TiO2 photocatalyst has been prepared by using a novel ultrasound assisted solution based chemical synthesis method. Further, degradation of methylene blue (MB) dye in aqueous solution was carried out by using hydrodynamic cavitation combined with H2O2 and Bi-doped TiO2 photo-catalyst. The effect of various operating parameters such as inlet fluid pressure, solution pH, addition of H2O2 and photo-catalyst on the degradation of MB dye has been investigated. The maximum extent of degradation of methylene blue was obtained at inlet pressure of 5 bar and pH around 2. The loading of H2O2 has been optimized at 1:20 molar ratio of MB:H2O2. Hydrodynamic cavitation and H2O2 has shown significant synergetic index of 11.79.However, less synergetic index of 1.46 was observed between hydrodynamic cavitation and Bi-doped TiO2 photocatalytic process for the degradation of methylene blue.

System II: Second system deals with ultrasound assisted synthesis of graphene-TiO2 nanocomposites (G-TiO2) by sol-gel method. The prepared reduced graphene oxide (RGO) was used as photocatalyst for the decolorization of malachite green (MG). Graphene oxide (GO) has been prepared by the modified Hummers-Offeman method in presence of ultrasonic irradiation. Decolorization of MG dye has been achieved using hydrodynamic cavitation and in combination with other advanced oxidation processes.The hydrodynamic cavitation was first optimized in terms of different operating parameters such as inlet pressure, and pH to get the maximum degradation of MG dye. In the hybrid techniques, combination of hydrodynamic cavitation with H2O2, G-TiO2, and G-TiO2/H2O2 have been used to get the enhanced degradation efficiency through hydrodynamic cavitation device. The maximum extent of MG dye decolorization around 99.4 % has been observed using hydrodynamic cavitation in conjunction with G-TiO2/H2O2 under the optimized conditions (inlet pressure 2 bar and pH value 8.5 in 90 minutes).

System III : Third system deals with the degradation of ternary dye (combination of dye includes methylene blue, methyl orange, rhodamine) in aqueous solution has been systematically investigated using independently hydrodynamic cavitation, combination of hydrodynamic cavitation (HC) and H2O2 and the combination of hydrodynamic cavitation (HC) with various other advanced oxidation processes such as Fenton, photo-Fenton, photoly tic and photocatalytic processes. Initially, the effect of different operating parameters such as inlet pressure to thecavitating device (2–8 bar) and operating pH (2–9) has been investigated. The substantial synergetic effect hasbeen observed using HC + H2O2 process, which confers the synergetic coefficient of 28.97. The hybrid process consist of HC + Fentonprocess significantly enhanced the rate of degradation of ternary dye, which leads to a completedegradation of ternary dye within 20 min of operation using the molar ratio of ternary dye: H2O2 as1:40 and the molar ratio of FeSO4.7H2O: H2O2 as 1:30.

System IV: Fourth system deals with the production of stable colloidal copper nanoparticles using microreactor and Advanced flow reactor®. In the both microreactors, copper nanoparticles were prepared by chemical reduction method in a copper sulfate solution using ascorbic acid as reducing agent. Ascorbic acid plays roles as reducing agent and antioxidant of colloidal copper, due to its ability to scavenge free radicals and reactive oxygen molecules. Temperature and concentration ratio of reducing agent to precursor, change in flow rates of the precursors influenced the synthetic progress and size of the copper nanoparticles. In both the microreactors size of copper nanoparticle decreases with the increasing flow rates. In capillary microreactor, copper nanoparticles with average size 270 nm were formed in the temperature range 75 oC - 80 oC and in advanced flow reactor® average size of 206 nm were formed in the temperature range 85 oC - 90 oC.

**CHEMICAL ENGINEERING**

Author : **Mr. BHASKAR BETHI**

Title of the thesis : **DEVELOPMENT OF HYBRID SYSTEM FOR WASTEWATER TREATMENT BASED ON HYDRODYNAMIC CAVITATION**

Guide : **Dr. SHIRISH HARI SONAWANE**

Degree : **Ph. D.**

Student ID No. : **714035**

**ABSTRACT**

This research work mainly deals with the decolorization/degradation of organic dye pollutants from aqueous streams using the advanced oxidation process (AOP) as a base technique. AOP’s involves the generation of hydroxyl radicals (•OH) and plays a key role in degradation and converting of organic pollutants into CO2, H2O, some short chain organic acids and intermediate compounds. Recently, hydrodynamic cavitation (HC) technique has been explored as a one of the emerging advanced oxidation technology (AOT) for degradation of various organic pollutants in the aqueous streams. In the present work, HC has been used a basic AOT. This work also demonstrated the combination of hydrodynamic cavitation with other AOP’s such as photocatalysis, hydrogen peroxide (H2O2), as well as the hydrogel adsorption, nanofiltration and Fenton process for the degradation/removal of dye pollutants from wastewater.

This thesis deals with five systems, the **first system** deals with an acoustic cavitation engineered novel approach for the synthesis of titanium di-oxide (TiO2), cerium (Ce) and iron (Fe) doped TiO2 nano-photocatalysts. As synthesized TiO2, Ce and Fe doped TiO2 nano-photocatalysts were characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis to evaluate their structure and morphology. Photocatalytic performance of both un-doped and doped TiO2 photocatalyst was investigated for the decolorization of Crystal Violet (CV) dye in aqueous solution at pH of 6.5 in the presence of hydrodynamic cavitation. Effect of catalyst doping with Fe and Ce was also studied for the decolorization of CV dye. The results show that, 0.8 % of Fe-doped TiO2 exhibits maximum photocatalytic activity in the decolorization study of CV dye due to the presence of Fe in the TiO2. Kinetic study was also carried out for the hybrid AOP (HAOP) and that followed the pseudo first-order reaction kinetics.

The **second system** deals with the decolorization of high concentrated Malachite Green (MG) dye (500 mg/L) in aqueous solution using a HAOP. HC setup consists of centrifugal pump having the power rating of 0.5 HP, 2 mm diameter of the orifice hole as a cavitation device and 9 W ultraviolet (UV) light were used in this study. It has been observed that MG dye was effectively decolorized up to 96 and 99.9 % at pH 8.5 and at an inlet pressure of 2 bar in 90 mins of reaction time using the HC+UV and HC+H2O2 respectively.

The **third system** demonstrates a novel hybrid technique (HC + hydrogels packed bed adsorption) for dye degradation and subsequent adsorption of dye molecules. HC was employed for the degradation of CV dye and subsequent adsorption of dye molecules have been carried out by using polymer hydrogels. Poly-acrylic acid (PAA)/nanocomposite hydrogels have been synthesized via ultrasound (US) assisted emulsion polymerization technique. Modified Bentonite clay was used as a cross-linker during the synthesis of PAA in the presence of US for the uniform dispersion of Bentonite clay in the hydrogel matrix and to improve the adsorption capacity of the hydrogels. The morphology of synthesized hydrogels has been studied by XRD and TEM analysis. Operational parameters such as effect of inlet pressure for CV dye removal, effect of Bentonite clay content in PAA hydrogel, effect of quantity of hydrogel loading in packed bed, effect of pH, and effect of the inlet flow rate of the packed bed of integral removal of CV dye in the hybrid system have been investigated. The combined process of HC and packed bed hydrogel adsorption demonstrated the higher percentage removal of the CV dye as compared to packed bed hydrogel adsorption alone. The synergistic effect of combined technique was evaluated based on the total organic carbon (TOC) removed from the dye solution.

The **fourth system** deals with the HAOP for the degradation of a mixture of dyes in aqueous media. In this work, a combination of H2O2 addition and HC for the degradation of ternary dye mixture were studied. H2O2 was used as an oxidizing agent to improve the degradation efficiency through the cavitation device. The independent effect of the H2O2 on the degradation of ternay dye was also quantified. It was observed that 65 % decolorization using HAOP while, 39 % using HC and 25 % using H2O2 alone were obtained. The mineralization (degradation) of dye solution was also evaluated by measuring the TOC. 51 % of mineralization was achieved using HAOP, whereas HC alone could yield only 28 % mineralization. Degradation of ternary dye mixture using HAOP followed the pseudo first-order reaction kinetics. The synergistic effect of HAOP over two independent AOP’s was quantified based on the kinetic rate of degradation.

The **fifth system** deals with the removal of organic pollutants form textile industry dye wastewater by the combination of HC, Fenton and ceramic nanofiltration membrane. In this work, the pore size of the membrane was reduced by the alumina boehmite sol-gel coating using wet impregnation and layer by layer technique. The pore size reduction was confirmed through the pure water permeate flux through the membrane before and after coating. Fenton process was employed along with combined HC and nanofiltration for extent of removal of organic pollutants from dye wastewater. HC combined with nanofiltration and drop wise addition of 2 mL/L of H2O2 has shown the 36.62 % of TOC removal in 90 min. HC combined with Fenton, nanofiltration and drop wise addition of H2O2 has shown the 58.85 % of TOC removal in 3 h for 0.28 g/L of Fenton and 2 mL/L of H2O2 (30 % (v/v)) addition.

The results obtained through these studies demonstrated the importance and contribution of the HC as a primary pretreatment technique for obtaining the maximum degradation of the organic pollutants in wastewater in conjunction with other treatment techniques. From these studies, it was observed that the HC can also be a useful technique for scaleup of wastewater treatment through the incorporation of number of orifice holes, increasing the size of the pipe and pump.

**CHEMICAL ENGINEERING**

Author : **Shaik Liyakhath Ahmed**

Title of the thesis : **Dynamic simulation of corrosion of dual phase alloy steel based on its constituent phase properties**

Guide : **Dr. T. SUNIL KUMAR**

Degree : **Ph. D.**

Student ID No. : **714034**

**ABSTRACT**

In this work single phase and dual phase steels are studied for corrosion characterization as well as predicting their corrosion rate by dynamic simulation approach. It is the aim of the project to predict dual phase alloy steel corrosion rate by using only the polarization characteristics of the individual phases. Initially the corrosion characterization is done by polarization technique in a flat cell with electrolyte as NaCl solution. The potential scan rate as well as the pre-immersion time is varied to study their effect on polarization curve. But it was found that ASTM standards can be implemented without loss of corrosion characteristics in detail. Other approaches like electrochemical impedance spectroscopy were also carried out and novel equivalent circuit for the dual phase alloy steel is proposed and validated.

Since, the goal is to simulate the micro-galvanic currents on metal surface immersed in electrolyte, the polarization curve is represented by Butler-Volmer equation which contains four parameters namely: icorr, Ecorr, α and β. These are normally obtained by Tafel slopes method graphically. As a novelty in this work, the polarization data is fitted to Butler-Volmer equation by using data fitting techniques of software such as MATLAB. By this way the ambiguity in drawing the Tafel slopes is eliminated.

The corrosion phenomenon at the metal-electrolyte interface is modeled by electric field driven ionic movement as the rate limiting step. Thus an assembly of metal and electrolyte is simulated in two dimensions. The metal interface is allowed to dissolve and form a corroded interface which keeps happening as the corrosion occurs. This gives an estimate of corrosion rate of the metal from simulations. It can be termed as a mechanistic model where cathode and anode locations are assigned randomly to simulate uniform corrosion in a single phase alloy. Similarly, for 50% austenite – ferrite distribution in super duplex stainless steel, the dynamic corrosion was simulated. It was found that, it gives an estimate of corrosion rate close to the immersion test results for a wide range of NaCl concentration in water. It was effectively shown that the corrosion rate from simulation is more exact than weighted average estimate of alloy steel using the corrosion rate of two individual phases.

Especially, super duplex stainless steel exhibits an increase and decrease trend in corrosion rate as a function of NaCl concentration in water. This aspect is also captured effectively using dynamic simulation approach.

**CHEMICAL ENGINEERING**

Author : **PRASHANT LALCHAND SURYAWANSHI**

Title of the thesis : **PRODUCTION OF FUNCTIONAL NANOMATERIALS USING MICROREACTOR AND THEIR APPLICATIONS FOR POLYMER ELECTROLYTE MEMBRANE (PEM) FUEL CELL**

Guide : **Dr. SHIRISH HARI SONAWANE**

Degree : **Ph. D.**

Student ID No. : **714151**

**ABSTRACT**

The main focus of this research work is to develop the functional nanomaterials/nanocatalyst for the polymer electrolyte membrane (PEM) fuel cell application. In this work, synthesis of platinum (Pt) and it‟s alloy was carried out by using micro reactor. Overall, research study deals with five different catalytic systems.

First system deals with the synthesis of ultra-small platinum (Pt) nanoparticles using borohydride reduction and polyol method, in a continuous flow microreactor. This method facilitated the synthesis of Pt nanoparticles less than 5 nm at room temperature, as opposed to the conventional high temperature synthesis. Further, the effect of capping agent and flow rate on particle size and aggregation of Pt nanoparticles is demonstrated. It is found that the flow rate of reactants in microreactor has a significant effect on size and crystallinity of Pt nanoparticles. TEM image shows that stable and narrow size distribution of Pt nanoparticles. Second system deals with, synthesis of iron oxide nanoparticles using continuous flow microreactor and advanced flow reactor (AFR®). Synthesis of iron oxide nanoparticles is carried out using the co-precipitation and reduction reactions in microreactor and AFR®.

Third systems deal with synthesis of Pt nanoparticles in microreactor doped on various supportive materials like Vulcan XC-72 carbon powder, reduced graphene oxide (r-GO) and metal oxide such as titanium dioxide (TiO2) used as a catalyst and its application for oxygen reduction reaction (ORR) study in PEM fuel cell. A metal oxide (TiO2) and rGO are the alternative catalyst support materials for carbon due to its tailored properties like corrosion resistance, strong metal-support interactions, improved surface area and higher electrochemical stability. A synthesized Pt NPs by formic acid reduction and exhibited a smaller in particle size, high dispersion and strong integration between particles and supports. Reduced graphene oxide supported Pt (Pt/rGO) demonstrated superior catalytic activity and higher electrochemical active surface area (EASA) than Pt/TiO2 and Pt/C due to their graphite layered structure and intrinsic catalytic properties.

Fourth system consist of continuous production of conducting nano-size polymer such as polyaniline (PANI) from polymerization of aniline was carried out in a fabricated spiral wound microreactor. The lowest particle size of 296.9 nm was obtained at 0.04 M concentration of aniline. PANI decorated onto the carbon support (PANI@C). As-synthesized a conducting polymer PANI decorated on carbon-based materials was found a promising support materials for nanoparticles synthesis (Pt/PANI@C) for next generation of energy conversion and storage devices. Therefore, the HNO3 treated Pt/PANI@C catalyst shows the superior activity, durability compared with Pt/C. Finally, it can be concluded that it is superior potential material for ORR in PEM fuel cell.

Fifth system deals with synthesis of carbon supported bimetallic (Pt-Ni or Pt-Mo) catalyst by chemical reduction method either by sodium borohydride or formic acid as a reductant from the respective metal precursors carried out in fabricated microreactor is presented. The bimetallic catalyst Pt-Ni/c or Pt-Mo/C shows higher catalytic activity and mass activity than Pt/C due to the synergetic effect of Ni, Mo, and Pt. Finally, it can be concluded that it is a superior and cost-effective solution to use bimetallic catalyst for PEM fuel cell application.

**CHEMICAL ENGINEERING**

Author : **Mr. UDAY DASHARATH BAGALE**

Title of the thesis : **DEVELOPMENT OF NANO HYBRID COATINGS USING ULTRASOUND ASSISTED ENCAPSUALTION APPROACH FOR CORROSION INHIBITION**

Guide : **Dr. SHIRISH HARI SONAWANE**

Degree : **Ph. D.**

Student ID No. : **714152**

**ABSTRACT**

The present work deals with development of self-healing corrosion inhibition coating using ultrasound assisted *in-situ* polymerization approach. Self-healing coatings are multi-component, which have been proposed as a way to long lasting corrosion protection of steel structures. The most promising technology route is based on nanocontainer and microcapsules, filled with active healing agents for marine application. The stable nanocapsules/nanocontainer synthesis and their dispersion in epoxy polyamide using sonochemical approach. The nanocapsules prepared by sonochemical approach resulted in spherical shape particle with smoother surface and enhanced stability during dispersion in epoxy coating. The results shows that the incorporation of nanocontainer/nanocapsules as additives into polymer matrices shows improved performance compared to neat coating.

The present work deals with three different types of self-healing coating systems, one among the development of an active corrosion inhibition coating of two pack epoxy polyamide system using halloysite nanocontainer. This work, deals with encapsulation of corrosion inhibitor in inorganic nanocontainer and its performance in terms of inhibition rate. Halloysite nanotubes were used as inorganic nanocontainer for encapsulating the active corrosion inhibitor. The benzotriazole loading up to 10 % (by weight) was achieved in inorganic nanotube of 50 nm external diameters and lumen of 15 nm. In order to control the release of the benzotriazole, encapsulated halloysite nanotubes are closed at both the ends of nanotube with solution of copper sulphate. The release of corrosion inhibitor was carried out for 18 h at different pH ranging from 3 to 10. The wt % of the benzotriazole encapsulated halloysite nanocontainer was varied from 2 to 10 and then dispersed in 2K clear coat epoxy-polyamide. EIS data of coating in terms of Bode plot and Nyquist plot shows better the corrosion resistance than standard epoxy-polyamide coating.

The second system consist of the production of nanocapsules containing a natural green corrosion inhibiting component. The natural corrosion inhibiting agent, ‘Neem oil (*Azadirachta indica*) was encapsulated in urea-formaldehyde polymeric shell using ultrasound assisted and conventional approach of *in-situ* polymerization. Synthesis of nanocapsules having spherical shape with inner smooth surface and rough outer surface was carried out using *in-situ* polymerization. In case of ultrasound assisted approach, the inner core has of 50-100 nm whereas, the conventional approach showed the thickness of 5 μm. Subsequently, nanocapsules were incorporated in clear epoxy-polyamide coating. The results are promising and shows better corrosion protection in terms of the electrochemical impendence analysis (EIS) data and Tafel plot. It was found that current density decreases from 0.0011 (for standard epoxy coating) to 5.22 x10-7A/cm2 for 4 wt % encapsulated nanocapsules in coating.

Third system deals with encapsulation of dibutyl phthalate (plasticizer) in urea-formaldehyde nanocapsules using ultrasound assisted *in-situ* polymerization and preparation of self-healing corrosion inhibition coatings. Methodology for synthesis sonochemical approach encapsulation of healing agent based nanocapsules was carried out in two different stages. The first one deals with the preparation prepolymer urea-formaldehyde solution and second one for the fabrication of nanocapsules using prepolymer solution. Prepared nanocapsules are spherical shape structure having inner smooth and outer rough surface. The particle size analysis confirmed the narrow particle size distribution with a mean size of 352 nm. Nanocapsules showed a good degree of dispersion stability in the aqueous phase. The performance of the coating was evaluated based on studies consist of the healing of the crack of high solid based surface coating. It was found that the current density decreases from 0.0011 (for standard epoxy coating) to 5.79 x 10-12 A/cm2 by the addition of 10 wt % encapsulated nanocapsules in the coating.