

The performance of a gas-inducing stirred tank reactor for Fischer-Tropsch synthesis: electrical process tomography analysis and computational fluid dynamics studies

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**The Performance of a Gas-inducing
Stirred Tank Reactor for Fischer-
Tropsch synthesis: Electrical Process
Tomography Analysis and
Computational Fluid Dynamics Studies**

by

Bawadi Abdullah

A thesis submitted in partial fulfilment of the
requirements for the degree of

Doctor of Philosophy

2011



School of Chemical Engineering
The University of New South Wales

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CURRICULUM VITAE

The author graduated from University of Wales, Swansea, United Kingdom with Chemical Engineering degree in 1997. From 1997, he worked in Samsung Corning (M) Sdn. Bhd. (Seremban, Malaysia) as a waste-water treatment plant engineer for almost 3 years. In 2000, he joined Universiti Teknologi PETRONAS (UTP), Malaysia as a training lecturer. A year later, he received the scholarship from UTP to pursue a master studies under the guidance of Associate Professor Pak K. Yuet in the area of Transport Phenomena in Dalhousie University, Canada. His thesis titled "*Modeling the effect of temperature induced surface tension gradient in coating processes*". He re-joined UTP as a full-fledged lecturer in Chemical Engineering Department in 2003. In March 2008, He received a full scholarship and study leave from UTP to pursue PhD studies under supervision of Professor Adesoji A. Adesina in School of Chemical Engineering in the University of New South Wales (UNSW) Australia. Research area involved computational fluid dynamics (CFD), electrical process tomography and Fischer-Tropsch synthesis (FTS) in slurry reactor, equipped with gas-inducing impeller.

Abstract

Gas-inducing stirred tank reactors (GISTs) are attractive for industrial chemical processes where efficient mixing holds the key to product yield and quality particularly in situations where the reaction has low conversion per pass as is the case for the Fischer-Tropsch synthesis (FTS) of hydrocarbons. However, these benefits can only be properly harnessed if there is a reliable set of quantitative relations between operating variables and the mixing attributes as well as reaction metrics. Therefore, in this project, the hydrodynamics and mass transfer in a multiphase system have been intensively investigated using electrical process tomography (electrical resistance tomography (ERT) and electrical capacitance tomography (ECT)).

Unlike conventional methods, tomography provides a visualisation of the interaction between different phases by generating cross-sectional phase distribution images of the vessel. The technique is non-invasive, using electrical signals corresponding to changes in the component distribution within the vessel with the aid of reconstruction algorithms. Various parameters such as stirring speed, particle size, solid loading, temperature, pressure, and partial pressure have been studied in both reactive and non-reactive systems.

In addition, computational fluid dynamics (CFD) software (FLUENT 6.3) was used to elucidate the hydrodynamic behaviour within the system. Dynamics bubble behaviour over time in GIST (gas-liquid system) was successfully modeled using common Laguerre equation that based on birth, growth and death (bubbles break-up and coalescence), where the onset of gas bubble dispersed in liquid starts about 0.2 s.

The dispersed phase holdup increased with stirring speed and solid loading (0-40 g L⁻¹). Global solid phase hold-up profile exhibited a sigmoid-shape with respect to the impeller Reynolds number, indicative of three solid suspension regimes across the stirring range (0 to 1200

rpm) investigated. It is evident that at stirring speeds above 800 rpm, vortex formation sets in and gas is pushed towards the impeller shaft causing a maximum gas hold-up in the immediate shaft vicinity. The magnitude of this maximum increased with agitation rate. Phase hold-up distribution and mass transfer profiles were adequately captured by generalized Chapman-Richards equations. The dependency of the model parameters on particle size was also obtained in all cases. Mass transfer coefficients (gas-liquid and liquid-solid) for GIST were superior to that of the externally gas-sparged gas-liquid system, suggesting that the gas-inducing impeller indeed enhances mixing performance and interphase mass transfer.

In the FT reaction, the steady-state gas phase hold-up dependency on temperature was shown to be due to contributions from both thermal expansion and reaction-induced changes in the liquid phase. The latter model was combined with the standard Arrhenius representation of the rate behaviour at a given feed composition, to yield a new relation that may be employed to evaluate online reaction rate from unobtrusive dispersed phase hold-up measurements if the reactor is endowed with ECT capabilities.

List of Publications

Book Chapter

1. **Bawadi Abdullah**, Chirag Dave, Tuan Huy Nguyen, Cyrus G. Cooper and Adesoji A. Adesina, *Fischer-Tropsch Synthesis Investigation in a Gas-Inducing Agitated Reactor Using Electrical Capacitance Tomography*, 2011, ACS publications, (edited by Arno de Klerk and David L. King), accepted.

Journal papers

2. **Bawadi Abdullah**, Chirag Dave, Tuan Huy Nguyen, Cyrus G. Cooper and Adesoji A. Adesina, *ERT-assisted analysis of dispersed phase hold-up in mechanically agitated vessel*. Chem. Eng. Sci., 2011, 66, 5648-5662.

3. Chirag B. Dave, **Bawadi Abdullah**, Viswanathan Arcotumapathy, Tuan Huy Nguyen, Cyrus G. Cooper and Adesoji A. Adesina, *Effect of aspect ratio on gas hold-up in bubble columns via electrical resistance tomography*, Inter. J. Chem. Eng., 2009 2(2), 183-193.

4. **Bawadi Abdullah**, Chirag B. Dave, Cyrus G. Cooper, Tuan Huy Nguyen and Adesoji A. Adesina, *Electrical capacitance tomography study of carbon monoxide hydrogenation in a slurry reactor*. Ame. Chem. Soc, Div Fuel Chemical, 2010, 55(2), 453

5. Chirag B Dave, **Bawadi Abdullah**, Dai-Viet N. Vo, Tuan Huy Nguyen, Cyrus G. Cooper and Adesoji A. Adesina, *ERT measurement of gas hold-up distribution in bubble column with coalescence inhibiting solutions*, Industrial & Engineering Chemistry Research, submitted.

6. **Bawadi Abdullah**, Chirag B. Dave, Cyrus G. Cooper, Tuan Huy Nguyen and Adesoji A. Adesina, *A study of gas-liquid mass transfer in gas-inducing stirred tank reactor using electrical resistance tomography*. J. of Chem. Tech. Biotech., to be submitted.

7. **Bawadi Abdullah**, Chirag B. Dave, Cyrus G. Cooper, Tuan Huy Nguyen and Adesoji A. Adesina, *CFD modeling in gas-inducing stirred tank reactor*. Inter. J. of CFD, to be submitted.

Peer-review conference papers

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of Chemical Engineering, 23rd – 27th August 2009, Montreal, Quebec, Canada

9. Chirag B Dave, **Bawadi Abdullah**, Dai-Viet N. Vo, Tuan Huy Nguyen, Cyrus G. Cooper and Adesoji A. Adesina, *ERT measurement of gas hold-up distribution in bubble column with coalescence inhibiting solutions*, 8th World Congress of Chemical Engineering, 23rd – 27th August 2009, Montreal, Quebec, Canada

10. Chirag B. Dave, **Bawadi Abdullah**, Viswanathan Arcotumapathy, Tuan Huy Nguyen, Cyrus G. Cooper and Adesoji A. Adesina, *Effect of sparger type and aspect ratio on gas hold-up in bubble columns via electrical resistance tomography*, CHEMECA, 27th and 30th September 2009, Perth, Australia

11. Cyrus G. Cooper, **Bawadi Abdullah**, Dai-Viet N. Vo, Tuan-Huy Nguyen, Frank P. Lucien, Adesoji A. Adesina, *An evaluation study of the Intrinsic reaction metrics of Co/Al₂O₃ Fischer-Tropsch Catalyst*, The 14th International Congress on Catalysis (ICC), Seoul, 13-18 July 2008.

12. Cyrus G. Cooper, **Bawadi Abdullah**, Tuan-Huy Nguyen, Dai-Viet N. Vo, Faisal Althenayan, Frank P. Lucien, Adesoji A. Adesina, *GTL fuel synthesis: Product distribution and generalised kinetic modeling for individual hydrocarbon species*, CHEMECA 2008, Newcastle, Sept 29-Oct 2, 2008.

13. **Bawadi Abdullah**, Chirag B Dave, Cyrus G. Cooper, Tuan-Huy Nguyen, Adesoji A. Adesina, *Hydrodynamics study in multiphase stirred tank reactor using ECT*. 21st International symposium on chemical reaction engineering, June 13-16 2010, Philadelphia, USA.

14. **Bawadi Abdullah**, Chirag Dave, Cyrus G. Cooper, Tuan-Huy Nguyen and Adesoji A. Adesina, *Electrical Capacitance Tomography (ECT) study of carbon monoxide hydrogenation in a slurry reactor*, Coal-, gas-, biomass- and waste-to-liquids conversion ACS Fuels Division program at the 240th ACS National Meeting , 22nd - 26th August 2010, Boston, USA

15. **Bawadi Abdullah**, Chirag B. Dave, Tuan Huy Nguyen, Cyrus G Cooper, Adesoji A. Adesina. *Unsteady-state CFD model for gas-liquid flow in a gas-induced impeller stirred tank reactor*, 5th International Symposium of Design, Operation and Control of Chemical Processes, July 25-28, 2010 Singapore.

16. **Bawadi Abdullah**, Chirag B. Dave, Tuan-Huy Nguyen, Cyrus G. Cooper and Adesoji A. Adesina, *An electrical resistance tomographic study of gas-liquid mass transfer in a continuous stirred tank reactor*, 6th World Congress on Industrial Process Tomography (WCIPT6), 6th - 9th September 2010, Beijing, China.

17. **Bawadi Abdullah**, Cyrus G Cooper, Tuan Huy Nguyen, Adesoji A Adesina, *Fischer-Tropsch synthesis using cobalt-based catalyst in a stirred tank slurry reactor*. CHEMECA, 26th - 29th September 2010, Adelaide, Australia.
18. Chirag B. Dave, **Bawadi Abdullah**, Tuan-Huy Nguyen, Cyrus G. Cooper and Adesoji A. Adesina, *ECT analysis for gas-oil and gas-solid systems in a bubble column*, The 5th International Symposium on Design, Operation and Control of Chemical Processes (PSE-ASIA 2010), 25th - 28th July 2010, Singapore.
19. Chirag B. Dave, **Bawadi Abdullah**, Tuan-Huy Nguyen, Cyrus G. Cooper and Adesoji A. Adesina, *Phase hold-up, mixing and mass transfer in a bubble column reactor using ERT analysis*, 6th World Congress on Industrial Process Tomography (WCIPT6), 6th - 9th September 2010, Beijing, China
20. Chirag B. Dave, Mohammad A. Iftekhhar, **Bawadi Abdullah**, Tuan-Huy Nguyen, Cyrus G. Cooper and Adesoji A. Adesina, *Phase holdup and axial liquid dispersion in a high aspect ratio bubble column using ERT analysis*, CHEMECA, 26th - 29th September 2010, Adelaide, Australia.
21. Chirag B. Dave, **Bawadi Abdullah**, Tuan-Huy Nguyen, Cyrus G. Cooper and Adesoji A. Adesina, *Hydrodynamics and mass transfer parameters in a water-filled shallow bubble column using ERT visualization*, 4th International Workshop on Process Tomography (IWPT4), 21-23th September 2011, Chengdu, China, paper accepted
22. **Bawadi Abdullah**, Chirag B. Dave, Tuan-Huy Nguyen and Adesoji A. Adesina, *Effect of particle size and agitation rate on phase hold-up characteristics in gas-inducing stirred tank reactor using ECT-based diagnosis*, , 4th International Workshop on Process Tomography (IWPT4), 21-23th September 2011, Chengdu, China, paper accepted.

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Nomenclature

Abbreviation	Explanation
ASF	Anderson-Schulz-Flory
BET	Brunauer-Emmett-Teller (surface area)
BPR	Back pressure regulator
CFD	Computational fluid dynamics
DAS	Data acquisition system
ECT	Electrical capacitance tomography
EPT	Electrical process tomography
ERT	Electrical resistance tomography
FID	Flame ioniser detector
FT	Fischer-Tropsch
FTS	Fischer-Tropsch synthesis
GIST	Gas-inducing stirred tank reactor
GC	Gas chromatography
GHSV	Gas hourly space velocity ($\text{L g}_{\text{cat}}^{-1} \text{h}^{-1}$)
GL	Gas liquid
GTL	Gas to liquid
LBP	Linear back projection
LTFT	Low Temperature Fischer-Tropsch
MRF	Multiple Reference Frames
rps	Revolution per second
ROP	Ratio olefin to paraffin
rpm	Revolution per minute

TCD	Thermal conductivity detector
TPO	Temperature-programmed oxidation
TPR	Temperature-programmed reduction
SBCR	Slurry bubble column reactor
STNR	Signal-to-noise ratio
VCCS	Voltage controlled current source
WGS	Water gas shift
XRD	X-Ray diffraction

Notation	Explanation
A_i	pre-exponential factor for component i
A_{orifice}	cross sectional area for gas exit orifice, mm^2
a	constant as function of w for the solid mixing time
b	constant function of w for the solid mixing time
c	empirical constant
$C_{D,0}$	drag coefficient in a stationary liquid
$C_{D \text{ Avg}}$	averaged drag coefficient
C_{DO}^*	impeller drag coefficient in the gas-liquid dispersion
conveying	
C_{DY}^*	impeller drag coefficient in the central zone
d_{32}	Sauter bubble column diameter
D_I	impeller diameter, m
D_T	tank diameter, m
d_s	particle diameter, m
d_p	bubble diameter

E_i^a	Individual activation energy for each species
F	Total molar feed flowrate (mol s^{-1})
Fr	Froude number, ($Fr=N^2D/g$)
g	acceleration due to gravity, m^2s^{-1}
h	submerge depth, mm
h_{f1}	energy loss in the turbulent field (continuous phase)
h_{f2}	energy loss during gas flow through the impeller
shaft from inlet	to exit
K	impeller speed loss coefficient
k	solid colloid formation constant, dimensionless
k_{ASF}	ASF rate constant, $\text{mol g}_{\text{cat}}^{-1}\text{s}^{-1}$
$k_L a$	volumetric mass transfer coefficient
$k_L a_0$	initial volumetric mass transfer coefficient
k_{radial}	solid colloid formation constant in radial coordinate, dimensionless
k_{centre}	solid colloid formation constant in the centre, dimensionless
M_p	effective particle number in a stable colloidal concentration
M	minimum particle number for solid cluster formation
N_{cs}	critical impeller speed, s^{-1}
N_s	impeller speed, s^{-1}
N_{js}	impeller speed for just suspended state of particles,
s^{-1}	
N_P	power number, dimensionless
$N_{P,GIST}$	power number for gas-induced stirred tank with no solid suspended, dimensionless

n	hydrocarbon carbon number
$\langle n \rangle$	average carbon number
n_p	number of pixels
ΔP the gas	manometric pressure drop between tank bottom and headspace (mm)
P	power consumption, W
P_i	partial pressure for species i
P_i^0	partial pressure of species i at start of transient
P_i^∞	partial pressure of species i at infinite time
P_0	power consumption without gas-entrainment impeller
Q_g	gas volumetric flowrate, m^3s^{-1}
r	reactor radius, mm
r_i	reaction rate of species i
r_p	propagation rate, $\text{mol g}^{-1}\text{s}^{-1}$
r_t	termination rate, $\text{mol g}^{-1}\text{s}^{-1}$
R	reactor radius, mm
Re_i	impeller Reynolds number, dimensionless
Re_G	gas Reynolds number, dimensionless
S_i	solubility coefficient, $\text{m}^3_{\text{L}}/\text{m}^3_{\text{G}}$
T	torque, Nm
Ta'	Taylor number, dimensionless
t_d	time delay, minutes
t'_{mix}	solid mixing time constant, dimensionless
W	impeller width, m
w	solid loading, (g L^{-1} of liquid)

We	Weber number, dimensionless
y_i	mole fraction of species i in product stream
ΔZ (mm)	change in liquid height before and during stirring

Greek	Explanation
α	local dependency of γ , dimensionless
β	gas-inducing enhancement factor
β_2	reactor geometry parameter, dimensionless
γ dimensionless	particle clustering activity in the liquid phase, dimensionless
γ_0 dimensionless	clustering frequency for solid in the liquid phase, dimensionless
$\gamma_{0,radial}$	clustering frequency for solid in the radial coordinate, dimensionless
$\gamma_{0,centre}$ dimensionless	clustering frequency for solid in the centre, dimensionless
δ	parameter defined in Equation (6.15), dimensionless
ε_D	dispersed phase hold-up, dimensionless
$\varepsilon_{D,max}$ dimensionless	dispersed phase hold-up at finite stirring speed, dimensionless
τ_{ppp} constant	non-dimensional dispersed phase mixing time constant
ε_G	gas phase hold-up, dimensionless
$\varepsilon_{G,0}$	initial gas phase hold up when there is no stirring

$\varepsilon_{G,max}$	gas phase hold-up at finite stirring speed, dimensionless
τ_{gpp}	non-dimensional gas phase mixing time constant
γ_G	exponent related to the gas bubbles clustering activity
ε_i	local solid voidage for the i^{th} pixel, dimensionless
$\overline{\varepsilon}$	average solid voidage for the entire cross-section, dimensionless
ε_l	liquid phase hold-up, dimensionless
ε_s	solid phase hold-up, dimensionless
$\varepsilon_{s,max}$	maximum solid phase hold-up due to fast stirring, dimensionless
ε_{s0}	solid phase hold-up at the vessel centre, dimensionless
θ	function of w in power consumption correction factor
κ	function of w in power consumption correction factor
k_ε	energy dissipation rate per unit mass, m^2s^{-3}
μ_l	liquid dynamic viscosity, Pa.s
μ_{water}	water dynamic viscosity, Pa.s
ξ	local dependency γ of in the wall region, dimensionless
ρ_g	gas phase density, $kg\ m^{-3}$
ρ_l	liquid phase density, $kg\ m^{-3}$
ρ_s	solid phase density, $kg\ m^{-3}$
σ_1	conductivity of continuous phase, $mS\ cm^{-1}$
λ	Kolmogoroff scale of turbulence

σ_2	conductivity of dispersed phase, mS cm^{-1}
σ_m	conductivity of mixture of continuous and dispersed phase, mS cm^{-1}
φ_c	permittivity of the continuous phase, Farad m^{-1}
φ_D	permittivity of the dispersed phase, Farad m^{-1}
φ_M	permittivity of the mixture, Farad m^{-1}
τ	mixing time constant, minutes
ω	olefin attenuation index
Λ	maximum ROP value
η	carbon number where maximum ROP produce
τ_{br}	bubble rise time constant, minutes
τ_{dpp}	characteristic dispersed phase particle mixing time, dimensionless
τ_{spp}	characteristic solid phase particle mixing time, dimensionless
Φ	vortexing constant
χ	Statistical parameter, dimensionless
Ψ	radial attenuating effect for solid phase hold-up, dimensionless
α_{BC}	net bubble collision frequency (s^{-1}) for the three cases (a)-(c)
α_{FT}	chain growth probability during FTS
α_{TGA}	transient solid conversion

1. INTRODUCTION

1.1. Background and Motivation

Within the last two decades, several investigators, including Joshi and co-workers [1-4], have reported the advantages of the gas-inducing stirred tank (GIST) in the provision of improved mixing and single gas conversion per pass over conventional agitators. Efficiency and effectiveness of mixing, and overcoming the relevant resistances to mass transport, are integral to product yield and quality in commercial scale projects. The importance of this is more so in processes with low single pass conversion (e.g. Fischer-Tropsch synthesis, FTS). Consequently, the potential value of reliable quantitative relations between operating variables, the mixing attributes and the reaction indices, is immense. To date, methods are heavily reliant on the “black box approach” with minimal consideration to the internal flow structure of the various phases. Recent studies have focused on the application of computational fluid dynamics (CFD) to investigate the complex interplay of different phenomena at local level [5-8]. Even so, the verification of CFD simulation results by independent non-intrusive measurement is absolutely necessary to strengthen confidence in the ability of these mathematical models for practical engineering utility. It is in this respect that tomographic techniques play a complementary role in substantiating computational results and perhaps more significantly, provide a platform for building mechanistically-based models since the finger-prints of various complex phenomena can be picked up by spatiotemporal changes in the physiochemical properties of the multiphase system when non-invasively probed. The need for a non-intrusive technique becomes more relevant for chemical processes involving high temperature and

pressure (e.g. slurry FT synthesis) due to the concomitant practical and safety issues.

The slurry FT reactor is particularly suitable for hydrocarbon synthesis from CO hydrogenation over Fe and Co catalysts because of its ability to achieve better control of the exothermic reaction, enhanced C_{2+} selectivity and better catalyst usage [9, 10]. However, the complex hydrodynamics involved and the impact of changing liquid physicochemical properties as a result of products dissolution in the liquid phase have led to compounded reactor analysis and scale-up challenges [11]. Possible variation in dispersed phase hold-up and spatial distribution may give rise to unexpected results even in the absence of mass transport resistances. The associated hydrodynamics, mixing and mass transfer characteristics have been examined using residence-time distribution (RTD) and computational fluid dynamics methods to secure correlations for design and scale-up purposes. In CFD, volume of flow (VOF) and k-epsilon models were employed. Nonetheless, VOF model was not suitable to study mass transfer due to inability of the phases to interpenetrate each others. While, k-epsilon turbulent model was not fitted for highly swirling motion that would caused unsteadiness to the final solution. However, to effectively eliminate or minimise this problem, the simulation runs must be started at very low speed and gradually increase the magnitude up to the desired speed level.

The increased gas recirculation also promotes solid mixing and hence better catalyst utilization when applied in a slurry reactor. However, the agitation rate must exceed the critical impeller speed, N_{CS} , given by the Sawant-Joshi criterion [12] for the gas-inducing stirrer before the benefits of enhanced gas recirculation may be realised. For a slurry reactor, N_{CS} , is well above the rotational speed necessary to ensure absence of gas absorption and external liquid-solid transport resistances.

In view of the product-induced changes in the fluid phase properties in a multiphase reactor – e.g. viscosity, density and surface tension - and

hence, phase hold-up variation with time-on-stream during reaction, a non-invasive evaluation of the reactor would provide useful insight into the coupling effect of transport processes and reaction metrics. Indeed, non-intrusive flow visualization of the reactor contents with time-on-stream may provide additional information to complement standard chromatographic exit gas phase composition analysis leading to better understanding and ability to carry out superior scale-up and modeling, for example, using computational fluid dynamics [4]. This is especially germane to FT operation in a mechanically-agitated slurry reactor fitted with a gas-entrainment impeller to improve gas recirculation and hence, CO conversion per pass.

Thus, in this project, the hydrodynamics and mass transfer in a multiphase system have been investigated using electrical process tomography. Unlike conventional methods, tomography provides a visualisation of the interaction between different phases by generating cross-sectional phase distribution images of the vessel. The technique is non-invasive, using electrical signals corresponding to changes in the component distribution within the vessel with the aid of reconstruction algorithms.

1.2. Scope and outline of this thesis

In general, this research project focuses on the use of a non-intrusive technique known as electrical process tomography to study the hydrodynamics and mass transfer of a gas-inducing stirred tank reactor (GIST) and to complement CFD modelling of the multiphase system. The aim of this thesis is to understand the influence of various parameters including stirring speed, particle size, solid loading, temperature, total pressure, and reactant partial pressure on hydrodynamics, and to some extent on mass transfer and the reaction rate under relevant industrial conditions. The acquired knowledge can be exploited to improve the performance of slurry reactors, which are increasingly used in industrial practice. The improved understanding of

this application of stirred tank reactors would lead to cost savings due to more efficient design.

In this thesis, the work on GIST is predominantly focused on three areas: hydrodynamics, mass transfer and FT reaction study. The structure of the thesis is outlined as follows:

Chapter 2 reviews various aspects of gas-inducing stirred tank reactors including FT synthesis that is directly applicable to the research scope.

Chapter 3 summarises and identify materials used, experimental assembly approaches and strategies of conducting research including CFD modelling are explained.

Chapter 4 describes preliminary experiments that were conducted before commencement of the actual experiments, to find optimum conditions and limitations. Characterisation of the equipment used also been discussed in this chapter.

Chapter 5 discusses the influence of stirring speed on hydrodynamics and mass transfer is discussed in detail for a gas-liquid system. Empirical models are proposed in relation to global and localised gas phase hold-up in GIST. The models show good agreement with the experimental data. Three types of reactor assembly were studied to investigate the efficacy of the gas-inducing impeller over conventional reactors. Effect of stirring speed on volumetric mass transfer coefficient, k_La , bubble size, Sauter mean bubble diameter and gas-liquid (GL) interfacial area are studied. The liquid side mass transfer coefficient is calculated from volumetric mass transfer coefficient and GL interfacial area. CFD modelling based on volume of flow (VOF) method is employed to gain better insight into hydrodynamics of GIST, in which the velocity profile in transient flow can be described by a common Laguerre model.

Chapter 6 provides a detailed study of the hydrodynamics and mass transfer of a gas-liquid-solid system in GIST is reported. A dispersed phase hold-up model based on Chapman-Richards model which can predict the dispersed phase hold-up in all three regimes is derived.

Chapter 7 describes the dynamic feedback between the fluid phase characteristics (such as dispersed phase hold-up, mixing time constants, etc.) and reaction metrics in gas-liquid-solid reactor using Fischer-Tropsch synthesis (FTS) as a case study using electrical capacitance tomography (ECT). The effect of various parameters such as pressure, temperature, reactant partial pressure, stirring speed as well as catalyst loading are investigated in a Parr reactor equipped with a gas-inducing impeller.

Chapter 8 summaries the main findings of this thesis. Recommendations are also proposed at the end of this chapter for future research.

Finally, appendices are included to provide a thorough account of data and calculations referred to in textual chapters.

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2 ■ Literature Review

2.1. General Consideration

This chapter aims to review various aspects of chemical engineering that relate to stirred tank reactors, namely hydrodynamics, mass transfer and reaction (slurry FT synthesis). The main focus of the collated literature is on reactors equipped with a gas-inducing impeller and non-invasive monitoring technique called tomography in order to provide an understanding of fluid dynamics in agitated multiphase systems. A literature survey of Computational fluid dynamics (CFD) is also provided to complement data analysis by electrical process tomography system.

2.2. Stirred Tank Reactors (STRs)

Mechanically-stirred vessels are commonly employed in the process industries for a variety of operations including pharmaceutical production, metallurgical processing, polymerisation and petrochemicals manufacturing [1-3]. Approximately half of the chemical industrial production worldwide used stirred tank vessels translating into more than \$1200 billion turnover per annum [4]. The mixing operation involved in stirred tank reactors can be as simple as fluids mixing to more complex operations such as Fisher Tropsch Synthesis (FTS), and may be operated as single-phase or multiphase depending on the purpose of the operation. In multiphase systems such as FTS; homogeneous mixing, suspension of catalysts, and gas dispersion are very important criteria. Optimum design can eliminate or greatly reduce unnecessary costs such as possible commissioning failures, lower production rate, increased downstream processing and down-time costs. Poor initial design was estimated to increase costs by 0.5-3.0% of total turnover. By the same

token, over-mixing also may incur additional costs due to over specification of the agitation power or mixing time [5].

There are two common multiphase operations involved in industrial applications; 1) gas-liquid and 2) gas-liquid-solid systems. According to Tatterson and co-workers [5], approximately 25% of reaction operations involved in industry occur between gas and liquid. Often, the contacting device of choice for this kind of operation is a mechanical-stirred vessel [6]. The most common criteria considered in choosing equipment are residence times of gas and liquid, the degree of conversion, safety and flexibility of the operation, and selectivity for desired products. Advantages of stirred tanks over other types of contacting devices include a well-mixed environment, relatively low concentration gradient and uniform pH and temperature. Further, the stirred tank reactor can give better control of bubble size distribution and gas dispersion compared to other equipment such as bubble columns, tray columns, and static mixers. In addition to better mixing performance, agitation also can enhance the mass transfer rate between gas and liquid. In gas-liquid-solid operation, agitation rate offers an effective way of suspending the catalyst in the liquid medium, which is a key condition in most 3-phase operations such as FTS.

There are two types of multiphase stirred tank reactor; 1) Conventional gas-sparged 2) Self-induced stirred tank reactors.

2.2.1. Gas-sparged stirred tank reactor (GSTR)

Industrial processes such as oxidation, chlorination and hydrogenation commonly use GSTR as a contacting device in gas-liquid operations. A few examples of these industrial processes are discussed briefly as follows [7]:

1) Oxidation: A typical application of oxidation is leaching for treatment of refractory gold ore. In this process, gold is bound up in grains of pyrite or arsenopyrite [8]. The reaction involves high temperature and pressure in an autoclave reactor which is divided into a number of compartments

separated by weirs. Each compartment is equipped with its own agitator and oxygen sparger.

2) Fermentation: Aerobic fermentation exploits micro-organisms to produce various products such as antibiotics, enzymes, amino acids, vitamins, yeast, flavour enhancers and thickening agents [9]. Adequate agitation helps to suspend the microorganisms, and provides a good environment for microorganisms to live by controlling pH and temperature. Air sparged from the bottom of the stirred tank supplies the necessary oxygen needed by microorganisms.

3) Hydrogenation: A common industrial process of hydrogenation is Fischer-Tropsch (FT) synthesis. Mechanical agitation is required to suspend the catalyst and provide a contact between solid catalyst and synthesis gas (H_2 and CO). Typically, high aspect ratio with multiple agitators with internal heat transfer coils are employed due to high operating pressure and exothermic reaction.

4) Bioleaching: In this process, micro-organisms such as bacteria and archaea species are used to extract metal from sulphide ores i.e. sulphidic gold, copper and cobalt [10]. These micro-organisms reduce ferrous ions to obtain their metabolic energy thus providing a pathway for the leaching process. Air that is sparged into the stirred tank provides the micro-organisms with necessary oxygen .

The examples above show that three-phase systems are the most common industrial application of GSTRs. To ensure the solid particles are suspended within the liquid phase, agitation rate and type of impeller are important factors in designing stirred tank reactors. In cases involving micro-organisms i.e. bioleaching and aerobic fermentation, an additional consideration of shear rate must be taken into account to avoid any damage to the micro-organisms.

In designing the gas-sparged stirred tank reactor, especially in industrial applications, selecting a proper impeller type and tank aspect ratio are crucial depending on the nature of the reaction operation. For example,

in hydrogenation of vegetable oil, multiple impellers with high aspect ratio are commonly used to obtain better residence time.

The typical gas-sparged stirred tank reactor comprises of a shaft with one or more impellers, baffles, and sparge pipe or distributor at the tank bottom. In certain operations, baffles may be excluded from the system as they inhibit proper cleaning or sterilisation e.g. fermentation process. Aspect ratio (T/L) often varies depending on the nature of the operation, for example in systems that need more gas residence time, higher aspect ratio is preferable and typically more than one impeller is employed on the same shaft. The internal heat exchange tube may be present in the form of a helical coil or vertical tube baffles for certain operations i.e. FTS. The most common impeller used in industry is known as the Rushton turbine. It was introduced by Rushton and co-workers [11] and later considered as a standard impeller design. A standard tank configuration includes cylindrical tank with flat bottom, depth, H , equal to diameter of the tank, T with baffle width, $B=0.1T$. The impeller diameter, D is normally $0.33T$ and centrally mounted with clearance, $C=0.33H$. This tank configuration is illustrated in Figure 2.1. The major advantages of the Rushton turbine are the additional strength given to the impeller by the disc in comparison to the open-bladed paddle, and avoidance of by passing of gas along the shaft [12]. However, the Rushton turbine requires much larger power consumption and has less axial circulation capability than critical in the case of solid particles suspended in liquid [13]. Therefore, other impellers such as Smith impeller, Lightnin A315, autoclaves and Scaba impeller, and the gas-inducing impeller have been developed over the years to overcome some shortcomings of the Rushton turbine.

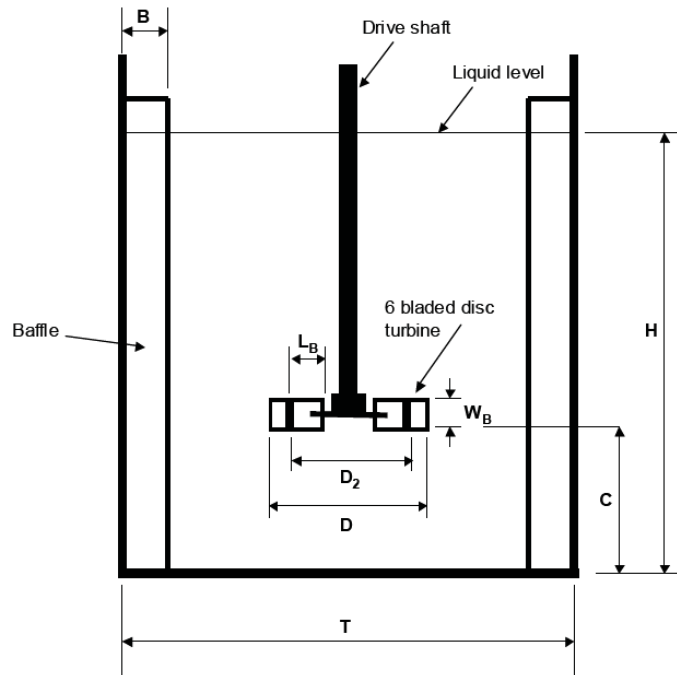


Figure 2.1. Standard configuration stirred tank with Rushton turbine [7]

2.3. Gas-inducing Stirred Tank Reactor (GIST)

Gas-inducing stirred tank reactors are attractive in multiphase systems especially when the conversion per pass is low. In the case of hazardous operation, it becomes critical to recycle the un-reacted gas back into the reactor. These operations include alkylation, ethoxylation, chlorination, hydrogenation, oxidation and many others [14]. A report provided by Roby and Kingley [15] gave additional reasons to employ a gas-inducing stirred tank reactor. The GIST renders redundant the external gas compressor used by GSTRs, reducing capital and operating expenditure.

2.3.1. Design

There are different designs of GIST depending on the nature of the operations and operating parameters. However, Mudale [16] has categorised the gas-inducing impeller based on the flow pattern in the impeller zone as;

Type 11 – single-phase flow (gas) at the inlet and outlet of the impeller zone.

Type 12 – single-phase flow (gas) at the inlet and two-phase flow (gas and liquid) at the outlet of the impeller zone.

Type 22 – two-phase flow (gas and liquid) at the inlet and outlet of the impeller zone.

The three different types of impeller design are illustrated in Figure 2.2.

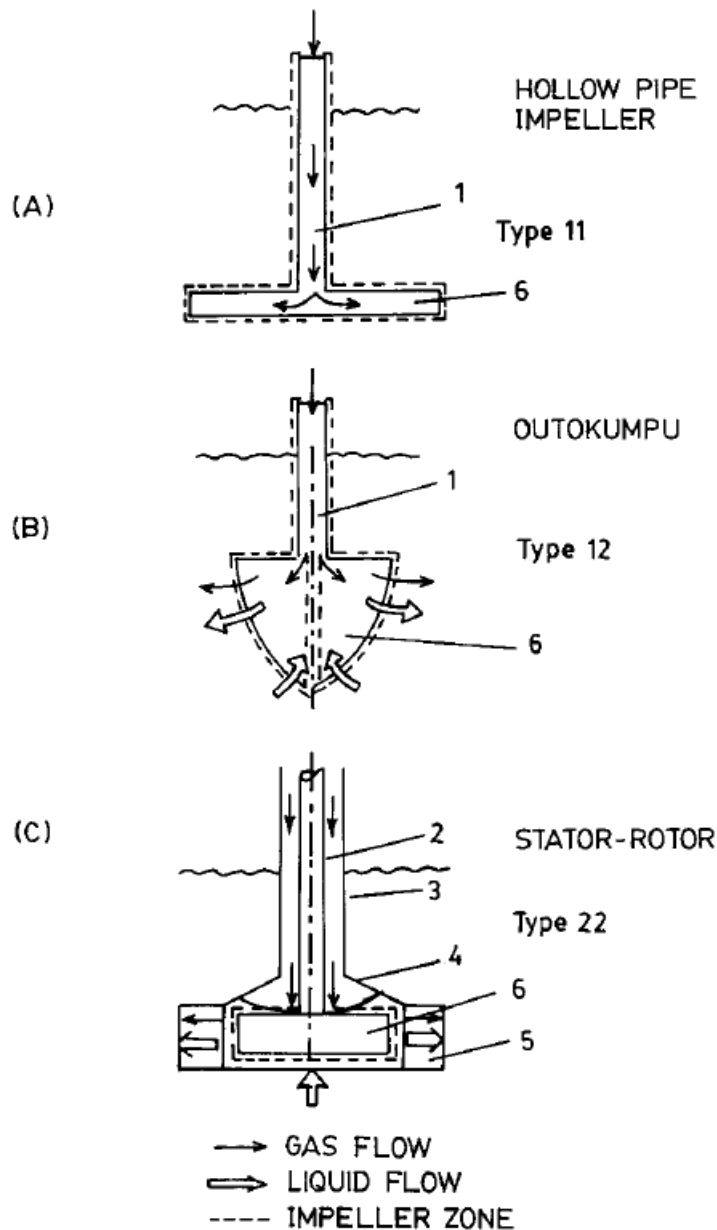


Figure 2.2. Three types of gas-inducing impeller design 1) hollow shaft, 2) solid shaft, 3) standpipe, 4) stator, 5) stator vanes, 6) impeller. [14]

In our project, the gas-inducing impeller design used falls under type-11 category, thus this review relates to type-11 only. A basic design consists of hollow impeller blades connected to a hollow shaft at the centre as shown in Figure 2.3. The gas-inducing impeller employs a pressure difference between the blade surface and the headspace. The local fluid at the blade surface accelerates away from the impeller region due to influx of the gas entrained from the headspace during rotation of the impeller thus causing a sudden pressure reduction. Gas induction starts when the pressure at the orifice falls to headspace pressure. This allows a recirculation of gas from the headspace back into the liquid.

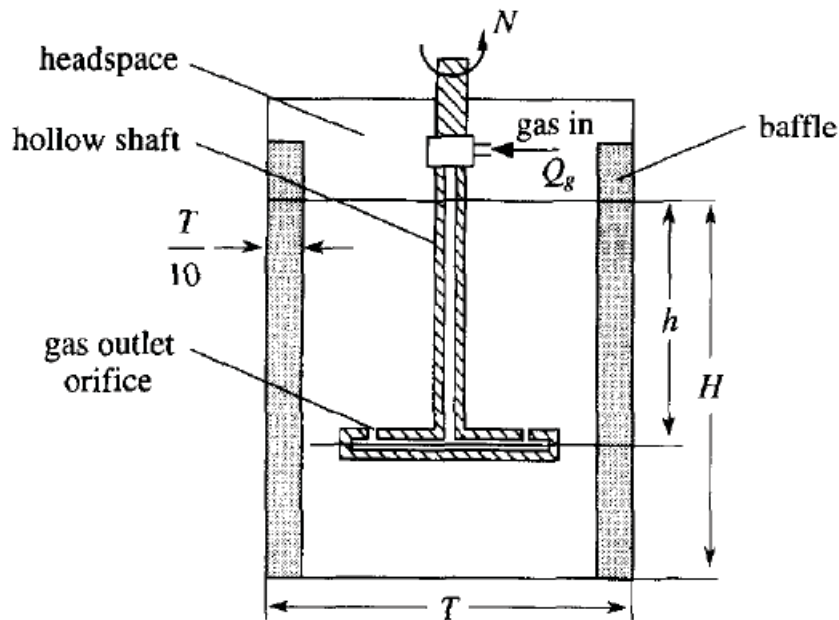


Figure 2.3. Design of gas inducing stirred tank reactor [17]

Deshmukh *et al.* [18] illustrated in Figure 2.4. the operating mechanism of the gas-inducing stirred tank reactor.

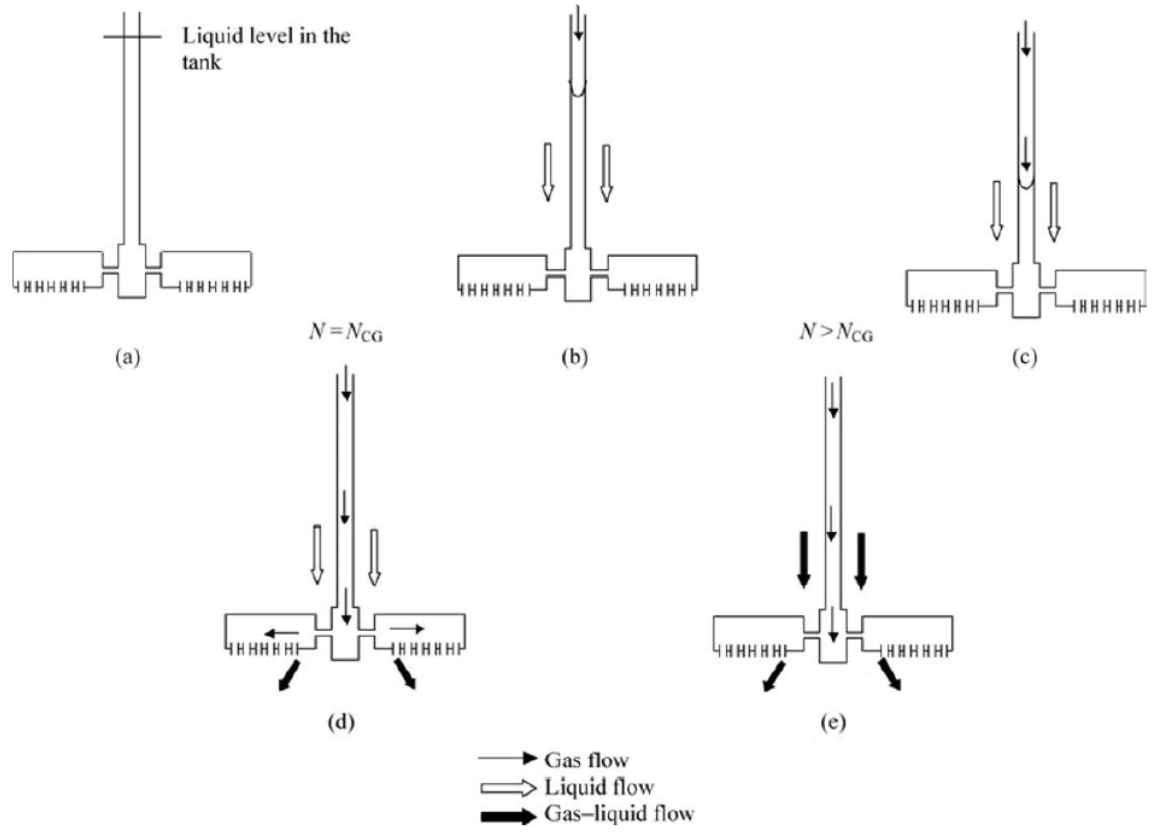


Figure 2.4. Mechanism of gas-inducing impeller [18]

2.3.2. Critical Impeller Speed

The speed of impeller at which gas induction commences is known as the critical impeller speed, N_{sc} . This parameter can be predicted using the relationship between velocity and pressure heads. Factors such as impeller geometry, physicochemical properties of the liquid, and shape of impeller blades may affect the N_{sc} . Martin's [19] work on establishing the relationship between differential pressure ($P_s - P_L$) and impeller tip velocity gave fundamental insight into critical impeller speed correlation with the local pressure. By measuring the reduction in local pressure using a manometer, a dimensionless parameter P' is given by

$$P' = 2g \left(\frac{h_s - h_L}{V^2} \right) \quad (2.1)$$

where h_s and h_L are the liquid head above the orifice without gas flow and liquid head outside the orifice respectively.

Nonetheless, Equation (1) does not give any relationship between impeller design, impeller speed, and local pressure. Evans et al.[20, 21] extended the work of Martin [19] to develop a relationship between local liquid velocity with impeller speed as

$$U = 2\pi N_s R (1 - K) \quad (2.2)$$

where N_s is impeller speed and K is blade slip factor. Values of pressure coefficient, C_p , and K were determined by independent experimental runs in the absence of gas induction [20]. The value of K has been found to be close to zero for both baffled and partially-baffled systems [19, 22] and we can safely assume that the value of K was zero in the present study. $C_p(\theta)$ was defined as

$$C_p(\theta) = \frac{2(P_0 + \rho_L gh) - P_i(\theta)}{\rho_L U^2} \quad (2.3)$$

Therefore, the difference between orifice pressure and headspace pressure is given by,

$$\Delta P = P_i - P_0 = \rho_L gh - \frac{1}{2} \rho_L U^2 (C_p - 1) \quad (2.4)$$

where P_i and P_0 are the orifice pressure and headspace pressure respectively, h is submersion depth, C_p is orifice pressure coefficient, U is the liquid velocity upstream of the orifice relative to the orifice velocity and given by Equation (2.2).

At the on-set of gas induction the driving force is equal to zero, thus from equation (2.4), the critical impeller speed, N_{sc} , is given by;

$$N_{sc} = \sqrt{\frac{gh}{2[\pi R(1-K)^2(C_p - 1)]}} \quad (2.5)$$

Equation (2.5) can be used to predict the critical impeller speed for a range of impeller blade designs and geometries[20, 22]. However, equation (2.3) fails to account for the effect of vortex in GIST. Therefore,

White and Villiers [23] reported the following correlation by assuming vortex formation adjacent to the impeller using a different method;

$$\frac{N_{sc}^2 D_I^2}{gh} = C \quad (2.6)$$

where D_I is the impeller diameter and C is an empirical constant with value of 0.23. The left hand side term in equation (2.6) is similar to Froude number ($Fr = N^2 D/g$). Sawant and Joshi [24] modified equation (2.6) by introducing the effect of liquid viscosity as

$$\frac{N_{cs}^2 D_I^2}{gh} \left(\frac{\mu}{\mu_w} \right)^{-0.11} = C \quad (2.7)$$

Based on the Equation (2.7), C value is 0.21 ± 0.04 . This equation is also valid for different types of reactors such as turbine impeller, Wemco flotation cells, Denver flotation cells, and shrouded turbine with a stator (type-12 and type-22) [25]. Other researchers such as Heim *et al.* [26] also used this equation to estimate a critical impeller speed for their system. Thus, we used Equation (2.7) to determine the critical impeller speed in our reactor.

2.3.3. Rate of gas induction

Rate of gas induction, Q_G , is one of the essential parameters in GIST generated by the impeller. Gas induction is zero at the critical impeller speed. As the impeller speed goes beyond the N_{cs} , gas induction increases in proportion to the pressure gradient. There have been several empirical correlations proposed to estimate the N_{cs} . Earlier work by Martin [19] proposed a Q_G correlation by implying the driving force of gas induction is proportional to the pressure gradient between the headspace and the local pressure at the orifice. Thus Q_G can be estimated by equating the pressure difference with the total resistive pressure drop due to friction in the hollow pipe, blades and orifice and is defined as;

$$Q_G = C_0 A_0 K_1 \sqrt{2g(-h_s) \left(\frac{\rho_L}{\rho_G} \right)} - 0.00085 K_1 \quad (2.8)$$

where K_1 is the empirical constant, C_0 and A_0 are orifice discharge coefficient and orifice area respectively. However, Equation (2.8) ignored the change in gravity head and is only applicable in fully developed turbulent flow with uniform cross section.

Baczekiewicz and Michalski [27] proposed a correlation for the maximum value of the ratio Q_G/V_L as;

$$(Q_G/V_L)_{\max} = (2.36 \times 10^{-4}) N_s^{1.53} \left(\frac{D_i}{T} \right)^{1.83} n_p^{0.26} \quad (2.9)$$

However, this correlation does not consider the physics of the process involved. Evans *et al.* [21] proposed a correlation based on equating the pressure driving force generated by rotation of the impeller to the pressure drop for the gas flow in the hollow-bladed agitator, thus

$$Q_G = C_0 A_0 \sqrt{\frac{2P_0 - P(\theta)}{\rho_G}} \quad (2.10)$$

As the gas starts to induce from the orifice, the average density in the vicinity of the impeller reduces considerably. Thus, the velocity head generated by the gas-inducing impeller is significantly lower. Therefore, the pressure driving force decreases to a large extent near this region. Thus, the average density, $\bar{\rho}$, is incorporated in the equation and defined as;

$$\bar{\rho} = \rho_L (1 - \varepsilon_G) \quad (2.11)$$

Absolute pressure on the blade surface is modified to account for the average density to yield

$$P(\theta) = (P_0 - P_L g S) - \frac{1}{2} \bar{\rho} C_p(\theta) [2\pi N_s R (1 - K)]^2 \quad (2.12)$$

Finally, by substituting Equation (2.11) into Equation (2.12), gives

$$Q_G = C_0 A_0 \sqrt{\left(\frac{\rho_L (1 - \varepsilon_G)}{\rho_G} + \varepsilon_G \right) C_P(\theta) [2\pi R N_s (1 - K)]^2 - \frac{2\rho_L g S}{\rho_G}} \quad (2.13)$$

Equation (2.13) reasonably successful in predicting the gas induction rate for a variety of operating conditions [14]. However, this model poorly predicts the gas induction rate at low speeds. Ever since, this model has been continuously modified by authors to account for different processes, for example, friction pressure drop in the hollow pipe and related kinetic energy, pressure drop required to overcome the surface tension forces for formation of bubbles. In this study, the rate of gas induction was calculated based on the Bernoulli equation and corroborated with the data collected via gas phase hold-up using ERT system (Appendix A2) that consequently used to estimate the average density that represent a true mixture of liquid and gas phases in the system. Table 2.1 summarises proposed models of gas induction rate for type 11 systems.

Table 2.1 Models for gas induction rate for type 11 system

Impeller type	Basis of prediction of Q_G	Accuracy	References
Hollow pipe and flatted pipe impeller	Empirical, flow correction factor K_1	—	Martin [19]
Hollow pipe	$(Q_G/V_L)_{\max} = (2.36 \times 10^{-4}) n^{1.5} \left(\frac{d}{D}\right)^{1.8} I^{0.26}$	—	Baczekiewicz and Michalski [27]
Hollow-bladed impeller	Blade slip factor K and pressure coefficient $C_p(\theta)$	10%	Evan <i>et al.</i> [21]
Hollow-bladed impeller	K , $C_p(\theta)$ and $\Delta P_T = \Delta P_p + \Delta P_0 + \Delta P_{KE} + \Delta P_\sigma$	20%	Evan <i>et al.</i> [28]
Two-bladed disc turbine orifice behind and off the blades	K , $C_p(\theta)$ and $\Delta P_T = \Delta P_p + \Delta P_0 + \Delta P_{KE} + \Delta P_\sigma$	20%	Evan <i>et al.</i> [29]
Hollow-bladed with multiple orifice	K , $C_p(\theta)$ and $\Delta P_T = \Delta P_p + \Delta P_0 + \Delta P_{KE} + \Delta P_\sigma$	—	—
Hollow pipe	$\frac{K_G}{K_\infty} = 1 - \exp(-C \text{Re}^{C_1} Fr^{*C_2})$	—	Heim <i>et al.</i> [26]
Hollow-bladed with multiple orifice	Similar to Evan <i>et al.</i> [20] and Forrester <i>et al.</i> [29]	—	Forrester <i>et al.</i> [17]
Hollow-bladed with multiple orifice	$Q_G = A_{\text{orifice}} \sqrt{\left[\frac{\rho_L (1 - \varepsilon_G)}{\rho_G} + \varepsilon_G \right] \left[(\pi D_s K)^2 - 2gh \right]}$	—	This study [30]

2.4. Dimensionless Groups and Correlations

In characterising stirred tank reactor performance, a number of dimensionless groups have been found useful. Many experimental studies have been conducted to determine the values of these dimensionless groups and how they vary with geometrical configuration and operating conditions. One of the most important descriptors is the impeller Reynolds number, Re_i , given by [5];

$$Re_i = \frac{\rho_L N_s D_i^2}{\mu_L} \quad (2.14)$$

For a stirred tank reactor, the power consumption is given in terms of power, number, N_p , defined as;

$$N_p = \frac{P}{\rho_L N_s D_i^5} \quad (2.15)$$

where P is power consumption and ρ_L is liquid density. Generally, in stirred tank reactors, N_p is found to decrease with increasing Re_i , while in the fully turbulent region ($Re_i > 10^4$), power number becomes constant for given tank and impeller geometry [5].

Various correlations have been proposed to predict the gas or solid hold-up, interfacial area, average bubble size and $k_L a$ values. Most of the correlations are developed under constraint number of impellers and tank configurations based on laboratory scales [31]. Measurement of gas hold-up in mechanical-agitated tanks was first initiated by Foust *et al.* [32] in 1944. Since then, various researchers have proposed correlations of gas phase hold-up [33-38] in which gas hold-up is given as a function of power consumption, superficial gas velocity. Calderbank [33] proposed the following equation for gas-liquid systems,

$$\varepsilon_G = \left(\frac{u_G \varepsilon_G}{u_B} \right)^{0.5} + \frac{0.0216 \left(\frac{P}{V_L} \right)^{0.4} \rho_L^{0.2}}{S_T^{0.6}} \left(\frac{u_G}{u_B} \right)^{0.5} \quad (2.16)$$

where u_B is terminal bubble velocity ($u_B=26 \text{ cms}^{-1}$) [39]. u_B also can be calculated using the following correlation [40]

$$u_B = 1.53 \left(\frac{S_T g}{\rho_L} \right)^{0.25} \text{ for } \text{Re}_G > 500 \quad (2.17)$$

Miller [41] modified Equation (2.16) by replacing term u_G/u_B by $u_G/(u_G+u_B)$ and broadening power consumption, P , to include both mechanical agitation and isothermal expansion due to kinetic power of the gas phase. Loiseau *et al.* (1977) proposed a correlation as given below;

$$\varepsilon_G = 0.011 u_G^{0.36} S_T^{-0.36} \mu_L^{-0.056} \left(\frac{P}{V_L} + \frac{P_G}{V_L} \right)^{0.27} \quad (2.18)$$

Another correlation was proposed by Hassan and Robinson [42] for gas phase hold-up and given as

$$\varepsilon_G = C_2 \left(\frac{Q_G N^2}{S_T} \right)^{C_3} \quad (2.19)$$

The most widely used equation for gas phase hold-up, proposed by Bakker *et al.* [43] is;

$$\varepsilon_G = C_h \left(\frac{P_G}{V_1} \right)^A v_{SG}^B \quad (2.20)$$

Where P_G is the gassed power, V_1 is the tank liquid volume, and v_{SG}^B is the superficial gas velocity. For water-air systems, $C_h=0.16 \pm 0.04$, $A=0.33$ and $B=0.67$. However, this correlation is based on experimental data that need to be tailored for specific applications.

Various authors have proposed correlations for average bubble size in stirred tank reactors [33, 44, 45]. In coalescing systems Calderbank [33] proposed that the bubble size may be given by;

$$d_B = 4.15 \frac{\sigma^{0.6}}{\left(\frac{P_G}{V_L}\right)^{0.4} \rho_L^{0.2}} \varepsilon_G^{0.5} + 0.0009 \quad (2.21)$$

where σ is the surface tension coefficient.

Usually, average bubble size is characterised by Sauter bubble diameter, d_{32} , which has the same ratio of area to volume. The Sauter mean bubble diameter, d_{32} , is defined as the ratio of the third and second moments and given as,

$$d_{32} = \frac{\int d^3 f(d) d(d)}{\int d^2 f(d) d(d)} \quad (2.22)$$

Barigou and Greaves [46] proposed the direct measurement of interfacial area with gas phase hold-up and Sauter mean diameter as given:

$$a = \frac{6\varepsilon_G}{d_{32}} \quad (2.23)$$

Another correlation proposed by Hughmark [47] for interfacial area is applicable in disc turbines;

$$a = 1.38 \left(\frac{g\rho_L}{\sigma} \right)^{1/2} \left(\frac{Q_G}{N_s V_L} \right)^{1/3} \left(\frac{N_s D_I^4}{g w V_L^{2/3}} \right)^{0.592} \left(\frac{dN_s^2 D_I^4}{\sigma V_L^{2/3}} \right)^{0.187} \quad (2.24)$$

It is reported by many authors that agitation rate can strongly influence volumetric mass transfer coefficient, $k_L a$ [48]. Bakker [43] proposed a correlation of $k_L a$ as a function of tank operating conditions, and given as

$$k_L a = C_{k_L a} \left(\frac{P_G}{V_L} \right)^a v_{sg}^b \quad (2.25)$$

For air-water systems, $C_{k_L a} = 0.0154 \pm 0.005$, $a = 0.6$ and $b = 0.6$. The overall mass transfer rate then can be calculated using,

$$\frac{dC_1}{dt} = k_L a (C_1^* - C_1) \quad (2.26)$$

where C_1 is the average concentration of gas dissolved in the liquid, and C_1^* is the saturation concentration.

Various parameters affect the $k_L a$ in mechanical-stirred tank reactors. Table summarises the dependency of $k_L a$ from different authors

Table 2.2 Study of gas-liquid mass transfer by different authors [49]

System	Solid type	Agitator description	Reference
Absorption of O_2 and CO_2 in water, glycol, and polyacrylamide solutions	—	—	Calderbank [33]
Absorption with reaction	—	Turbine propeller	Mehta and Sharma [50]
Desorption of O_2 in aqueous glycerol	—	Six-blade turbine 10 cm diameter	Yagi and Yoshida [51]
Hydrogenation of rapeseed oil	0.1% Ni catalyst, $d_p=10^{-3}$ cm	Six-blade turbine	Bern <i>et al.</i> [52]
Desorption of He from organic liquids	Polypropylene, sugar, and glass bead (25-50 μ m)	Turbine, $D_I=1/3D_T$	Joosten <i>et al.</i> [53]
Absorption of O_2 in sodium sulfite solution using cobaltous ions as catalyst	—	Turbine	Botton <i>et al.</i> [54]
Absorption of CO_2 in	—	Six-blade	Hassan

NaOH solution and turbine and
simultaneous Robinson
desorption of O_2 . [42]

Calderbank and Moo-Yong [55] proposed separate correlations for k_L and a ;

$$k_L = 0.42 \left[\frac{(\rho_L - \rho_G) \mu_L g}{\rho_L^2} \right]^{1/3} \left(\frac{D \rho_L}{\mu_L} \right)^{0.5} \quad (2.27)$$

and

$$a = \frac{1.44 \left(\frac{P}{V_L} \right)^{0.44} \rho_L \left(\frac{u_G}{u_B} \right)^{0.5}}{S_T^{0.6}} \quad (2.28)$$

while Yagi and Yoshida [51] also proposed a correlation for $k_L a$ in the form of:

$$\frac{k_L a D_1^2}{D} = 0.06 \left(\frac{D_1 N_s}{g} \right)^{0.19} \left(\frac{\mu_L}{\rho_L D} \right) \left(\frac{\mu_L u_G}{S_T} \right)^{0.6} \left(\frac{N_s D_1}{u_G} \right)^{0.32} \quad (2.29)$$

Bern *et al.* [52] proposed the $k_L a$ in an agitated slurry reactor for hydrogenation of oil in a gas-liquid system as;

$$k_L a = 1.099 \times 10^{-2} N_s^{1.16} u_G^{0.32} V_L^{-0.521} \quad (2.30)$$

Litmans *et al.* [56] also proposed a relatively simplified correlation for $k_L a$ expressed as

$$k_L a = \alpha \left(\frac{P}{V_L} \right)^{m^*} \varepsilon_G^{0.67} \quad (2.31)$$

For values of $P/V_L < 8000 \text{ Wm}^{-3}$, $\alpha = 0.618$, $m^* = 0.605$, while $\alpha = 1.215$, $m^* = 0.315$ for $P/V_L > 10000 \text{ Wm}^{-3}$.

The most recent correlation developed by Kavic and Heindel [57] is based on studies in a mechanical-stirred reactor equipped with six-blade Rushton impeller while gas was sparged using a ring sparger located at the bottom of the tank, with dimensions: $D_T = 0.211$ m, $D_T/T = 0.35$. Their correlation is given by

$$k_L a = 0.04 \left(\frac{P_G}{V_L} \right)^{0.47} u_G^{0.6} \quad (2.32)$$

They found that Equation (2.32) also matched data collected for a range of different vessel sizes ($0.211 \text{ m} < D_T < 2.7 \text{ m}$.)

The effect of solid particles on $k_L a$ has not been discussed extensively in the open literature. Slessor *et al.* [58] and Joosten *et al.* [53] have investigated the effect of solid particles on $k_L a$. They found that at low solid concentration (<10%) the $k_L a$ value was unaffected. However, at high concentrations, the $k_L a$ value was reduced considerably by the presence of solid particles. Tamhankar and Chaudhari [59] also found that solid particles showed no effect on $k_L a$. They investigated the effect of $k_L a$ in a mechanical-stirred reactor containing acetylene in water with suspended solid particles. Figure 2.5 shows the effect of $k_L a$ as a function of solid phase hold-up for various types of solid particles in a slurry reactor.

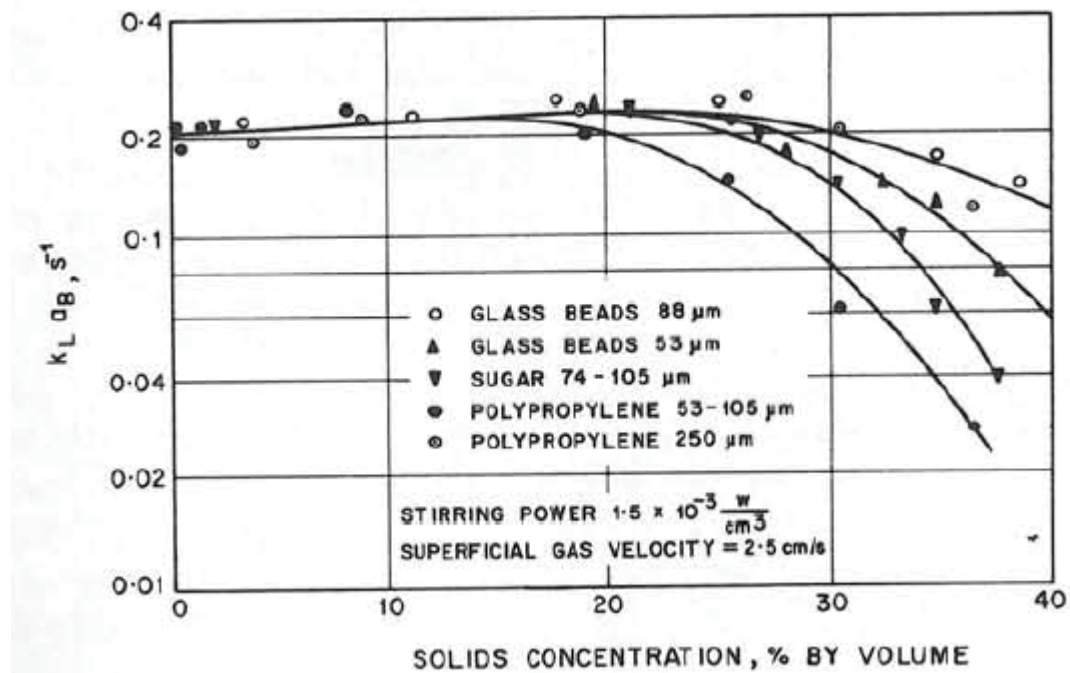


Figure 2.5 The volumetric gas liquid mass transfer coefficient as a function of solid phase hold-up for different solid particles. [53]

There are many other published correlations of this type that cover different types of impellers and operating conditions i.e. temperature and pressure [31]. However, these correlations may be suitable for specific conditions and/or functions of different variables, and sometimes gave conflicting results. Moreover, these correlations may not work well in non-standard stirred tank reactors and are extremely hard to generalise for different liquids and gases.

2.5. CFD application in Stirred Tank Reactors.

With the advancement of computers, CFD modelling has become an increasingly prominent and useful tool for investigation of fluid dynamics behaviour in various systems, in particular stirred tank reactors. CFD can provide valuable data that is unattainable via experimentation. However, it should be noted, experimental investigation is still a crucial step in validating the accuracy of CFD simulation.

2.5.1. Basic principle in CFD and governing equations

The most fundamental equations in CFD are conservation of mass and momentum equations for a single phase, given by [60];

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (2.33)$$

$$\frac{\partial (\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla P + \nabla \cdot (\mu_L (\nabla \mathbf{u} + \nabla \mathbf{u}^T)) + \rho \mathbf{g} \quad (2.34)$$

where,

ρ = fluid density

$\mathbf{u}$ = velocity vector

P = dynamic pressure

t = time

μ_L = liquid viscosity in laminar flow

Equations (2.33) and (2.34) apply to the simple case of laminar flow of a single phase fluid. However, most practical industrial problems involve more complex multiphase systems. We still can use these equations without any modification via direct numerical solution (DNS) but generally, DNS is impractical because it needs tremendous computer resources. Therefore, averaged forms of these equations are usually solved. It is nearly impossible to obtain exact solutions regardless of whether exact or averaged forms of the conservation equations are used. Thus, a numerical routine is required to solve these equations [61]. The geometry of interest is discretised into a number of cells and equations are solved using iterative methods which include spectral, finite element and finite volume techniques. Finite volume methods are commonly used. Then, the geometry needs to mesh either using body fitted or regular, and structured or unstructured meshes.

To assist in solving the set of Navier-Stokes equations, generalised software packages have been developed and commercialized, such as

FLUENT, CFX, and star-CD. The modeling in this study was performed under the frame work of FLUENT version 6.3.

In industrial applications, most of the flow problems involve turbulent flow in which the flow displays unsteady state fluctuations and formation of turbulent eddy structures. Thus, a turbulent model is introduced based on approximate methods. FLUENT provides several choices of turbulence models, namely [62]:

1. $k-\varepsilon$ models

- standard $k-\varepsilon$ model
- Renormalisation-group (RNG) $k-\varepsilon$ model
- Realisable $k-\varepsilon$ model

2. spalart-Allmaras model

3. $k-\omega$ models

- standard $k-\omega$ model
- shear stress transport (SST)

3. Reynolds stress models

- Linear pressure-strain RSM model
- Quadratic pressure-strain RSM model
- Low-Re Stress-omega RSM model

3. v^2-f model

4. Detached eddy simulation (DES)

5. Large eddy simulation (LES) model

However, no single turbulence model is suitable for all the classes of problems. The selection of turbulent model depends on the physics of the flow of interest, established practice for the specific class of problems, level of accuracy required, and the computational time and resources available. The most common turbulence model used is standard $k-\varepsilon$ model. In this model, Reynolds stress is assumed to be

given in terms of turbulent viscosity, μ^T , and the mean flow velocity gradient according to;

$$\rho \overline{\mathbf{u}'\mathbf{u}'} = \mu_T (\nabla \mathbf{U} + \nabla \mathbf{U}^T) - \frac{2}{3} \rho k \mathbf{I} \quad (2.35)$$

where $\mathbf{I}$ is the identity tensor and k is turbulent kinetic energy per unit mass and can be expressed in terms of fluctuating velocity component, $\mathbf{u}'$, as;

$$k = \frac{1}{2} \overline{\mathbf{u}'^2} \quad (2.36)$$

Turbulent viscosity, μ^T is defined as,

$$\mu_T = C_\mu \rho \frac{k^2}{\varepsilon} \quad (2.37)$$

where, ε is the rate of dissipation of turbulent kinetic energy per unit mass and C_μ is a constant which has value of 0.09 [62].

Variables k and ε in the turbulent model are calculated based on the conservation of equation [62] and given as,

$$\frac{\partial(\rho k)}{\partial t} + \nabla \cdot (\rho \mathbf{U} k) = \nabla \cdot \left[\left(\mu_L + \frac{\mu_T}{\sigma_k} \right) \nabla k \right] + \Pi - \rho \varepsilon \quad (2.38)$$

$$\frac{\partial(\rho \varepsilon)}{\partial t} + \nabla \cdot (\rho \mathbf{U} \varepsilon) = \nabla \cdot \left[\left(\mu_L + \frac{\mu_T}{\sigma_\varepsilon} \right) \nabla \varepsilon \right] + C_1 \frac{\varepsilon}{k} \Pi - C_2 \rho \frac{\varepsilon^2}{k} \quad (2.39)$$

where C_1 , C_2 , σ_k , σ_ε are model constants and Π is production of turbulent kinetic energy by mean velocity gradients, given by,

$$\Pi = (\mu_L + \mu_T) \nabla \mathbf{U} \cdot (\nabla \mathbf{U} + \nabla \mathbf{U}^T) - \frac{2}{3} \nabla \cdot \mathbf{U} [(\mu_L + \mu_T) \nabla \cdot \mathbf{U} + \rho k] \quad (2.40)$$

In applying boundary conditions near the wall for turbulent flow with k - ε model, the approach of wall functions to model the boundary layer is

considered. This approach is formulated using the concept of universal law of the wall [63-65] in which a constant stress is assumed in the near-wall region and eddy scale is proportional to the distance from the wall. A relationship is obtained between the shear stress at the wall, τ_w , and the velocity component parallel to the wall in the adjacent node, $u_{t,adj}$, given as,

$$\tau_w = \frac{\rho C_\mu^{1/4} \kappa k_{adj}^{1/2}}{\ln(E y_{adj}^+)} |u_{t,adj}| \quad (2.41)$$

where κ is Von Karman constant, E is the roughness constant, C_μ is a constant with value 0.009, k is turbulent kinetic energy in the cell adjacent to the wall, and y_{adj}^+ is the scaled distance to the wall, given by,

$$y_{adj}^+ = \frac{\rho C_\mu^{1/4} k_w^{1/2}}{\mu} y_{adj} \quad (2.42)$$

where, y_{adj} is the distance from adjacent cell centre to the wall. This equation represents the boundary conditions for the tangential velocity component. However, the transport equation for turbulent dissipation rate, ε , is not solved adjacent to the walls, rather, its value is derived via the relation:

$$\varepsilon = \frac{C_\mu^{3/4} k_{adj}^{3/2}}{k y_{adj}} \quad (2.43)$$

In order for the wall function to be valid, the first cell centre adjacent to the wall must lie within the boundary layer. Therefore, it is required that non-dimensionalised distance to the wall for each neighboring cell should fall in the range $11 < y_{adj}^+ < 300$ [66].

This k - ε model is used in this study due to its generality and applicability to a wide range of situations. More complicated models have been developed, for instance Reynolds stress model, where the modelling

equations are calculated using all the normal and shear stresses individually. However, the main drawback of this model is that seven equations need to be solved instead of two using $k-\varepsilon$ model. Therefore, an enormous amount of computational time and added complexity of the equations to be solved.

Apart from the turbulence model, other aspects of CFD modeling that affect accuracy are related to the numerical methods employed to solve the equations. The discretisation method related to spatial and temporal gradients is an important aspect in CFD simulation. Spatial discretisation is related to the estimation of convective terms in governing equations. An algebraic function is required in calculating the convective flux describing the spatial variation between cell centres in the discretised grid, and known as a differencing scheme. The degree of accuracy of this scheme is often referred in the term of order. Higher order reflects smaller truncation error, thus it should be preferred. However, there is no direct connection between the order of method to the accuracy of a solution on a given grid [67]. Furthermore, the more accurate schemes tend to be significantly less robust and computationally expensive [62].

Similarly, a temporal discretisation scheme (first or second order implicit scheme) is used when a transient simulation is carried out. Again, the choice of the scheme affects the accuracy of the solution. In this study, second order implicit method was used.

In FLUENT, differencing schemes for convective terms include upwind, central differencing, hybrid, power law, second order upwind, quadratic upwind differencing (QUICK) and total variation diminishing (TVD). By default, the hybrid differencing scheme is used where central differencing is employed if Peclet number is less than 2, otherwise upwind differencing is used.

In modelling multiphase systems, a number of approaches are available. It is impractical to model directly the bubbles or particles individually due to highly computational expensive [7]. The most common and accurate approach is applying Eulerian-Eulerian equations. This approach defines

each phase as a local volume fraction and separate equations are solved simultaneously for conservation of mass and momentums for each phase. The generalised form of Eulerian-Eulerian equations is given below;

$$\frac{\partial(\alpha_i \rho_i)}{\partial t} + \nabla \cdot [(\alpha_i \rho_i \mathbf{U}_i) + \nabla(D_i \alpha_i)] = S_i \quad (2.44)$$

$$\begin{aligned} \frac{\partial(\alpha_i \rho_i \mathbf{U}_i)}{\partial t} + \nabla \cdot (\alpha_i \rho_i \mathbf{U}_i \mathbf{U}_i) = & -\alpha_i \nabla P_i + \alpha_i \rho_i \mathbf{g} + \\ \nabla \cdot [& \alpha_i (\mu_{L,i} + \mu_{T,i}) (\nabla \mathbf{U}_i + (\nabla \mathbf{U}_i)^T)] + \mathbf{F}_i + \mathbf{A}_i + \mathbf{T}_i + \mathbf{L}_i + S_i \mathbf{U}_i \end{aligned} \quad (2.45)$$

Where i represents phase i ($i=1$ for continuous phase and 2 for dispersed phase), S_i is a source term, $\mathbf{g}$ is gravity vector in buoyancy force term, D_i is turbulent diffusivity coefficient for volume fraction, $\mathbf{F}_i$ is the drag force, $\mathbf{A}_i$ is added mass force, $\mathbf{L}_i$ is the lift force and $\mathbf{T}_i$ is the turbulent dispersion force.

For gas-liquid systems, turbulent in the gas phase is generally neglected. In gas-liquid systems, the drag force is the most important factor and the balance between the drag force and buoyancy force determine the slip velocity of a bubble or particle. The drag force is given as

$$\mathbf{F}_2 = -\mathbf{F}_1 = -\frac{3}{2} \alpha_2 \rho_1 \frac{C_D}{d} |\mathbf{U}_2 - \mathbf{U}_1| (\mathbf{U}_2 - \mathbf{U}_1) \quad (2.46)$$

It is imperative to calculate drag coefficient, C_D , which is an empirical constant. Various authors have adapted different approaches in evaluating C_D .

Another multiphase model that is widely used in gas-liquid systems is the volume of fluid (VOF) model. The VOF method, developed by Nichols and Hirt [62], is well suited to model the flow of liquid coupled with the movement of a gas-liquid interface by solving local-instantaneous conservation equations and boundary conditions. This method employs an algorithm to track the free surface moving through a computational

grid. The VOF method can model two or more immiscible fluids by solving a single set of momentum equations and tracking the volume fraction of each of the fluids throughout the domain. The VOF formulation relies on the fact that two or more fluids (or phases) are not interpenetrating. For each additional phase, the volume fraction of the phase is introduced as a variable in the computational cell. In each control volume, the volume fractions of all phases sum to unity. The fields for all variables and properties are shared by the phases and represent volume-averaged values. Thus, the variables and properties in any given cell are either purely representative of one of the phases, or representative of a mixture of the phases, depending upon the volume fraction values. In other words, if the q^{th} phase volume fraction in the cell is denoted as φ_q , then the following three conditions are possible:

$\varphi_q = 0$: the cell does not contain any of the q^{th} phase.

$\varphi_q = 1$: the cell is full of the q^{th} phase

$0 < \varphi_q < 1$: the cell contains the interface between the q^{th} phase and one or more other fluids. Based on the local value of φ_q , the appropriate properties and variables will be assigned to each control volume within the domain.

Another important issue in gas-liquid systems is local bubble size, d_B . A range of bubble sizes exist in the stirred tank reactor. In common practice, bubble size is specified by mean diameter. The mean bubble diameter may vary spatially within the vessel and overall size diameter may be used. The simplest assumption made available in the literature is to prescribe the bubble size based on empirical data. A more complicated approach is to include sub-models to predict the local bubble size based on the dynamics of bubble break-up and coalescence. Regardless of which approach is taken, the momentum conservation using mean diameter only uses one single equation, thus all the bubbles move at a single, average slip velocity.

2.5.2. Review of CFD simulations in stirred tank reactors

The development of CFD modelling in mechanical-stirred tank reactors has been reviewed by Haris et al [68], and Brucato et al [69]. CFD investigations related to mechanical-stirred tank reactors can be traced back to the late 1970s in which the CFD modelling used very simplistic models. However, thanks to the rapid development in computer technology over the years, more advanced techniques have been developed and used. One problem of CFD simulation is the need for very large computer memory and computation time, necessary to resolve 3-dimensional and complex 3-D flow structures in stirred tanks. Another problem related to stirred tanks is development of a proper technique to deal with impeller rotation in baffled tanks. The earliest approach was to model the impeller as a 'black box' by some sort of momentum source in the volume swept by the impeller. By adopting such techniques, empirical data are required for specifying the impeller. Brucato *et al.* [69] found later that the impeller boundary conditions are not a property of the impeller, but rather the area surrounding the impeller. Other simulations which adopted the impeller boundary conditions approach include Ranade et al. [70, 71] who simulated both a radial flow turbine and axial flow pitched blade turbine. Bakker [72] also adapted the same approach for predicting the flow of a Rushton turbine and pitched blade turbine. Another approach is to use a rotating frame of reference. In this model, baffles are modeled as a momentum sink. Harley et al used this method but disregarded the relative motion between the impeller and baffles which restricted themselves to laminar flow conditions. It appears that the real effects of baffling was not satisfactorily simulated. Another method proposed by Brucato *et al.* [73] is based on the steady-state approximation. In this approach, the vessel is divided into two overlapping zones, the inner zone represents the impeller region while the outer zone represents the remaining bulk of the tank including the baffles. In this approach, it simulates the flow in the inner zone as a frame of reference rotating zone. The flow of the outer zone is then

calculated in the normal inertial reference frame, to obtain an estimation of the velocity and turbulence quantities. A second procedure is then carried out in the inner zone. This procedure is repeated until satisfactory convergence is achieved. This method predicts flow fields reasonably well but the trailing vortices were not resolved. Finally, there is another method to simulate the whole flow of the vessel, called the multiple frames of reference (MFR) method. In this method, a steady-state approach is considered to avoid the large computational requirement of other methods. The flow domain is divided into two zones; the inner zone being assigned to the rotating frame of reference with the impeller and outer zone being the fixed inertial reference frame. In the inner zone, two forces are included in momentum equations, namely centrifugal and Coriolis forces. The flow is simultaneously solved in both domains, and information is exchanged at the interface taking into account the change in reference frame. Unlike the inner-outer method, there is no overlapping between the zones. Luo *et al.* [74] applied this method in the same tank that previously used moving grid simulation. They found that the predicted velocity showed reasonably good agreement with experimental measurements. This method required one tenth the computational time as compared to moving grid yet gave better prediction. This method has become a method of choice by researchers in particular for applications that involve rotating impellers [66, 74-78]. In this study, MFR is used to simulate the rotating gas-inducing impeller in a stirred tank reactor.

Sahu *et al.*, [79] used CFD modelling to develop rational design procedures for CSTRs in which impeller design geometry was related to flow field produced and developed a link between flow field and process objectives. In their study, five different designs of axial flow impellers were investigated. They used zonal modelling where the vessel was divided into a few zones for predicting the flow characteristics in regions far away from the impeller, where previous researchers found numerical predictions to be unsatisfactory. They found the predicted values of dimensionless radial and axial velocity were in good agreement with

experimental values, even though the tangential velocity showed a mixed trend. Predictions of turbulent kinetic energy, k , were significantly improved using zonal modelling. However, the prediction of turbulent energy dissipation rate, ε , which was estimated from impeller velocity and length scale calculated from auto correlation, was unsatisfactory. Revstedt *et al.*, [80] conducted similar modelling on a CSTR with a liquid volume of 0.64 m^3 , in which the effect of impeller type, viz dual Rushton and dual 6SRGT impellers, were studied using large eddy simulations (LES). They found that under equal power input, tip velocity provided proper scaling parameters when comparing similar turbine geometries. However, this finding was contradicted by the work of Sheng *et al.*, [81]. They also provided axial flow numbers as a function of liquid medium viscosity and the impact of the liquid medium viscosity on the blending time. Validation and verification of a process is a trial and error procedure. A simulation can be used to predict the performance of the process and also validate the process by comparing the experimental data. Along with experimental data, if images or animations of real-time analysis can be obtained, it can help improve product yield and uniformity, minimise input process material, reduce energy consumption and lower occupational exposure to plant personnel

Murthy *et al.*, [76] simulated multiphase flow using an Eulerian-Eulerian approach with standard $k-\varepsilon$ turbulence model in a gas-inducing stirred tank reactor. They used the multiple reference frames (MRF) approach in FLUENT 6.2 to model impeller rotation. The predicted three phase flow model was compared with the experimental data provided by Chapman *et al.* (1983) and Rewatkar *et al.* (1991). They found that the model closely predicted the critical impeller speed over the design and operating conditions. Kasat *et al.*, [82] simulated gas-liquid flows in a stirred tank reactor with dual Rushton turbines. They also used the MRF approach to simulate impeller rotation in a stirred reactor. The CFD model was used to predict three flow regimes: L33-VC (upper impeller-lower impeller), S33-VC (Dispersion- Vortex clinging) and VC-VC (vortex

clinging-vortex clinging) regions. They found good agreement between simulated results and experimental data for all three flow regimes.

Kerdouss et al., [83] predicted spatial distribution of gas hold-up, average local bubble size and flow structure in a double turbine stirred tank. The simulation of dispersed gas and bubble dynamics in the turbulent water was conducted using an Eulerian-Eulerian approach with dispersed $k-\varepsilon$ turbulence model.

The finite volume method uses the integral form of the conservation equations as its starting point in order to ensure global conservation. Finite volume in CFD can accommodate any type of grid and is therefore suitable for handling complex geometry.

Lopes and Quinta-Ferreira [84] employed VOF method to simulate the catalytic wet oxidation of Phenolic waste water in a trickle-bed reactor. They used unsteady-state operation to evaluate the dynamic behaviour of total organic and temperature profiles. The discrepancy of 1.5% between the experimental and modelling results show a good agreement between the two. Akiti *et al.* [85] also used VOF approach in determining the flow field in stirred tank reactor equipped with down-pumping hydrofoil impeller. The authors found CFD prediction gave reasonably good results as compared to previously published experimental data [86]. While, Bai *et al.* [87] employed similar simulation technique to predict hydrodynamics and residence time distribution (RTD) in industrial-scale stirred tank reactors that equipped with 2-and 3-stage agitators in which MRF method was used to model the agitation of stirrers.

In this study, the VOF approach has been employed based on volumetric fraction of each phase in grid cells. Relatively little research has been published on this subject, however, it is considered to be a critical aspect in understanding complex hydrodynamics of gas-inducing stirred tank reactors.

2.6. Fischer-Tropsch Synthesis (FTS)

The last half of the 20th century has witnessed three main generations of Fischer-Tropsch (FT) reactors: the fixed bed, fluidised bed and the slurry reactors. Reactor selection/design is a vital step, as it invariably affects the final product quality. Of the several aspects considered in selection of a reactor, its ability to effectively remove heat generated by the reaction is an important consideration [88]. The FT reaction is a highly exothermic one, generating in the order of 165-204 kJ of energy per mole of carbon monoxide reacted [89, 90]. This would effectively result in a theoretical adiabatic reactor temperature of 1600 K at complete conversion [91]. This is in the order of 1000-1100 K above the desired operating temperature for Fischer-Tropsch synthesis (FTS). High temperature leads to a low chain growth probability, α , which results in formation of relatively short chain products and enhances methane yield [89]. This effectively defeats the purpose of the reaction, which is primarily to convert gas to liquid fuels (i.e. C₄₊ hydrocarbons). In addition to this it also causes greater carbon deposition and particle fragmentation, overall resulting in decreased catalyst life [89, 90].

2.6.1. The Fixed Bed Reactor

Of all the different reactor modules used in FTS, the fixed bed reactor has undergone the greatest number of design modifications. The earliest fixed bed designs comprised of a rectangular box packed with catalyst, with water filled cooling tubes passing through the catalyst bed. Subsequent modifications of this reactor led to the development of the adiabatic bed reactor (single, then multiple), and the multi-tubular fixed bed reactor. The multi-tubular arrangement typically incorporates use of double concentric tubes, with the catalyst packed in the annulus, and surrounded by boiling water on both sides. The benefits of this arrangement are two-fold: it offers better isothermality of the reactor than its predecessors, while simultaneously also generating process steam for the plant. The relatively recent versions of the multi-tubular fixed bed

reactor operate on moderate per-pass conversion with gas recycle facility [91].

Fixed bed reactors have improved extensively over the decades, however, this reactor configuration faces some intrinsic drawbacks. Firstly, the packed bed characteristics cause a high-pressure drop across the bed and thus results in high gas compression costs. This is a very significant ongoing liability and hence, discourages the employment of the fixed bed reactor [89, 91].

The greatest dilemma, however, with the fixed bed reactor is poor heat removal characteristics. The fixed bed reactor is deficient in this respect, and the rate impeding section is the packed catalyst bed. Low gas throughputs, combined with lack of solids' mixing results in poor heat removal characteristics of the fixed bed reactor. Consequently, temperature gradients and non-isothermal conditions prevail in a fixed bed reactor [88-90, 92]. This scenario leads to broad distribution of low molecular weight products. As mentioned above, an increase in temperature decreases α_{FT} , the chain growth probability, and hence results in shorter chained products. Thus a reactor possessing non-isothermal characteristics is expected to support a range of parallel reactions that result in non-homologous reaction products. As a result, the fixed bed reactor shows poor product selectivity, which again suggests its use for Fischer-Tropsch synthesis is disadvantageous. [89-91].

Several more drawbacks exist for the fixed bed reactor. The employment of large size particles for the packed bed due to pressure drop constraints, results in intra-particle mass transfer limitations [88, 90, 91]. Due to inferior heat removal capacity, periodically local hot spots prove to be unavoidable in fixed bed reactors. This results in increased carbon deposition, sintering, and eventually catalyst deactivation and bed plugging [89-91].

2.6.2. Fluidised Bed Reactors

Fluidised bed reactors came into operation due to shortcomings of the fixed bed reactor. The pressure drop across the bed is much lower than in fixed bed configurations. This allows employment of smaller size catalyst particles, which practically eliminates the intra-particle mass transfer limitation. However, its greatest gain is the use of smaller size particles combined with higher gas velocity and constant mixing consequents in a high degree of isothermality of the reactor. Hence fluidised bed reactors offer high product selectivity and throughput [89, 91]. However, fluidised beds too possess some intrinsic weaknesses in relation to Fischer-Tropsch synthesis. A fundamental issue is the production of heavy hydrocarbon products. Given that the reaction takes place on the catalyst surface, generation of any high boiling products would result in their condensation on the particle surface, which in turn would lead to agglomeration and therefore defluidisation of the bed [89, 91]. As stated above, the chain growth probability, α_{FT} , is a function of the temperature, and hence, the fluidised bed reactor must be operated at relatively high temperatures to avoid the possibility of particle agglomeration. Sie and Krishna (1999) have formulated a condition to be fulfilled, in order to avoid particle agglomeration and subsequent loss of fluidisation. Another prominent setback of fluidised bed reactors is extensive catalyst attrition. Continuous collision of solid particles with internal surfaces of the reactor, as well as with others of the kind, in an agitated gas phase, causes significant catalyst attrition and production of fines. This poses problems with regard to catalyst carry over (loss of catalyst) and demands greater efforts for gas-solid separation.

2.6.3. Slurry Reactors

Of the major types of reactors used in FTS, slurry reactors have shown greatest promise. The majority of the weaknesses of the other two reactor configurations are overcome in the slurry reactor. It is a three-phase system, wherein the solid catalyst is suspended in an inert liquid

medium (often comprising of the FT product itself), while reactant gases are bubbled through the bottom. It is immediately evident that this reactor should have the best heat removal potential, as the principal heat removal medium is a liquid rather than gas which offers far superior heat transfer characteristics. Combined with efficient mixing of the slurry by the up-flow of gases, the reactor operates in highly isothermal conditions, thereby offering very high product selectivity [88, 93]. The potential to accommodate significantly higher catalyst loadings ensures higher single pass conversion and throughput [89]. In addition to the above, the slurry reactor also overcomes the problems encountered with the fluidised bed reactor. It is well adapted to production of heavy, high boiling, liquid products, which is in fact the basis for its functioning. Also, the liquid medium acts as a physical buffer surrounding the catalyst particles, and thus minimises attrition. While existence of the liquid medium may challenge inter-particle mass transfer, Sie and Krishna [91] have demonstrated that it is not a concern for reactors operated in the churn-turbulent regime.

Although the slurry reactor has demonstrated potential to overcome the weaknesses of the other types, it too faces some significant obstacles in commercial operations. The most critical of these is the separation of the catalyst from the inert liquid medium [88, 94]. The constant complaint is that filters used for the purpose get clogged much sooner than desired [95]. Attrition although much less than fluidised beds, has more severe detrimental impacts in slurry reactors. This is because solid-liquid separation is far more demanding than solid-gas separation [91, 96]. The problem cannot be solved by merely using larger size particles, since the key factor is the production of finer particles. Larger particles may reduce the occurrence of clogging, however it is imperative to rid the liquid product stream of catalyst particles completely. Also, larger particles have greater probability of attrition than smaller ones.

2.6.3.1. Slurry Bubble Column Reactor

The most common slurry based reactor on the industrial scale is in the form of the slurry bubble column (SBCR). The first commercial large-scale application was introduced by Kolbel in the 1950's at RheinpreuBen Company and later was adapted by Sasol plant in South Africa in the early 1990's [97]. Typical SBCR design includes a reactor shell with internal tubing to control reaction temperature by generating steam. Catalyst is suspended in the liquid medium, typically molten wax/paraffin oil while the synthesis gas is introduced through a distributor at the bottom of the reactor. The liquid product of mainly high molecular weight, is collected from a port within the slurry bed while the gaseous products including unreacted gases exit from the top of the SBCR [98, 99]. A typical slurry bubble column reactor used in FT synthesis is illustrated in Figure 2.6. Usually, the FT synthesis operates in the low temperature Fischer-Tropsch (LTFT) regime in order to optimise hydrocarbon production. The main, inherent benefits of SBCR compared with other reactor types are that the catalyst is suspended in a liquid medium and provides better heat transfer within the reactor thus eliminating any hot spots. Other benefits include a) suitability for production of high molecular weight products, b) operation at relatively low reaction conditions c) better catalyst longevity, d) simple design e) high throughput per reactor f) relatively low capital cost. [98, 99] provide comprehensive advantages of SBCR in FT synthesis.

However, the SBCR possesses some major challenges such as attrition and separation of fine catalyst from the liquid medium. Separation is usually performed by filtration using wire mesh filter which results in the filter been clogged up by the fine catalyst particles.

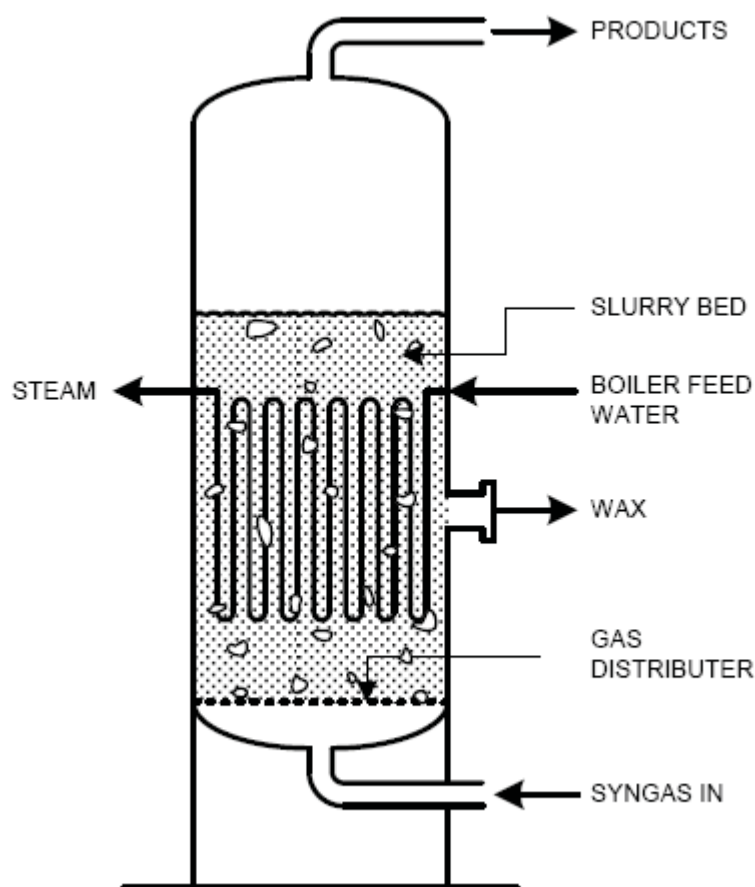


Figure 2.6 Schematic diagram of 3-phase bubble column slurry reactor [100]

2.6.3.2. Slurry stirred tank reactor

There is limited literature that deals with slurry stirred tank reactor FTS. Bukur and co-workers [93, 95, 101] have used a mechanical-stirred tank reactor in their studies of FTS. More recently, Cooper *et al.* [102, 103] have used a continuous stirred tank reactor (Parr reactor) to study FTS using molten wax as the liquid medium and various catalyst types i.e. cobalt and molybdenum supported with alumina in their study. Figure 2.7 shows the Parr reactor used in their study. Due to the nature of FTS with high pressure and high temperature, there is no available literature that studies the hydrodynamics of FTS during experimentation as far as the author knows. Thus, with the aid of electrical tomography, for the first time, we investigate in-situ electrical capacitance tomography (ECT)

diagnosis of the Fischer-Tropsch reaction in a gas-inducing stirred tank reactor (similar reactor to Cooper *et al.* [103]). The objective was to determine the relationship between reaction metrics and dispersed phase hold-up characteristics with time-on-stream.

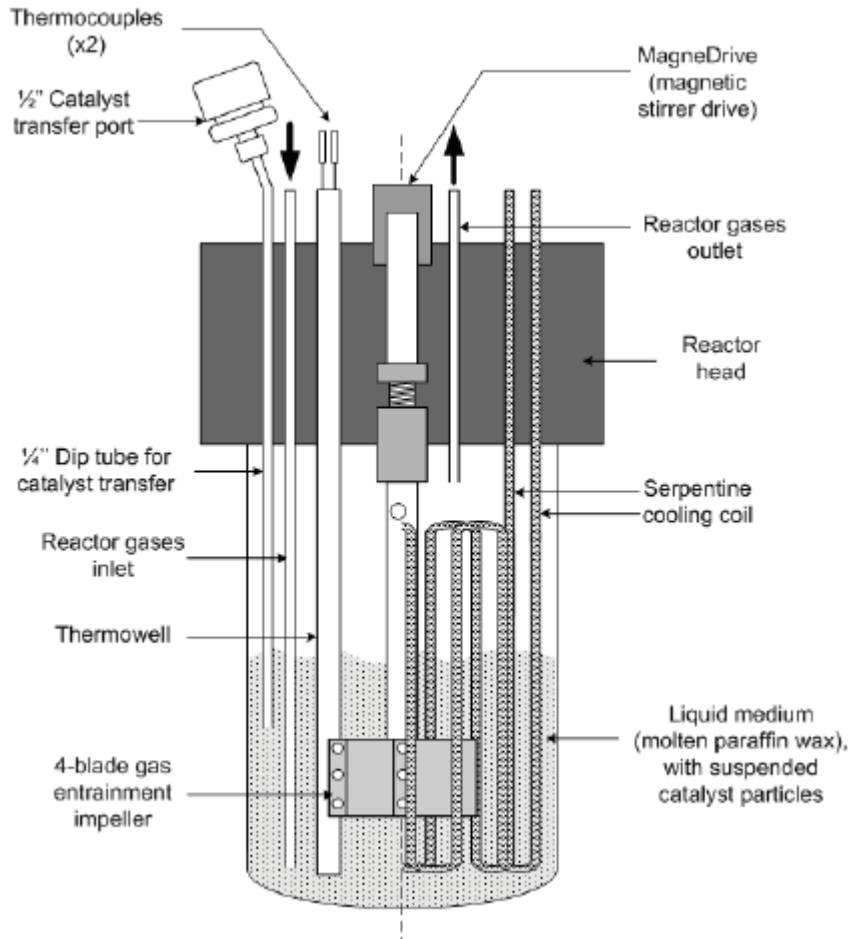


Figure 2.7 Schematic diagram of slurry Parr reactor in FTS [103]

2.7. Process tomography

Process tomography employs sensory measurements rooted in the electrical (e.g. capacitance, resistance and inductance modes), acoustic (ultrasound) [104], optical [105] and radiation (gamma, positron emission and X-ray [106]) stimulus-response character of the system of interest. Boyer *et al.* [107] have given a detailed and instructive review of various tomographic (as well as important intrusive) techniques for the

measurement of multiphase flow system characteristics and conditions or criteria which must be satisfied for deployment in meeting specific process diagnostic objectives. Although medical tomography has been well established for over two decades and credited for the significant advances made in the early detection and treatment of cancers as well as pathological fetal development, applications to industrial process systems are relatively recent as evidenced by papers in the proceedings of the triennial World Congress on Industrial Process Tomography [108].

2.8. *Electrical Process Tomography*

Electrical process tomography (EPT) consists of electrical resistance tomography (ERT) (sometimes known as electrical impedance tomography (EIT)) and electrical capacitance tomography (ECT). The underlying principle of these two types of EPT equipment is quite similar. ERT employs the different electrical conductivity of materials of interest while ECT uses electrical permittivity changes within the system of two fluids (in the case of 2-phase flow) [109]. Unlike other types of tomography equipment, EPT is relatively affordable, and gives fast response (up to 200 frames per second) for on-line process monitoring in process industries [110].

2.9. *Electrical Resistance and Capacitance Tomography*

2.9.1. *Apparatus*

An ERT or ECT system comprises three main parts (cf. Figure 2.8) as:

1. Sensors
2. Data acquisition system (DAS)
3. Image reconstruction

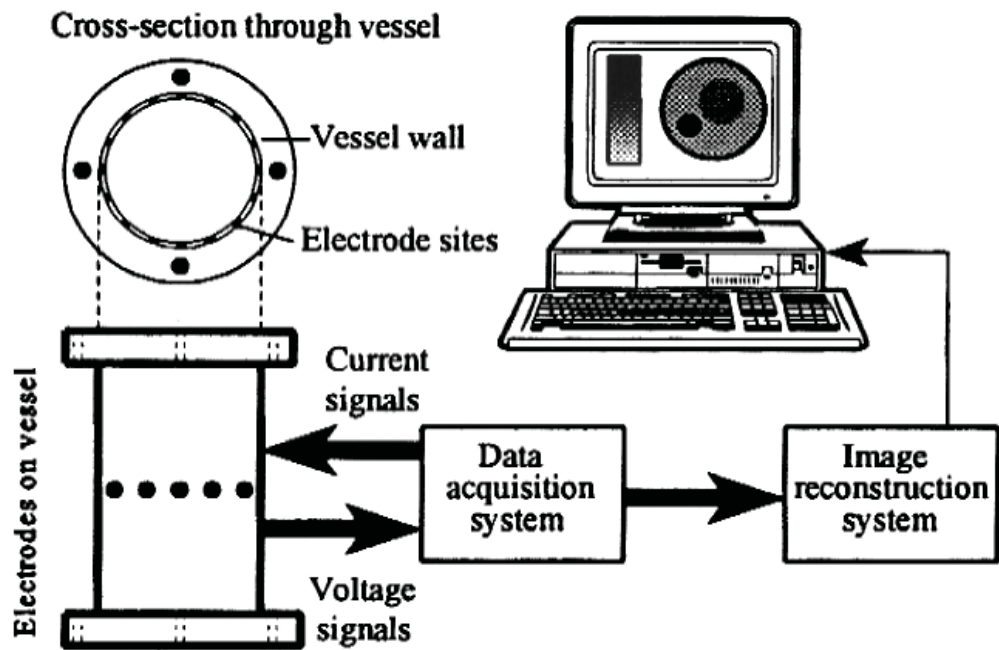


Figure 2.8 Schematic diagram of ERT/ECT system [111]

2.9.2. ERT/ECT Sensors

Electrode material can vary depending on the process of interest. However, the fluids being analysed must be less conductive than the electrodes [112]. Typically, the electrodes are made of stainless steel, brass or silver palladium alloy and may be coated with ceramics or other materials depending on the operating conditions. A special coating may be needed for high pressure and high temperature conditions for electrodes as in the present study. Dimensions of the electrodes should be chosen based on the vessel diameter, range of conductivity to be measured, velocity of the materials and imaging speed requirement [110]. However, a requirement of minimum surface area needs to be fulfilled to ensure an even current density is generated within the plane of interest [113, 114]. Typically, ERT electrodes are small, in contact with the fluid media in the vessel or pipeline; they are regarded as invasive but non-intrusive. Finally, the length of signal-carry cable between the electrode and current injection/voltage measurement circuitry has to be considered when building the sensors into the vessel. This criteria is to

avoid undesirable stray capacitance and current leakage, which consequently results in distorted signals. Figure 2.9 shows the typical ERT sensor design including measuring protocol.

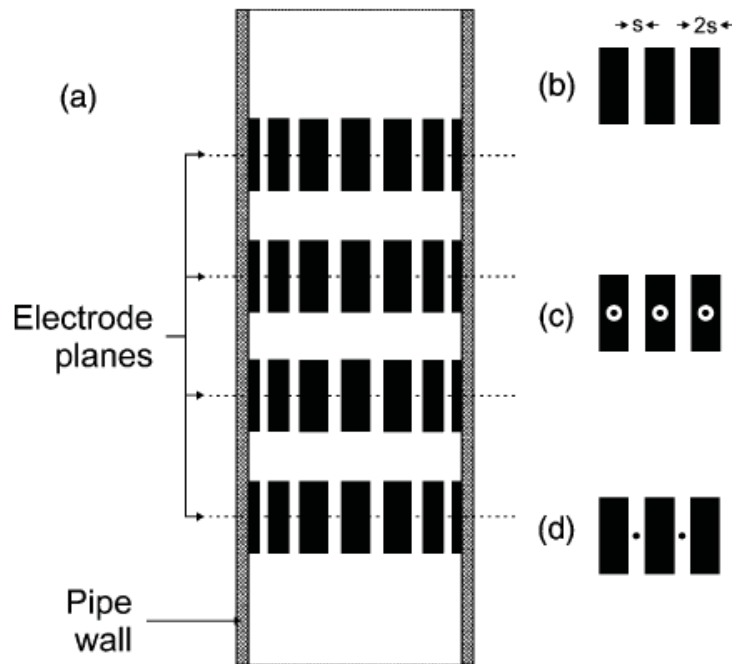


Figure 2.9 Schematic diagram of ERT sensor design showing a) diagram of a 4-plane b) the optimum 2:1 ratio between the width of electrode and gap size for adjacent measurement protocol c) nested measurement configuration using rectangular source and circular detect electrodes d) interleaved electrode configuration, using rectangular source and circular detect electrodes [115]

Ideally, the electrodes are arranged at equal intervals around the periphery of the vessel to map any changes in resistivity across the vessel, as shown in Figure 2.10. This criteria is paramount because the algorithm used in image reconstruction assumes the positioning of electrodes based on a defined interval, otherwise the data are not normalised prior to image reconstruction [113].

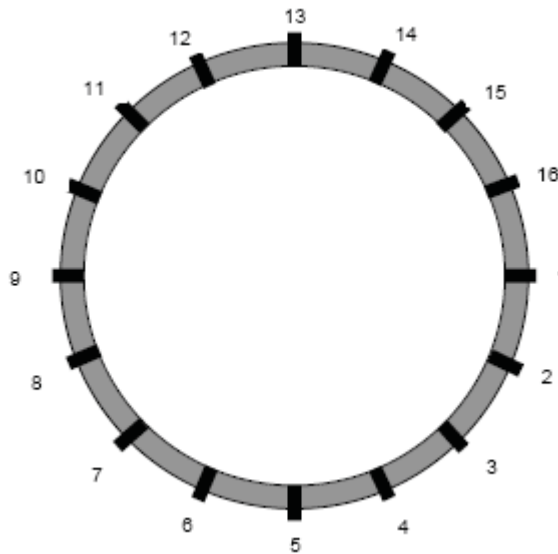


Figure 2.10 Schematic diagram of electrode arrangement [116]

Alternatively, the electrodes could be arranged around a square cross-section and vertical series of electrodes. The electrodes are connected to the DAS by co-axial cable, which assists in reducing the effect of extraneous environmental noise and interference. The outer sheath of the co-axial cable is coupled to the feedback path of a voltage buffer to provide further noise immunity and the inner core is capacitively coupled to the input of the voltage buffer. A spare electrode, referred to as the ground electrode, positioned away from the measurement electrodes but in contact with the internal fluid is required to ensure all voltage measurements are fixed against a common ground source.

In ECT, 12 electrode plates are mounted on the periphery of the process vessel as illustrated in Figure 2.11. Typical electrode length is 100 mm.

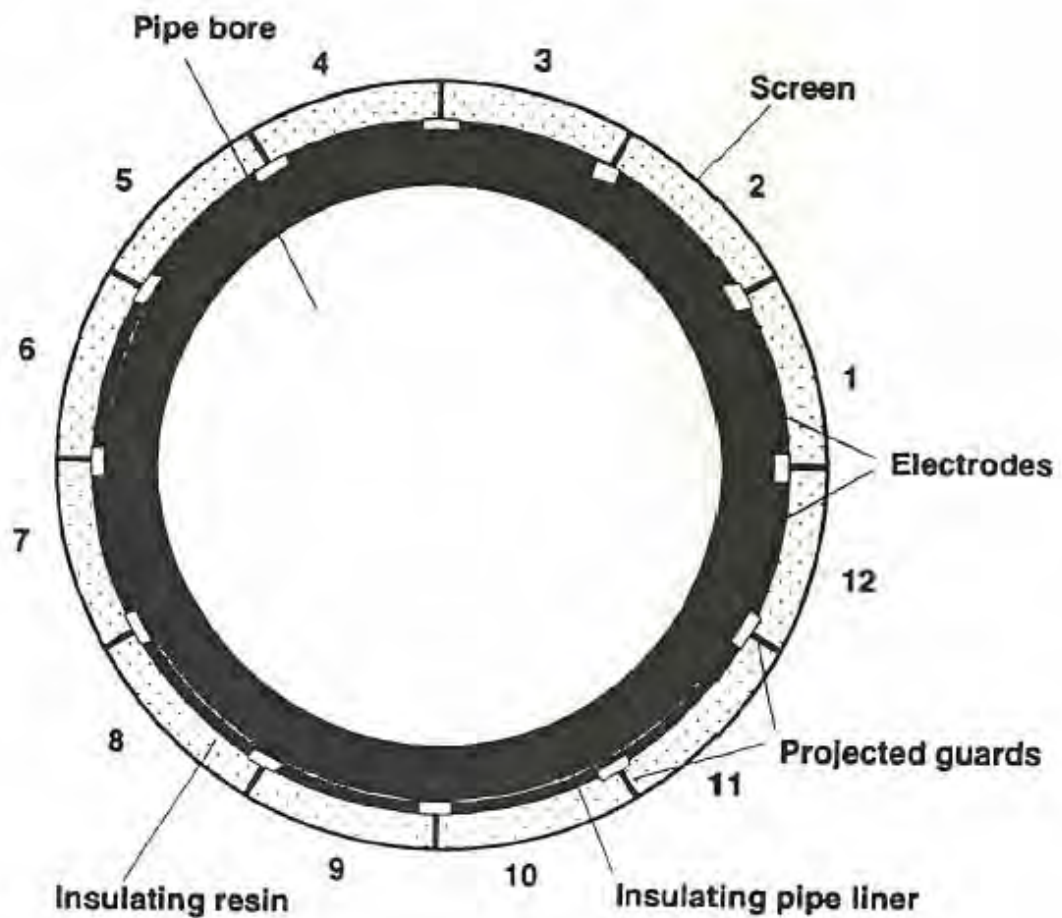


Figure 2.11 Cross-sectional structure of the imaging ECT sensor [112]

Projected guards are placed between neighbouring electrodes to eliminate the capacitance between the back surfaces of adjacent electrodes. This reduces the standing capacitance which is insensitive to the dielectric distribution inside the pipe/vessel.

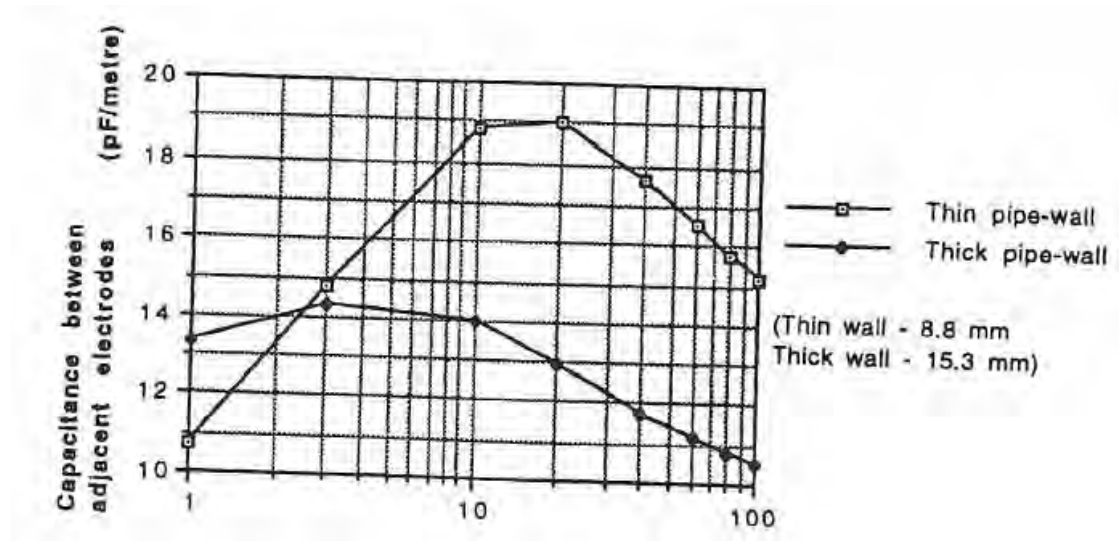


Figure 2.12 The capacitance between adjacent electrodes vs. the relative permittivity inside the pipe/vessel bore for different pipe-wall thicknesses [112].

There are several parameters to be carefully selected to ensure the sensor performs at its best. Among them is the wall thickness of the insulating pipe/vessel. If it is too thick, the capacitance between the adjacent electrodes would not respond accordingly to the permittivity increase inside the pipe/vessel. Figure 2.12 illustrates the effect of wall thickness on capacitance within the pipe/vessel. However, if the wall is too thin, there is significant reduction in mechanical strength, and the measurements experience uneven sensitivity distribution inside the pipe/vessel, causing a relative decrease in system sensitivity towards the centre of pipe/vessel.

2.9.3. Data Acquisition system (DAS)

The Data Acquisition System (DAS) is responsible for obtaining the quantitative data relating the state of the conductivity distribution within the vessel or pipeline. The data must be collected quickly and accurately in order to track small changes of conductivity in real-time thus allowing the image reconstruction algorithm to provide an accurate measurement of the true conductivity distribution. The DAS consists of a portable unit containing four Eurocard-sized printed circuit boards (PCBs) attached to a 64-way digital backplane (the analogue signals are carried on the front

panels via co-axial cables) which perform the following functions: measurement, de-modulation and control; sinewave generation and synchronization; multiplexer control; and power supply as shown in Figure 2.13.

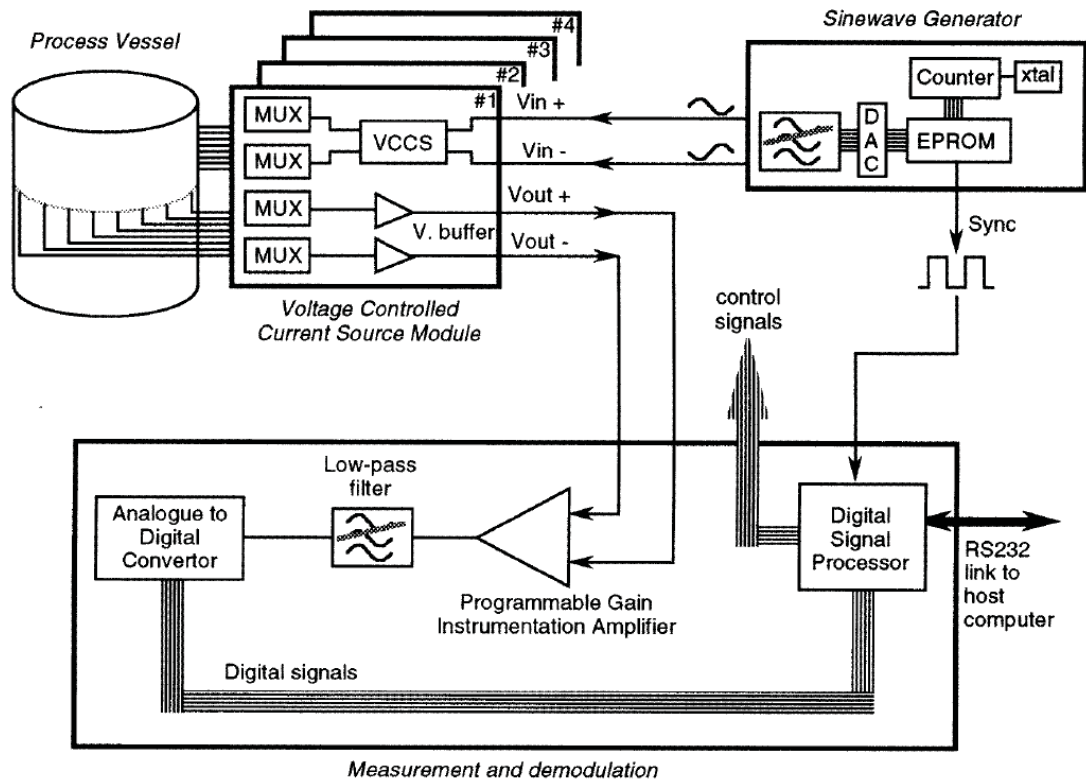


Figure 2.13 The typical ERT data acquisition system (DAS) [110]

At least three out of four eurocards are connected to remotely voltage-controlled current located close to the electrode in the process vessel. The DAS communicates with the host computer via a fast bi-directional RS 323 in this case, which receives and transfers logged data to image reconstruction. The function of each component in the DAS will not be discussed here in detail as Dickin and Wang [110] gave an excellent review on this subject.

The data collection strategy is critical in DAS for obtaining reliable and accurate data, thus the mechanism of probing the conductivity distribution within the vessel via boundary electrodes is crucial to obtain

the maximum amount of information. There are four main strategies, which will be discussed in this section as follows:

1. Adjacent
2. Opposite
3. Diagonal
4. Conducting boundary

2.9.3.1. Adjacent strategy

This strategy is commonly applied and recommended for sensors with insulating boundaries with 16 electrodes arranged at equal intervals around the periphery of the sensor [117]. The adjacent strategy applies a current through two neighbouring electrodes and voltage is measured from remaining pairs of neighbouring electrodes. This process is repeated until all independent measurements have been made.

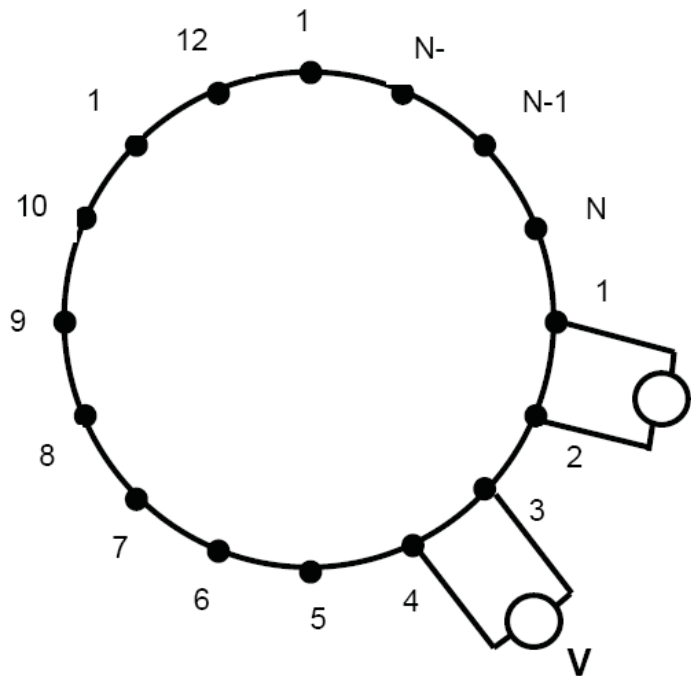


Figure 2.14 Adjacent strategy [117]

It is quite simple to demonstrate that the number of independent differential voltage measurements for an N electrode system, is $L=N(N-$

3)/2. In the case of 16 electrodes as in this study, we have $L=104$ measurements.

2.9.3.2. Opposite strategy

This strategy applies current through diametrically opposed electrodes as seen in Figure 2.15 in which the voltage reference is the electrode adjacent to the current-injecting electrode. The voltages are measured with the relation to the reference voltage for all electrodes except for the current-injecting ones.

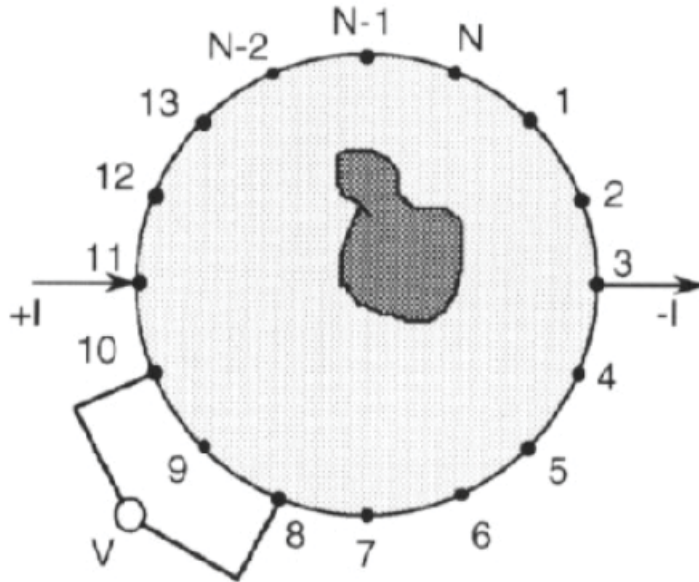


Figure 2.15 Opposite strategy [110]

The subsequent data set is obtained by switching the current to the adjacent pair of opposite electrodes (in clockwise direction) and voltage reference electrode is changed accordingly. The voltages are measure repeatedly in a similar fashion until all independent measurements have been made.

The main advantage of this strategy is that it has less sensitive conductivity changes as the current flows through the central part of the region. However, the number of independent current projections is significantly less than of adjacent method. Breckon and Pidcock showed that the number of independent measurements, $M=N/4(3N/2-1)$. For

similar electrodes, $N=16$, this method only produces, $M=92$ as compared to $M=104$ for the adjacent method. This strategy will reduce the image resolution by 23% relative to the adjacent method[113].

2.9.3.3. Diagonal strategy

This strategy is also known as the cross method [114] as currents are injected between electrodes separated by large dimension as displayed in Figure 2.16.

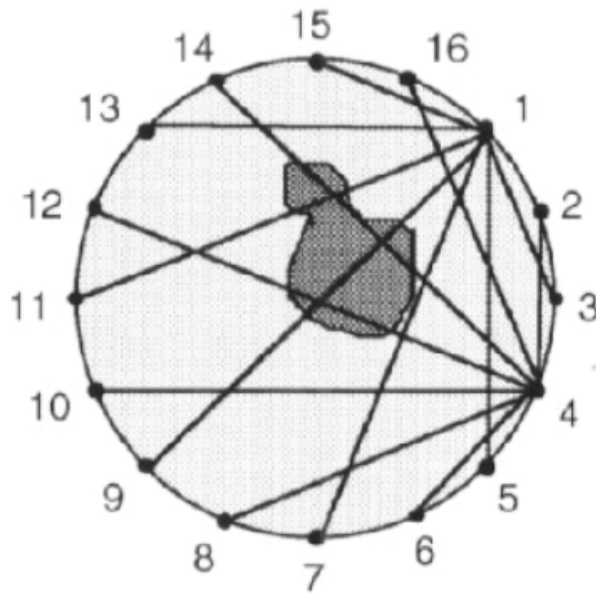


Figure 2.16 Diagonal strategy [110]

This strategy offers better uniform current distribution as compared to the adjacent method. It allows twice the measurements as each measurement contains 1 fixed electrode as current reference and the adjacent electrode (example of electrode 2 in diagram) is voltage electrode. The voltages from all electrodes are measured with respect to electrode 2. In the subsequent measurement, the current reference has changed from electrode 2 to 4 and voltage electrode from 2 to 3. This process is repeated until all independent measurements have been made. For the case of 16 electrodes, a total of 182 data points are produced.

2.9.3.4. Conducting boundary strategy

This measurement strategy enables ERT to be applied to pipelines and vessels with conducting boundaries, for example, stainless steel pipes. Unlike other strategies discussed previously, this measurement strategy only employs two electrodes as seen in Figure 2.17. The large surface area of the conducting boundary acts as a current sink, reducing common-mode voltage across the measurement electrode. Thus, there is a significant reduction of voltage as compared with the adjacent strategy.

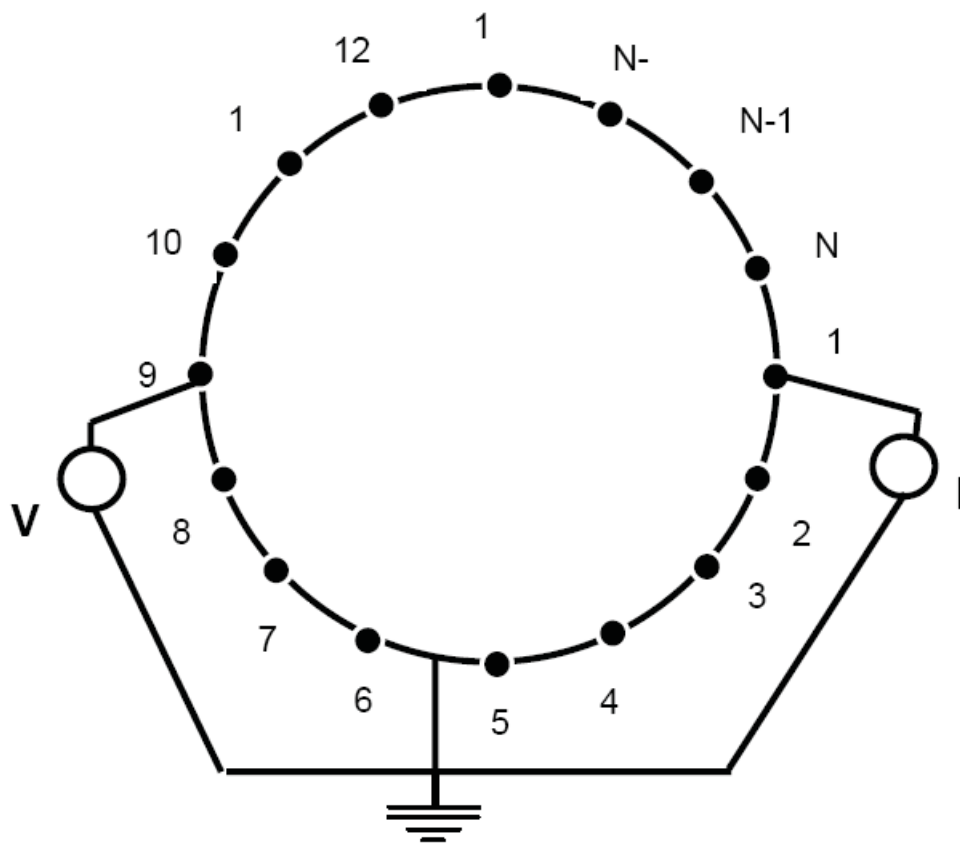


Figure 2.17 Conducting boundary strategy [117]

Meanwhile, an earthed conductivity boundary strategy reduces the effects of electromagnetic interference. Nonetheless, the major

drawback of this strategy is the amplitude of measurement voltage is significantly low compared to the adjacent strategy.

In selecting which is the best strategy to be employed, one needs to consider the size and shape of the vessels, location and conductivity of fluids used. It is necessary to choose the measurement strategy that has high sensitivity to conductivity changes in the region of interest. Thus, in our study, the adjacent measurement strategy was used. The error associated with this measurement strategy is between 1-5% [112].

2.9.4. Image Reconstruction

The most common image reconstruction algorithm in electrical process tomography is linear back projection (LBP). LBP offers fast and reasonably accurate image reconstruction [118]. LBP is considered a qualitative and non-iterative image reconstruction algorithm. It is based on the potential difference, calculated by the forward solver, between two-equipotentials on the boundary that is back-projected to a resistivity value in the area enclosed by two lines for all possible measurement combinations [119].

The image reconstruction process involves determining the electrical conductivity for each pixel within the image. However, insufficient electrical measurement information at the boundary of the process vessel does not allow the inverse problem to be solved directly. First, it is necessary solve the forward problem, either by direct measurement or computation. Poisson's equation is used to calculate the voltage, $V(x,y)$ given by:

$$\nabla \cdot (\sigma(x,y)) \nabla V(x,y) = 0 \quad (2.47)$$

where, σ is conductivity of material. Finite element method (FEM) is used to solve Poisson's equation by reducing it to a series of simultaneous equations describing the behavior of 316-pixels. In the event that adjacent measurement is used, 14 electrodes are employed for current

injection. Therefore for the i th current injection, FEM converts the solution to the following set of linear equations:

$$Av_{(i)} = b_{(i)} \quad (2.48)$$

where,

$$i=1 \dots 14$$

A = matrix of $N \times N$

b = $N \times 1$ vector

and b is the boundary conditions. The inverse problem is to determine the conductivity distribution from boundary voltage measurements. LBP algorithm back projects the voltage measurements to conductivity values within the pixels for all possible measurements using a sensitivity map calculated by the FEM. Thus, the image is reconstructed via matrix/vector multiplication and displayed on the computer as seen in Figure 2.18.

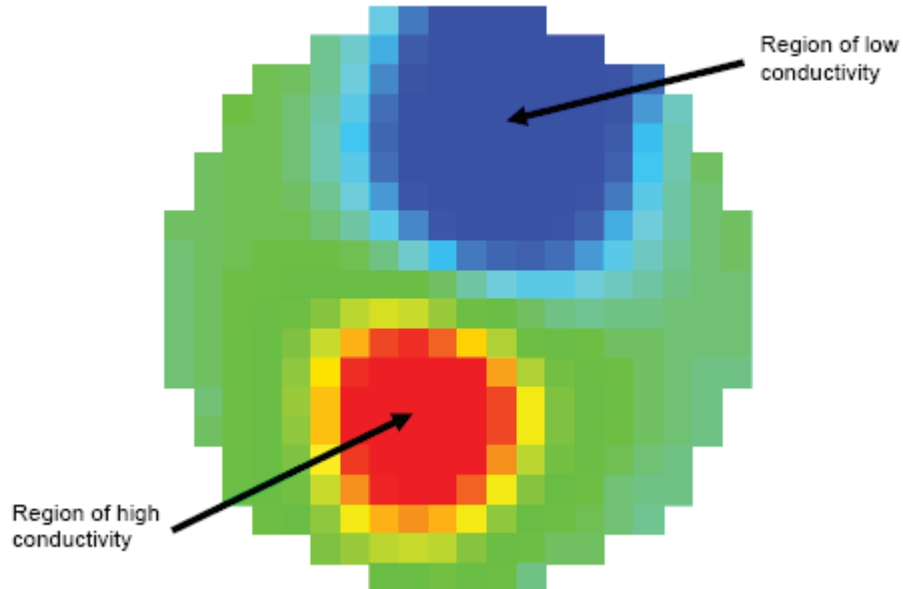


Figure 2.18 Sample of tomogram showing high and low conductivity regions [117]

2.10. Application of Process Tomography

Process tomography can be applied in multi-phase flow systems for obtaining both qualitative and quantitative data. Unlike conventional methods, process tomography offers a non-intrusive way to gain cross-sectional profiles of materials or velocities in the process vessel of interest as a function of time and space [120].

Jafari and Mohammadzadeh [121] reported that mixing in the GIST is closest to that of an ideal CSTR although it may be plagued by large dead zones (up to 16.7%) at low liquid flow rates and significant bypassing (as high as 10%) at high liquid flow rates. Mixing time and homogenization energy analysis were based on an invasive RTD method. Ford *et al.* [122], have, nonetheless, employed X-ray computed tomography to obtain qualitative understanding of the recirculation regions. They only provided global gas phase hold-up correlation which limited application to the narrow range of impeller speed (350-700 rpm) used.

Conway *et al.* [123] and Hichri *et al.* [48] investigated gas-liquid mass transfer in gas-induced stirred tank slurry reactors. Hampel *et al.* [124] employed gamma-ray tomography to investigate the two-phase flow in a stirred tank reactor using gas-inducing 6-blade turbines. Due to additional complexities associated with three-phase flow, there is a paucity of information on the hydrodynamics and mixing in gas-liquid-solid GISTs. In view of the stated advantages of the GIST over conventional spargers and recycle systems, especially in relation to commercial gas-liquid-solid operations where low gas conversion per pass or hazardous gases are anticipated, it is essential to provide reliable correlations usable for design and scale-up based on non-intrusive system characterisation such as that offered by process tomography.

Rodgers *et al.*, [125] employed electrical impedance tomography (EIT) to monitor the performance of an industrial-scale stirred-tank reactor (200-litre capacity) for the precipitation of barium sulphate. They found that

the mixing curve is linked to the structure and evolution of plume during a semi-batch reaction. Data arising from this investigation revealed the limitation of finite element methods in the analysis of the precipitator performance. This suggests that prior or concurrent tomographic studies are essential in developing realistic numerical models for the complex hydrodynamics in a multiphase stirred reactive system. Bolton *et al.*, [126] have also investigated the flow pattern evolution and distribution inside a novel radial flow packed bed reactor using electrical resistance tomography (ERT). Data acquired from the 8-plane $\times$ 16-electrode sensor ERT configuration permitted conductivity measurements in the 3D-space from which local flow velocity, flow pattern uniformity and radial distributive properties were obtained. More recently, Razzak *et al.* [105] determined the phase hold-up distribution in a gas-liquid-solid circulating fluidised bed using ERT. They observed that the radial distribution for solid hold-up has a minimum in the central region and increased towards the wall while an opposite trend was observed for the gas hold-up. Since electrical tomographic applications are characterised by fast response dynamics, rapid flow evolution may be reliably tracked. This has been used to advantage in fluidisation, bubble column and stirred tank hydrodynamics and modelling studies [120, 127, 128].

The quality of fluidisation in both lab-scale and industrial size gas-solid fluidised bed dryers has also been studied as a function of solid loading, particle size and density using gamma-ray tomography, GRT [129]. Similarly, Guida *et al.* [130] have examined the mixing of concentrated suspensions of coarse glass particles in a stirred tank with the aid of positron emission particle tracking. Velocity field and spatial distribution of both liquid and solid phases were obtained. While this brief review of representative tomographic investigations of multiphase flow processes demonstrates the merits of non-invasive techniques for clearer understanding of the mechanisms involved in gas-liquid-solid hydrodynamics, it is useful to provide quantitative correlations between multiphase flow metrics (phase hold-up distribution, degree of phase homogenisation or uniformity, mixing time, etc) and antecedent

hydrodynamic operating variables suitable for tunable design objectives or optimal process operation especially in the pharmaceuticals, environmental and clean energy production industries where mechanically-stirred vessels are commonly used. A gas-induced stirrer is an especially attractive mode of agitation for many gas-liquid-solid reactive systems where low gas conversion per pass may be detrimental to process efficiency.

Shaikh and Al-Dahhan [131] used computed tomography in a small diameter bubble column and observed that an increase in pressure delayed the transition in the flow regimes over a large range of superficial gas velocities. Parasu Veera [132] used gamma ray tomography to obtain radial void fraction distribution in a bubble column. Utomo *et al.* [133] used ultrasonic transmission method and iterative filtered back projection-based image reconstruction to investigate and analyse gas and particle distribution in a dispersion bubble column system of air-water-TiO₂ where the TiO₂ particle loading caused an increase in gas hold-up and a helical rising bubble flow was observed. Supardan *et al.* [134] investigated time averaged gas hold-up distribution in a small diameter bubble column using ultrasonic computed tomography and observed that an air-glycerol 10% solution system had more gas hold-up than the air-water system. Hubers *et al.* [135] applied x-ray computed tomography in a large bubble column, where at low cellulose fibre mass fraction in the air-water system, gas hold-up increased at the centre and near the walls of the column and the vice versa effect when cellulose fibre mass fraction was increased. Wu *et al.* [136] applied x-ray computed tomography with an image reconstruction method based on genetic algorithm to conduct fast measurement of multiphase flow dynamics. Schmitz and Mewes [137] used electrical process tomography (high time resolution) to measure void fraction distribution in a bubble column at high pressure and temperature using a worst case scenario, where during process breakdown, there is a sudden decrease of pressure and the liquid level in the column swells and a blowdown of liquid and gas from the column occurs.

Gunjal *et al.*, [138] developed a successful model of a trickle-bed reactor using CFD. They were able to predict the fraction of liquid hold-up suspended in the bed coupled with periodic operation. The results obtained from CFD all agreed well with the experimental data. The model was used to understand the hydrodynamics of trickle bed reactors. For chemical engineering applications such as bubble column and fluidized bed reactors, flow regimes, mixing and separators and pneumatic transport, electrical process tomography is used not only to study process dynamics but also to act as an on-line monitoring and controlling sensor for chemical reactions and variations in operating conditions. Electrical process tomography involves producing cross-sectional (slice) images based upon variations in factors such as permittivity and conductivity. Off-line and on-line monitoring are the two types of monitoring in electrical process tomography and are the reason for the difference in the implementation of tomography in experimental analysis and industrial production processes. In experimental analysis, observations of transport dynamics are made via off-line monitoring and measurement, so data-processing time is slow and high spatial resolution is needed for high quality data. In industrial production processes, on-line monitoring measures distribution of material properties and so data-processing time has to be fast in order to control the dynamics. High temporal resolution is needed to not only monitor the process but also obtain information and control by intervening during operational stages. Therefore tomography plays an important role in controlling the process in the case of hazardous situations resulting from failure or malfunction [115, 139].

Due to the sensitivity of the ECT sensor to organic compounds and solids, the majority of ECT research and application is in pneumatic conveying of solids [140] and fluidised beds [141, 142] where permittivity of the continuous phase is very high compared to the dispersed phase. Bennett *et al.* [143] conducted ECT measurements on air - double distilled water flow in a bubble column where the organic or water has high permittivity and the gas (air) has low permittivity. Flow regimes can

be characterised by visualising contours of gas volume fraction throughout axial sections constructed from stacked and interpolated tomograms. Due to high sensitivity and low noise, ECT sensors can be used to measure inter-related hydrodynamic aspects such as bubble size and bubble size distribution, bubble swarming and radial gas concentration profile. Bennett *et al.* [143] used ECT to image low water fraction foams to distinguish between different phases (aerated water, dense foam and air) and highlighted the potential to apply the technique to complex three-phase flow reactions (Fischer-Tropsch synthesis in a bubble column). Warsito and Fan [127] developed a 3-D image reconstruction technique for ECT imaging based on a neural network multi-criterion optimisation to image real time flow structures of bubble plume spiral motion and investigate large scale liquid vortex dynamics and gas volume distribution. The spiral bubble plume motion from a single gas nozzle and spiral liquid vortices dominated the transient flow structures. The bubble plume oscillated back and forth away from the central axis of the column as it rose from the gas nozzle and as it rose higher, it moved towards the centre due to either the increasing gas velocity or the presence of solid suspension.

2.11. Concluding remarks

The information provided in this chapter was used as a basis to effectively design the experimental assembly and provide better interpretation to data analysis in subsequent chapters (Chapters 5-7). More so, some information that seem contradict were evaluated and examined in this study.

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3 ■ Experimental and Modelling Details

3.1. General Consideration

This chapter provides details of equipment and materials employed during hydrodynamics and mass transfer studies with the aid of non-intrusive tools i.e. ECT and ERT including the application of CFD as a complementary tool to investigate the hydrodynamics of gas-inducing stirred tank reactor (GIST). Moreover, the equipment and material related to the catalyst preparation and characterisation as well as reaction studies in FT synthesis also briefly discussed.

3.2. Electrical Process Tomography Study in a Stirred Tank Reactor

The employment of various tomography techniques for medical applications has been prevalent and in fact well established for over two decades, especially in the fields of fetal development and early detection of cancers. Success of this technique in medicine has highlighted its potential for application in other disciplines, and in particular encouraged research into electrical process tomography for industrial applications. The behaviour of multiphase and multi-component flow processes is reflected in the velocity profiles and phase hold-up distribution inside the vessel. Consequently, it is important to have reliable and accurate correlations between operating variables (such as fluid flow rate, stirring speed and solid loading) and these multiphase system properties in order to optimise the design and performance for tailored applications.

3.2.1. *Electrical Process Tomography apparatus*

3.2.2. ERT/ECT sensors

The sensors are structured in such a way that the electrodes are in contact with the column contents to detect change in electrical conductivity/permittivity in the course of the operation. The circular sensors, which are mounted inside the vessel along the wall, are composed of stainless steel with 16 electrodes ($1 \times 1 \text{ cm}^2$) for ERT and 12 electrodes ($8 \times 2 \text{ cm}^2$) for ECT as shown in Figure 3.1.

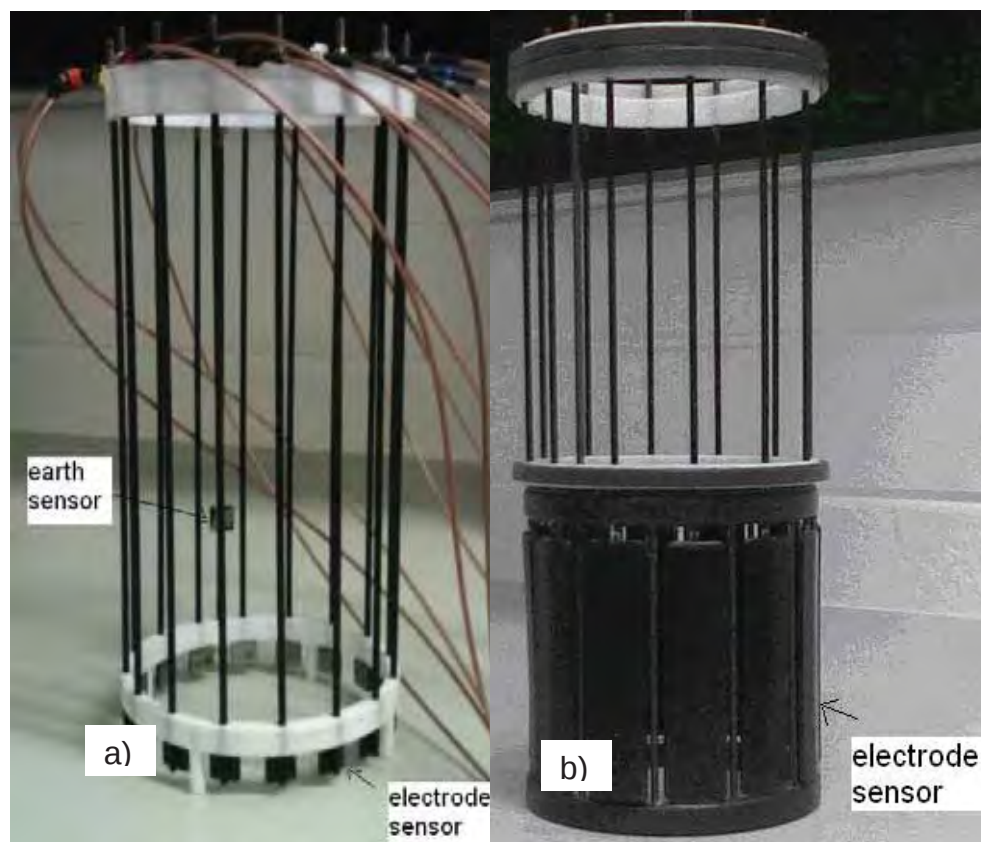


Figure 3.1 Electrode sensors for a) ERT and b) ECT

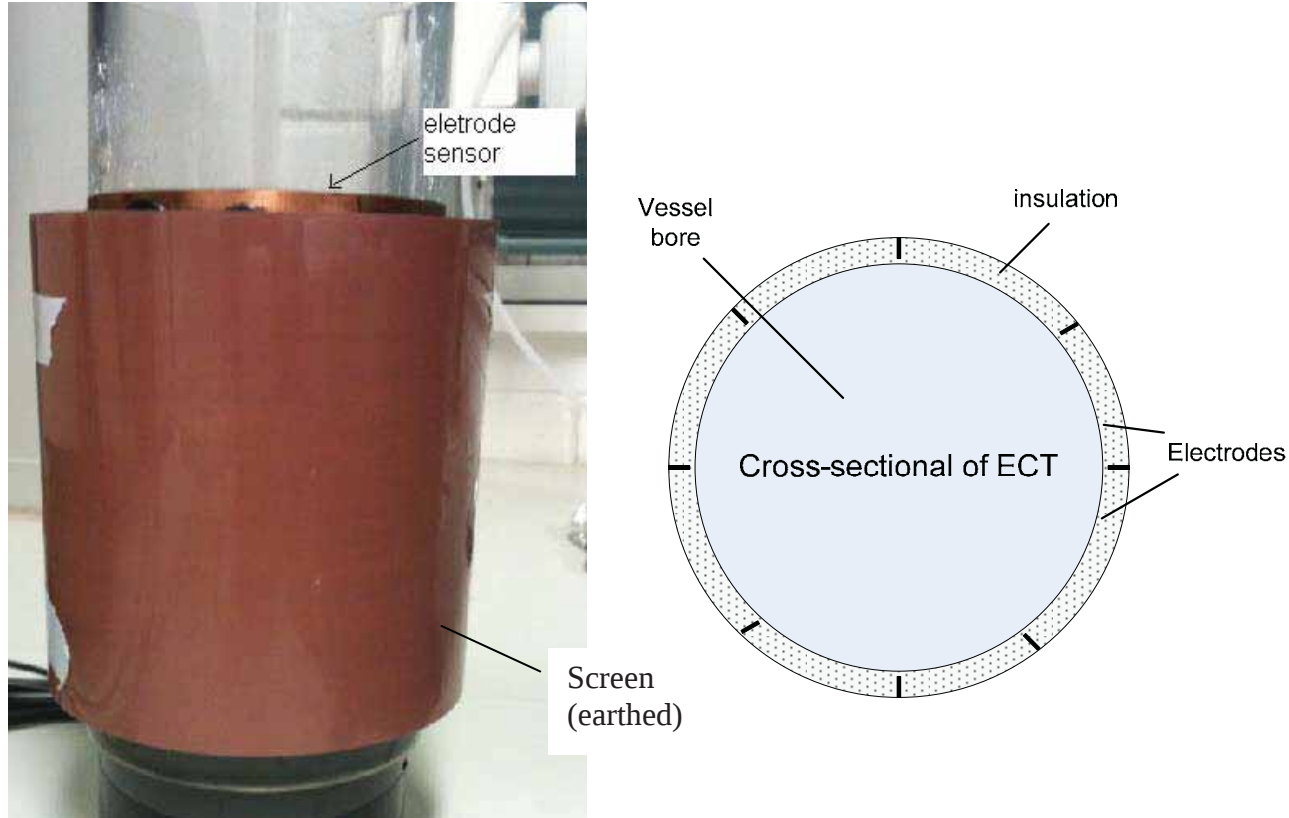


Figure 3.2 Example of 12-electrode belt fitted to the vessel exterior.

Another type of ECT sensor, used in this study is 12-electrode belt which was fitted tightly to the vessel exterior as depicted in Figure 3.2. The overall screen (earthed) is used to protect the sensor from any possible interferences from external electromagnetic fields [1].

3.2.3. Data acquisition system (DAS)

DAS is responsible to obtain the quantitative data within the vessel in the form of conductivity or/and permittivity. In this study dual tomography M3000 module from Industrial Tomography System Ltd., Manchester, UK is used as shown in Figure 3.3. This system mainly consists of electrode module attached to each electrode on the process vessel (voltage-to-current converter or voltage controlled current source – VCCS), differential input amplifier, voltage generator, and micro-controller, which connected to image reconstruction computer. The summary of DAS flow chart function for each component is depicted in Figure 3.4.

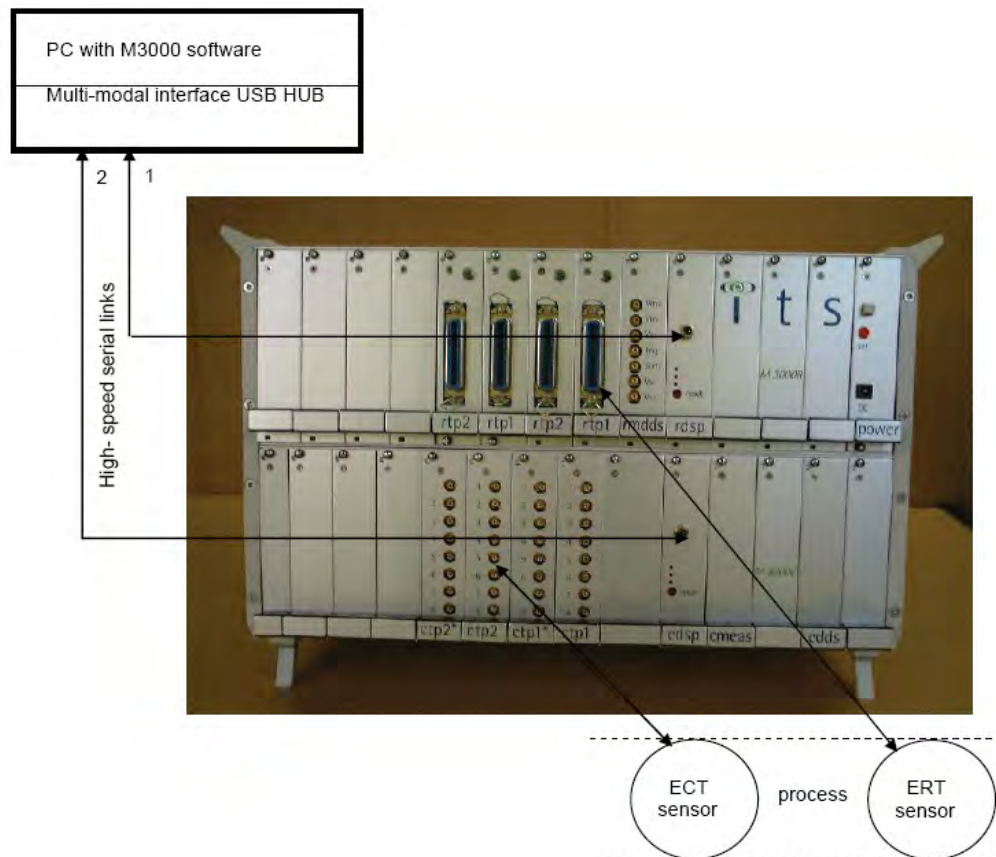


Figure 3.3 M3000 multi-modal data acquisition system [2].

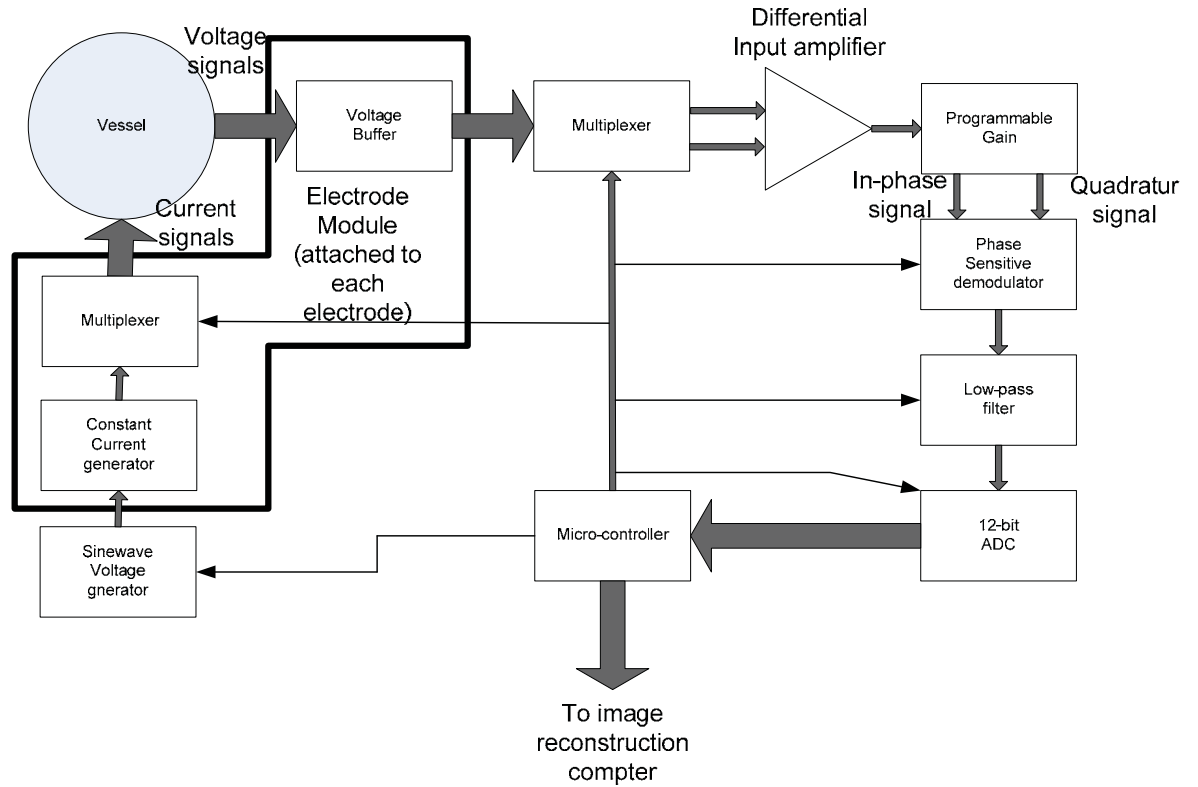


Figure 3.4 Components of data acquisition system (ADS)

This dual-modality unit M3000 capable of operating both ERT and/or ECT. The system is equipped with variable voltage outputs in order to reduce signal-to-noise ratio (STNR) to accommodate the possible variation of process vessel sizes. Nonetheless, we only used a fixed tank size for all the experimental runs i.e. 100 mm ID. Normal adjacent protocol is employed for probing the conductivity or permittivity within the vessel. The electrodes are arranged around the vessel boundary as shown in Figure 3.5.

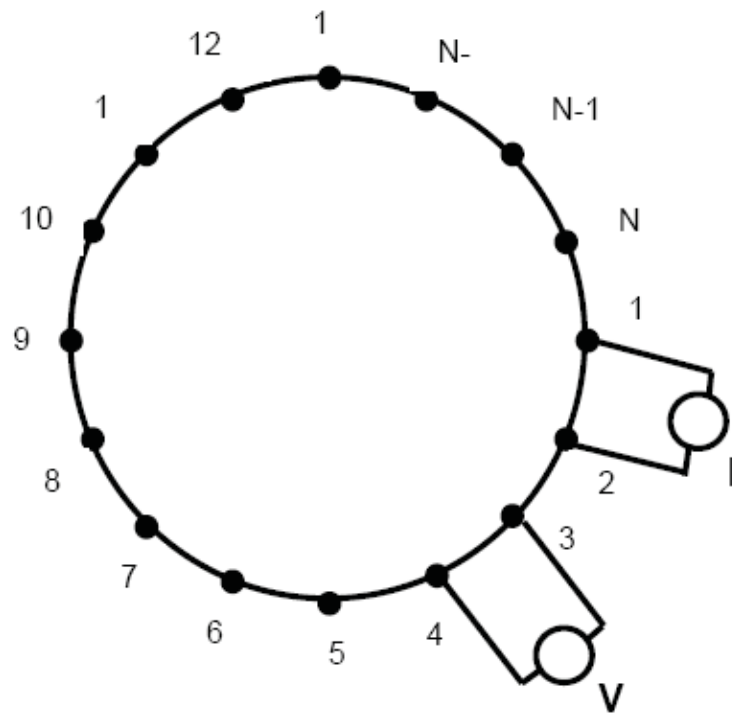
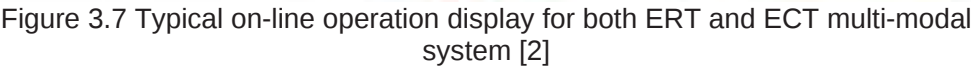
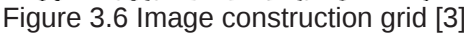


Figure 3.5 Normal adjacent protocol [3]

3.2.4. Image reconstruction

The M3000 system supplies independent time-stamped data using a qualitative, non-iterative algorithm based on a linear back-projection (LBP) algorithm and thus provides fast image reconstruction for real time imaging of moving processes of the dispersed phase in the measurement plane. A square grid ($20 \times 20 = 400$ pixels) represents the vessel interior cross-section. Nonetheless, a few pixels lie outside the vessel circumference and the circular image is, therefore, reconstructed using 316 pixels inside the vessel from the 400 pixel square grid as shown in Figure 3.6. The colour variation of tomograms will be displayed from blue to red in which represent low and high conductivity/permittivity respectively as seen in Figure 3.7.



3.3. Non-reactive Experimentation

3.3.1. Gas-inducing stirred tank reactor geometry

A flat-bottomed stirred tank made of clear plexiglass (ID = 100 mm and height = 277 mm) equipped with an axial gas-entrainment impeller (gas-inducing impeller) as shown in Figure 3.8, was used for all runs. The agitator shaft was a stainless steel hollow rod into which a 5 mm gas inlet hole (at 230 mm) was drilled for gas headspace suction into the liquid phase via 3 gas dispersion (exit) ports (3.175 mm ID) located at the tip of each of the 4 blades of the impeller. The latter (diameter = 50 mm) was made from brass or polypropylene (ECT experiment) and positioned at 90 mm above the tank bottom with blade width of 19 mm.

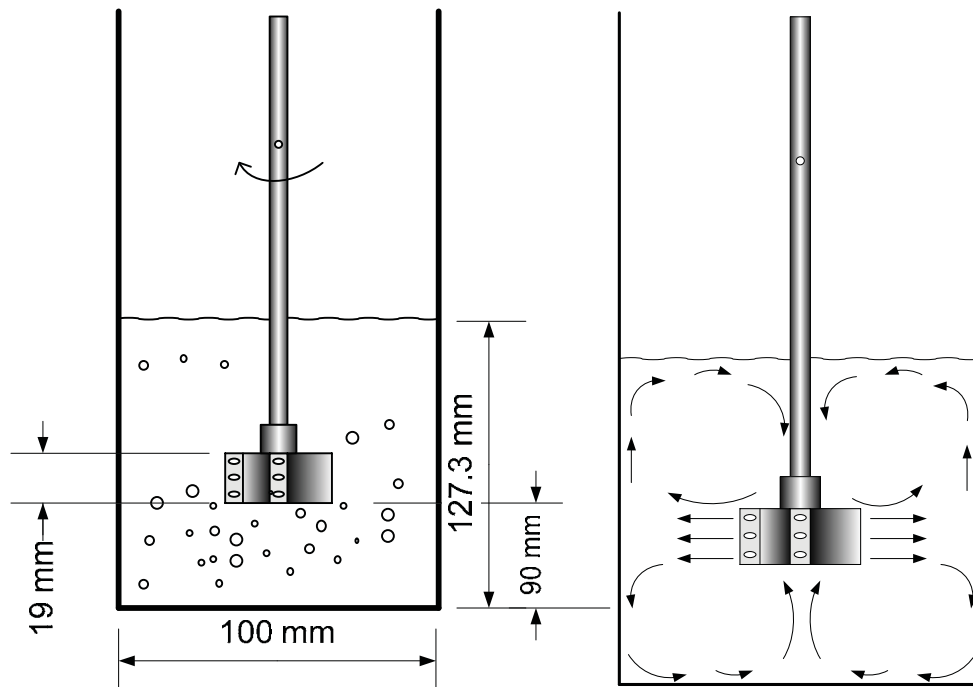


Figure 3.8 Schematic diagram of gas-inducing impeller

3.3.2. Gas-liquid system

Electrical resistance tomography (ERT) is well-suited for systems where the continuous phase is electrically conductive while the dispersed phase is either non-conducting or insulating. The continuous phase in this study was tap water and air as the dispersed phase. The advantages of

a Gas-inducing Stirred Tank Reactor (GIST) only come into effect after a critical rotation speed, N_{sc} , has been attained for gas flow and dispersion to commence. As will be discussed in a subsequent section, the hydrodynamic and mixing characteristics of the conventional non-gas entrainment stirrer is a special case of the gas-inducing mechanical agitator. The present tank system was also fitted with circumferential wall baffles in the form of 8 PVC rods. These rods are to reduce the formation of vortex within the vessel tank, thus promoting better mixing.

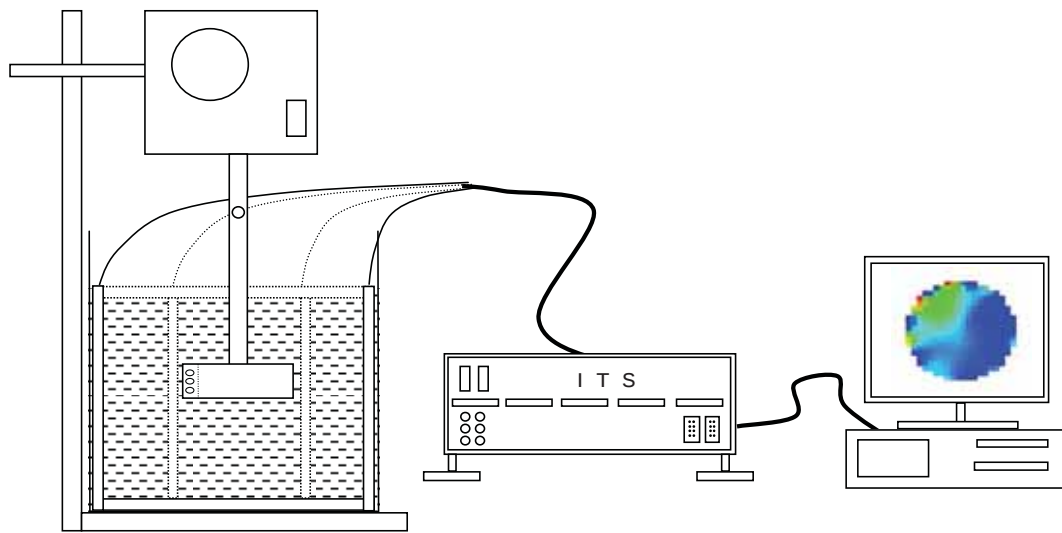


Figure 3.9 Experimental setup

Experimental runs were conducted for gas-liquid using impeller speeds ranging from 200 to 1200 RPM. The dimensionless impeller Reynolds number, Re_I , is defined as

$$Re_I = \frac{\rho N_s D_I^2}{\mu} \quad (3.1)$$

where,

μ = viscosity of liquid ($\text{kg s}^{-1} \text{m}^{-1}$)

ρ = density of liquid (kg m^{-3})

N_s = angular stirring speed (s^{-1})

D_I = impeller diameter (m)

such that the minimum impeller Reynolds number, Re_i , was 10^4 . As a result, hydrodynamic conditions inside the stirred tank may be regarded as being in the turbulent regime. 1 litre of water was used in the tank for all runs. Transient tomograms over a 10-second interval were obtained at 10 frames per second to ensure excellent spatiotemporal resolution for each run.

The dispersed phase hold-up, ε_d , was obtained from electrical conductivity values using the Maxwell relation [4]:

$$\varepsilon_d = \frac{2\sigma_1 + \sigma_2 - 2\sigma_m - \sigma_m \left(\frac{\sigma_2}{\sigma_1} \right)}{\sigma_m - \left(\frac{\sigma_2}{\sigma_1} \right) + 2(\sigma_1 - \sigma_2)} \quad (3.2)$$

where

σ_1 = conductivity of the continuous phase

σ_2 = conductivity of the dispersed phase

σ_m = local conductivity of the mixture as measured by ERT.

In the case of gas-liquid experiments, σ_2 was deemed negligible (air conductivity)

There are 2 impeller designs in this study viz.

- a) The gas-inducing impeller
- b) The non gas-inducing impeller with the same dimensions.

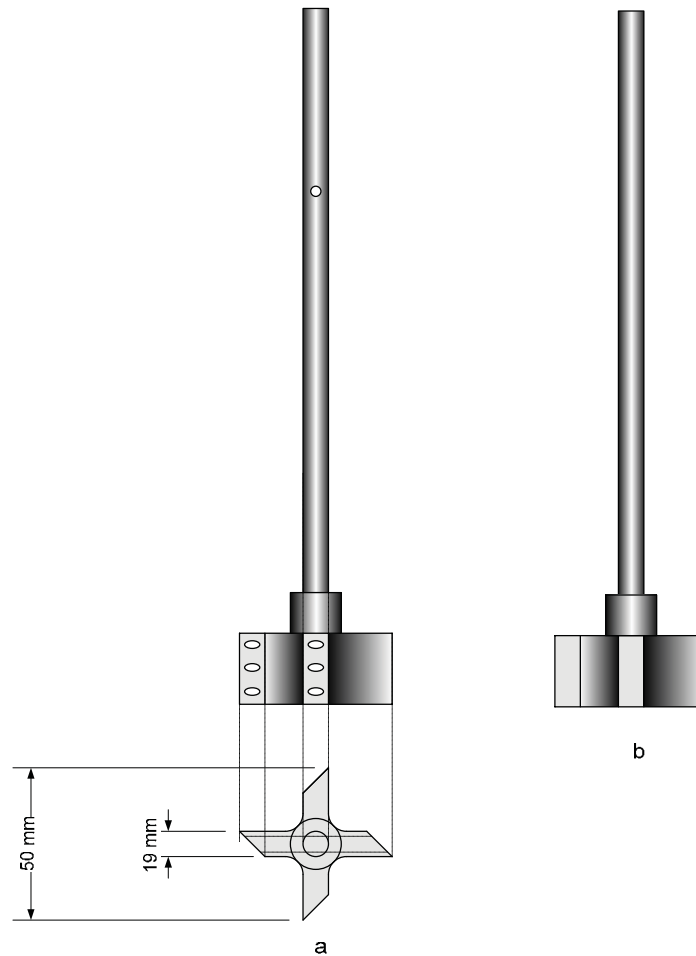


Figure 3.10 Impeller designs a) Gas-inducing impeller b) Non gas-inducing impeller

A sparger distributor (cf. Figure 3.12) is located at the bottom of the vessel to provide uniform gas dispersion into the liquid. The pore size of the sparger is 10 μm .

3.3.3. Bubble size distribution

Experiments were carried out for 3 cases to investigate the efficacy of GIST over conventional stirred tank reactor, namely;

- a) Conventional (non-gas inducing impeller) stirrer with external gas-sparging. The standard impeller design was the exact replica of the gas-inducing impeller.
- b) Gas-induced impeller in the absence of external air-sparging
- c) Combined gas-inducing impeller with external gas-sparging

Bubble size distribution was determined from the average of 4-5 photographs (of the vessel and its contents as illustrated in Figure 3.11 taken using a digital camera (Nikon D3000) with each shot containing 50-60 bubbles – assumed to be spherical. The actual bubble size, d_{Bi} , was then estimated from the similarity relation:

$$\frac{\text{Actual bubble diameter, } d_{Bi}}{\text{Bubble diameter in photograph}} = \frac{\text{Actual impeller width}}{\text{Impeller width in photograph}} \quad (3.3.3)$$



Figure 3.11. Stirred tank reactor equipped with gas inducing impeller (case b)

3.4. Mass Transfer study

3.4.1. Gas-liquid system

In this experiment, gas-liquid mixing was carried out in a 2-litre plexiglass cylindrical column (ID= 100 mm) fitted with a bottom stainless steel sintered plate (10 μm holes) as gas distributor. Gas (O_2 or N_2) was supplied through the liquid phase (1 litre of nanopure water) as shown in Figure 3.12. The gas-inducing impeller, was positioned at 60 mm above the tank bottom with a diameter, D_i , of 50 mm. Each blade of the impeller has three gas exit ports (3 mm orifice). The gas inlet port on the

shaft was located 50 mm above the liquid surface. Furthermore, the runs were conducted in an air-conditioned lab at a controlled temperature of 20 ± 0.5 °C. Prior to data collection, the ERT system was calibrated for the two extreme cases, namely; low calibration with the ERT fully exposed to the pure continuously flowing liquid (water) phase which has relatively low electrical signal resistance, and high calibration when the ERT sensor was fully immersed in a flow of pure gas (O_2) which has a much higher electrical resistance.

Mass transfer measurements were made using a dynamic method [5-7]. Initially, nitrogen gas was passed through to deoxygenate the liquid phase. Purified compressed air ($\geq 99\%$) and agitation were introduced to the system and the dissolved oxygen concentration was recorded using a calibrated TPS Dissolved Oxygen Probe. The stirring speed was varied between 50–1200 RPM for this study. Due to the fast response of the oxygen probe, the instantaneous O_2 concentration in the liquid phase may be written as:

$$C_L^* - C_L(t) = (C_L^* - C_{I0})e^{-k_L at} \quad (3.4)$$

where C_L^* is the equilibrium oxygen concentration, C_L is the oxygen concentration at time t , and C_{I0} is the initial concentration at $t=0$. All the measurements were taken at room temperature of 20 ± 0.5 °C.

Concurrent with the dissolved oxygen monitoring, transient ERT measurements were obtained by ITS Tool Suite software. Tomograms from the reconstructed images were subsequently analysed to gain insight into the vessel hydrodynamics during agitation. Experiments were carried out for three cases, namely;

- a) conventional (non-gas inducing impeller) stirrer with external gas-sparging. The standard impeller design was the exact replica of the gas-inducing impeller.

- b) gas-induced impeller in the absence of external air-sparging and,
- c) combined gas-inducing impeller with external gas-sparging.

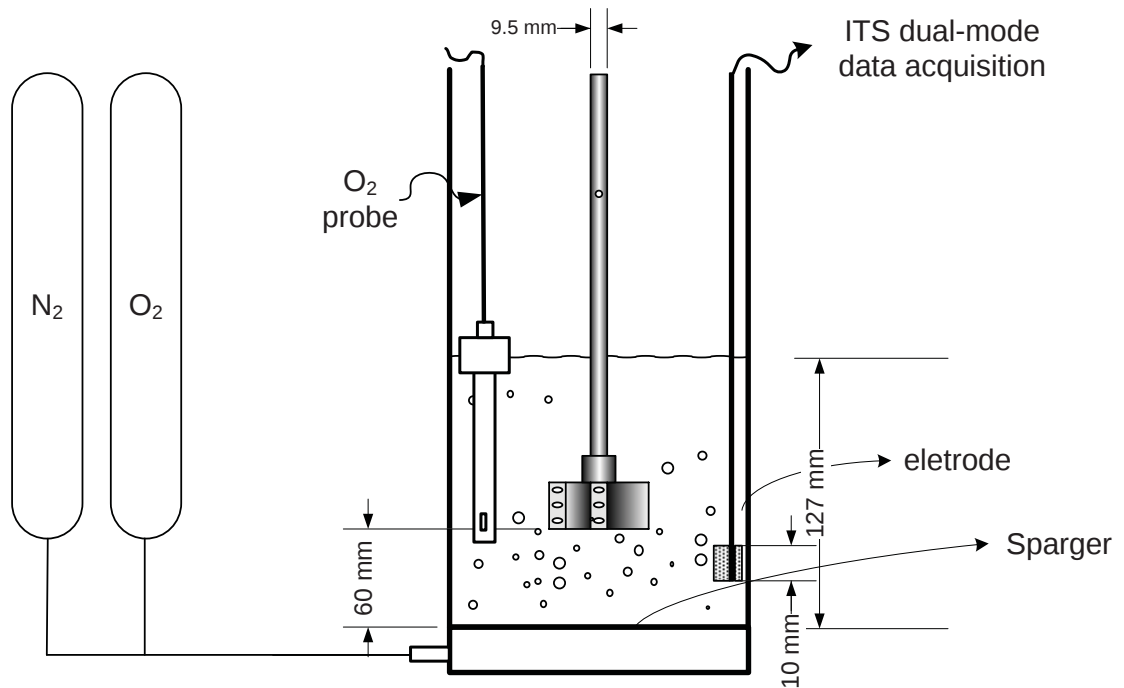


Figure 3.12 Mass transfer experimental setup

The runs which involving external gas-sparging - cases (a) and (c) were performed using air at a flowrate of 1 L min^{-1} .

3.4.2. Gas-liquid-Solid system

The experimental set-up for gas-liquid-solid system is similar to gas-liquid system (cf. Figure 3.9) except an addition of solid particle with average particles size of $75 \mu\text{m}$ was used for all runs. ERT measurement was employed to understand the hydrodynamics within the reactor vessel non-intrusively.

3.5. Effect of stirring speed and catalyst loading

Experimental runs were conducted using impeller speeds ranging from 200 to 1200 RPM (at 6 levels) for 4 different alumina particle loadings (10, 20, 30 and 40 g L⁻¹). For the gas-liquid-solid runs, dispersed phase conductivity, σ_2 , was taken as the conductivity of alumina particles (10⁻¹¹ mS cm⁻¹).

3.6. Effect of particle size

In this experiment, it was necessary to employ ECT rather than ERT, as an organic liquid was used (paraffin oil) as the continuous phase. The stirred tank vessel was made from a flat-bottomed acrylic (polymethyl methacrylate) cylinder with inner diameter, D_T of 100 mm and height, 190 mm. The tank was equipped with an axial gas-entrainment impeller made of polypropylene which had negligible influence on capacitance measurements. The impeller has a diameter, $D_I = 0.5D_T$ and was located at a distance of $0.6D_T$ above the vessel bottom. Alumina particles (with 4 different mean sizes, 45, 90, 200 and 425 μm) were used as the solid phase. The liquid (continuous) phase was paraffin oil kept at a level of $1.4D_T$ (i.e. 1000 ml oil) in all runs. Each of the four impeller blades has 3 gas exit ports ($0.035D_T = 3.15$ mm holes) thus permitting gas recirculation between the bulk liquid phase and the headspace. The reactor vessel was also snugly fitted peripherally with baffles in the form of 8 PVC rods to promote better mixing. The ECT sensor unit consisted of a 12-electrode belt, which was fitted to the vessel exterior. The sensor was connected to the ITS M3000 module for data collection.

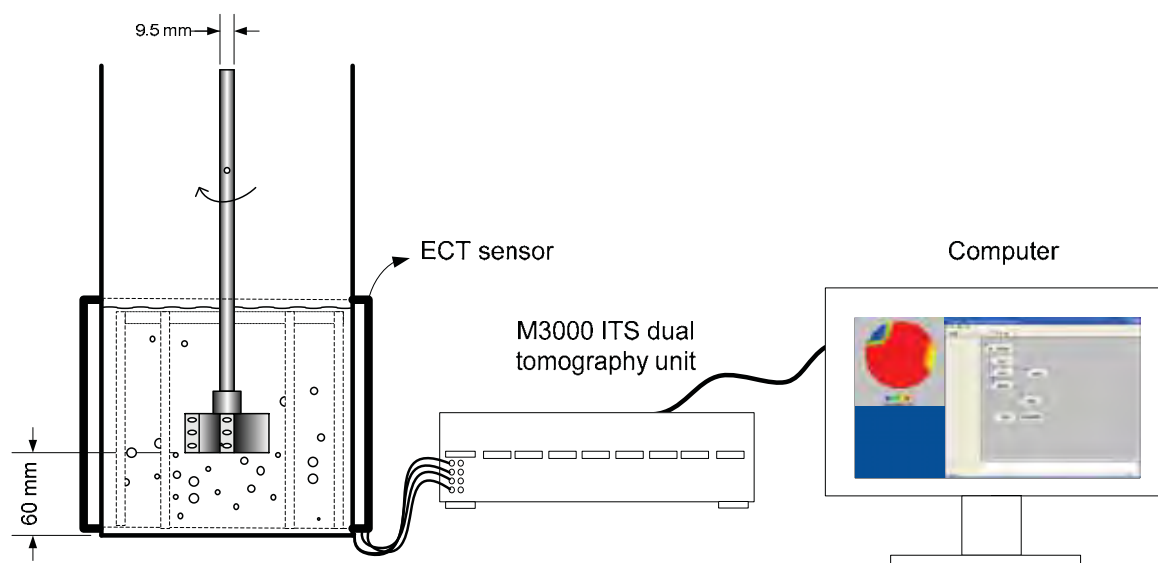


Figure 3.13 ECT experimental setup

3.7. Slurry reactor Fischer-Tropsch (FT) synthesis

To facilitate data acquisition and process monitoring, the experimental setup was connected to a DELL personal computer.

3.7.1. Chemicals

A list of chemicals used in this project is provided in Table 3.1. All the chemicals were either obtained from Sigma-Aldrich Chemicals (Sydney, Australia), or Ajax Finechem (Sydney, Australia) with the exception of the spray-dried γ -alumina obtained from Saint-Gobain NorPro (USA).

Table 3.1 Specification of chemicals used

Chemical	Formula	Purity/Conc.	Application
Gamma alumina	$\gamma\text{-Al}_2\text{O}_3$	Industrial grade	Catalyst preparation
Cobalt nitrate	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	> 99.0%	Catalyst preparation
Nitric acid	HNO_3	70% wt/wt	Catalyst preparation

Paraffin oils	Industrial grade	FTS medium and continuous phase for ECT
---------------	------------------	---

To prepare 5 M standard HNO_3 , nitric acid solution had to be diluted before using for catalyst preparation. Cobalt nitrate hexahydrate is deliquescent, and thus was stored as a 0.2 gCo ml^{-1} standard solution. Water used in preparation of all the standard solutions was purified by a NANOpure Diamond UV system (Barnstead International, USA), after passing through a Distinction distillation unit (Bibby Sterling Ltd., UK).

3.7.2. Gases

All gases used in this thesis were either provided by BOC gases or Linde Gas Australia and listed in Table 3.2 together with their purity and application. Compressed town air, further purified by a hydrocarbon and moisture removal trap containing $5\text{\AA}$ molecular sieve and calcium sulphate (Alltech Associates Inc.) was used during catalyst drying and calcination as well as for the Flame Ionisation Detector (FID)

Table 3.2. Gases manifold, their purity and application

Chemical	Purity/Conc.	Application
H_2	99.99%	activation, FTS, TPR, FID gas
CO	99.99%	activation, FTS
N_2	99.99%	diluent for FTS, carrier gas for H_2 -chemisorption, tomography study NH_3 -TPD, and adsorbate for BET-PV-PSD
He	99.999%	carrier gas for GCs, CO_2 -TPD, and BET-PV-PSD
Ar	99.999%	Carrier gas for TGA
10% NH_3/N_2	10% NH_3 in N_2	NH_3 -TPD

	balance	
10%H ₂ /N ₂	10% H ₂ in N ₂	H ₂ -chemisorption balance
10%CO/He	10% CO in He	CO-chemisorption balance
10%CO ₂ /He	10% CO ₂ in He	CO ₂ -TPD balance
CH ₄ standard	1% CH ₄ in Ar	routine GC standard gas balance
C ₁ -C ₅ standard	1% each (<i>n</i> -alkane/alkene)	GC calibration
Air	Instrument grade	Catalyst drying, calcination, TPO, FID gas

3.7.3. Catalyst preparation

Even though catalyst design was not the main aim of this study, great care was taken in catalyst preparation steps to ensure a high level of reproducibility and achieve the optimum activity of catalyst as shown in Figure 3.14.

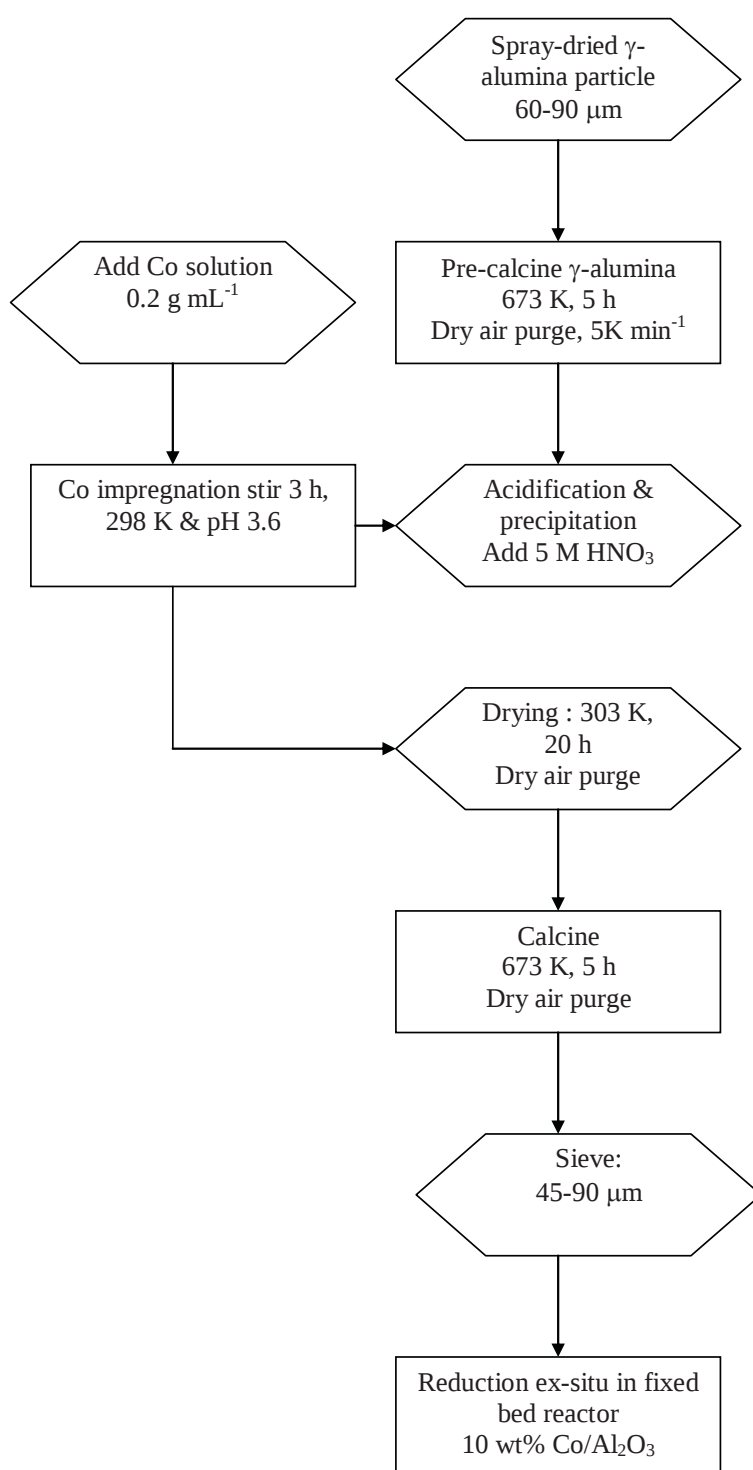


Figure 3.1. Catalyst preparation steps flowchart

While cobalt supported alumina catalyst is widely employed in industry and its physicochemical properties are available in the open literature, the different preparation methods may produce catalysts with different physicochemical properties. Hence preparation methods may ultimately become key parameters of the catalyst performance.

3.7.4. Catalyst support

Catalyst support plays an important role in offering better metal dispersion that consequently affect reaction characteristics such as selectivity, longevity, and regenerability. Imparting higher surface area is one of the primary roles of supports employed in any catalytic reaction process. In this respect, alumina and silica are the materials of choice in many commercial applications. In FT, alumina gives better metal dispersion but lower reducibility while silica offers higher reducibility and lower dispersion [8]. With respect to the wet impregnation method, support surface groups significantly affect adsorption of active species, and consideration of support surface chemistry is imperative in order to optimise desired characteristics i.e. metal dispersion, reducibility, distribution within catalyst pores, etc.

3.7.5. Impregnation steps

Impregnation may be categorised into two types: incipient wetness impregnation and wet impregnation. In incipient wetness impregnation, the volume of the precursor added is just enough or slightly less than the volume required to fill the intra-particulate pores of the support. In wet impregnation, the volume of precursor used is in excess of the pore volume of the support. The method of impregnation affects the characteristics of support-metal interactions in different ways:

- a) Crystallisation of precursor salt during solvent evaporation. (immobilised species unchanged)

b) Electrostatic interaction followed by ion exchange or electrostatic adsorption (inner sphere of immobilised species unchanged)

Catalyst synthesis was carried out using spray-dried γ -alumina as a support with particle size of 60-90 μm obtained from Saint-Gobain Norpro Corporation. The support was pre-treated at 673 K with dry air at 5 K min⁻¹ for 5 h to remove moisture and volatile organics that may arise from the manufacturing process. A standard cobalt nitrate hexahydrate solution (Aldrich Chemical) of concentration 0.2 g_{Co} ml⁻¹ as a salt precursor was added to the alumina support to prepare 10 wt% total metal loading. Impregnation was carried out at 298 K for 3 h under constant stirring and pH (5 M HNO₃ solution as pH control) using a Metler-Toledo T90 Titration Excellence system.

A sub-isoelectric pH (=3.6) impregnation was employed to create a positive alike charged support-precipitating pair that would have better metal dispersion and simultaneously reduce the undesirable metal-support interactions [9, 10]. Subsequently, the impregating slurry was dried in the oven at 303 K for 20 h. Dried catalyst was then calcined in the oven at 673 K for 5 h at a rate of 5 K min⁻¹. Air used in calcining and drying processes was purified by a organic and moisture removal trap containing 5Å molecular sieve and calcium sulfate (Drierite®), supplied by Alltech Associates Inc. (division of Grace Davison, Australia). Finally, the calcined catalyst was sieved to 45-90 μm using Retsch AS 200 Analytical Sieve Shaker before charging into a 1/2" stainless steel fixed bed reactor. The activation was carried out at 623 K for 8 h using a heating rate of 5 K min⁻¹ in 5% CO/H₂ mixture with 50% N₂ as diluent. High purity research grade H₂, CO and N₂ were used in all runs. Gas flowrates were controlled and metered via calibrated mass flow controllers (Brooks 5850E).

3.8. Catalyst characterization

In this section, we provide a brief review of the various characterization techniques employed including the underlying theory for determination of catalyst properties.

3.8.1. Surface area and pore characteristics

The surface area and pore characteristics (volume and average diameter) are the most basic physical properties of heterogeneous catalysts yet are critical in determining the activity, selectivity and mass transport parameters. The information on total pore volume and overall isotherm of catalysts may give an insight into the internal mass transport for both reactants and products within the catalysts. The Brunauer-Emmett-Teller (BET) is the most common method for the determination the surface area and pore size. The BET surface area is based on the relationship between the volume of gas adsorbed and total area of adsorbent, applicable for a measurement of surface area for both mesoporous and macroporous materials, and given as

$$\frac{P}{V_s(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1)P}{V_m c P_0} \quad (3.5)$$

where,

P = gas pressure

P_0 = saturation pressure of adsorbate gas at adsorbent temperature

V_s = volume of gas adsorbed

V_m = volume of gas adsorbed for monolayer coverage

c = a constant characteristic of the adsorbate-adsorbent system

We can calculate the volume of gas adsorbed for monolayer coverage by plotting $P/V(P_0 - P)$ versus P/P_0 that yields a straight line with the slope

$(c-1)/V_m c$ and intercept $1/V_m c$. Then, by assuming the cross-sectional area of the adsorbate gas is that of N_2 , $16.2 \text{ \AA}^2$, the specific surface area is given by;

$$S_A = \frac{m_m N_A a_a}{M_a} \quad (3.6)$$

S_A = total surface area of the sample ($\text{m}^2 \text{g}^{-1}$ sample)

N_A = Avogadro number (6.023×10^{23} molecules mol^{-1})

m_m = mass of adsorbed monolayer per unit mass of sample (g g^{-1} sample)

a = cross-sectional area of adsorbate molecule ($16.2 \times 10^{-20} \text{ m}^2$ for N_2)

M_a = molecular mass of adsorbate (g/mol)

While the total pore volume is calculated from the total volume of gas adsorbed and by assuming the pores are completely filled with liquid adsorbed, N_2 , thus; the volume of liquid N_2 ;

$$V_{liq} = \frac{PV_{ads} V_m}{RT} \quad (3.7)$$

where,

T = ambient temperature (K)

P = ambient pressure (1 atm)

V_{ads} = is the total volume of gas adsorbed at the relative pressure closest to unity

V_m = molar volume of the liquid adsorbate ($34.7 \text{ cm}^3 \text{mol}^{-1}$ for liquid N_2).

The pore volume distribution can be either derived from adsorption or desorption point of the isotherm but the desorption curve gives better results due to its occurrence closer to thermodynamic equilibrium i.e. lower relative pressure. Thus the pore radius, r_p is calculated as;

$$r_p = r_k + t_a \quad (3.8)$$

where r_k is Kelvin radius of pore and t_a is the thickness of the adsorbed layer.

In this study, BET surface areas and pore size measurements for both calcined catalyst and alumina support were obtained from a Quantachrome Autosorb-1 unit at 77 K as shown in Figure 3.15. Prior to the analysis, the catalyst sample was degassed for approximately 30 minutes at 298 K before heating up to 573 K for 3 hrs. The sample tube was re-weighed due to changes in weight from residual and volatiles lost during degassing process before transferring to the analysis station. The Autosorb-1 unit automatically computed the pore size distribution using software ASI WIN.



Figure 3.15 Quantachrome Autosorb-1 unit

3.8.2. Thermogravimetric Analyses (TGA)

A Thermo Cahn TherMax unit equipped with TG-2121 analyzer (cf. Figure 3.16) was used to for themogravimetric analysis of catalyst calcination, reduction and oxidation behaviour. Approximately 70 mg of catalyst sample was used for each analysis. Temperature-programmed calcination was carried out at 673 K for 5 h and a heating rate, β , of 5 K min⁻¹ using high grade instrument air (99.5% purity). During calcination procedure, weight loss is observed as depicted in Figure 3.17. Activation energy of the precursor composition was obtained by varying the heating rate between 1-20 K min⁻¹. Subsequently, temperature programmed reduction (TPR) was carried out at 673 K for 5 h and a heating rate of 5 K min⁻¹. Temperature was ramped up to 973 K during the TPR analysis with a mixture of 50% Ar/H₂ at 70 ml min⁻¹. Subsequently, temperature programmed oxidation (TPO) was carried out at a heating rate of 5 K min⁻¹ up to 973 K using high grade instrument air at a flow of 55 ml min⁻¹.



Figure 3.16 TGA unit

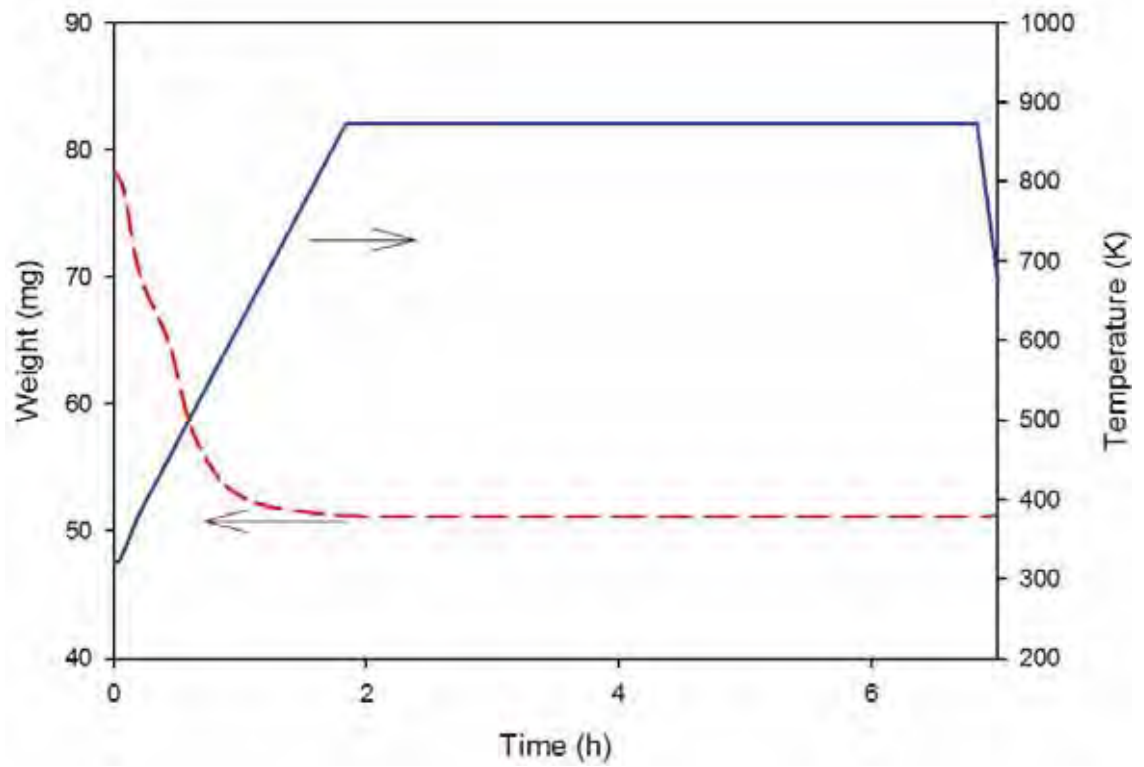


Figure 3.17 Typical weight loss during profile during calcination process

3.8.3. Temperature-Programmed Desorption (TPD)

TPD was performed to characterize the intrinsic nature of the acid and basic sites of the catalyst surface using ammonia and carbon dioxide respectively. A mixture of 10% NH_3/N_2 at 423 K was used in programmed- NH_3 desorption analysis using the Micromeritics AutoChem 2910 system, while CO_2 TPD was executed at 323 K using 10% CO_2 in He in the same unit to obtain acid and basic sites respectively. Approximately 0.2 g of catalyst was used for each analysis. To ensure complete saturation of catalyst with the probe molecule is achieved, the adsorption was done for 60 minutes at 423 K. A purge step using carrier gas (N_2 for NH_3 and He for CO_2) at 40 ml min^{-1} for 30 minutes at the adsorption temperature was performed to eliminate any weakly bonded NH_3 and CO_2 molecules. Subsequently, temperature programmed desorption started at a rate of 10 K min^{-1} up to 873 K and maintained at that temperature for 60 minutes. The sample was then cooled to 423 K and allowed to equilibrate before mixing with NH_3 for 60 minutes, followed by purging for the same duration. NH_3 -TPD used ramping rates of 10, 15, 20 and 30 K min^{-1} while CO_2 -TPD was executed at rates of 5, 10, 15, 20, 25, and 30 K min^{-1} . Both desorption temperatures were ramped up to 973 K.

The heat of desorption, $-\Delta H_{des}$ (J mol^{-1}), was derived from the following relationship;

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{-\Delta H_{des} A}{RC}\right) + \frac{(-\Delta H_{des})}{RT_p} \quad (3.9)$$

where,

- A = amount of probe molecule adsorbed at saturation ($\text{mol g}_{\text{cat}}^{-1}$)
- R = universal gas constant
- C = constant related to the desorption rate

The site concentration was calculated by assuming the total flowrate of desorbed species in the outlet was the same as the inlet flow of carrier gas as;

$$\text{site conc} = \frac{\int \frac{y_i Q}{22414} dt}{m} \quad (3.10)$$

y_i = mole fraction of desorbed gas in the outlet stream

Q = total outlet volumetric flowrate (ml min^{-1}) at STP

m = mass of sample (g)

3.8.4. Hydrogen Chemisorption

H₂ chemisorption was performed to evaluate the metal dispersion, cobalt active area and crystallite size on a Micromeritics AutoChem 2910 as depicted in Figure 3.18.



Figure 3.18 Micrometric AutoChem 2910 unit

Outlined procedure of H_2 chemisorption is as follows:

1. Approximately 0.4 g of catalyst sample was loaded into the sample holder (sandwiched between quartz wool).
2. Instrumental grade of 10% H_2 in N_2 balance was passed through the catalyst specimen at heating rate of 2 K min^{-1} to 873 K for reduction process. At this temperature, the specimen was kept isothermally for 5 hours in order to achieve optimum reduction level.
3. Subsequently, the catalyst sample was cooled down to room temperature using Ar and followed by re-heating to 383 K for 30 minutes at heating rate of 2 K min^{-1} .

4. A series of H₂ pulses were injected to catalyst sample every 5 minutes after a stable TCD signal was observed as illustrated in Figure 3.19.
5. The dissociation of H₂ on the metal atoms was occurred as:

$$H_2 + 2M \rightarrow 2M - H$$
6. Finally, unabsorbed H₂ was monitored through the TCD detector that then evaluated for the chemisorption profile derivation.

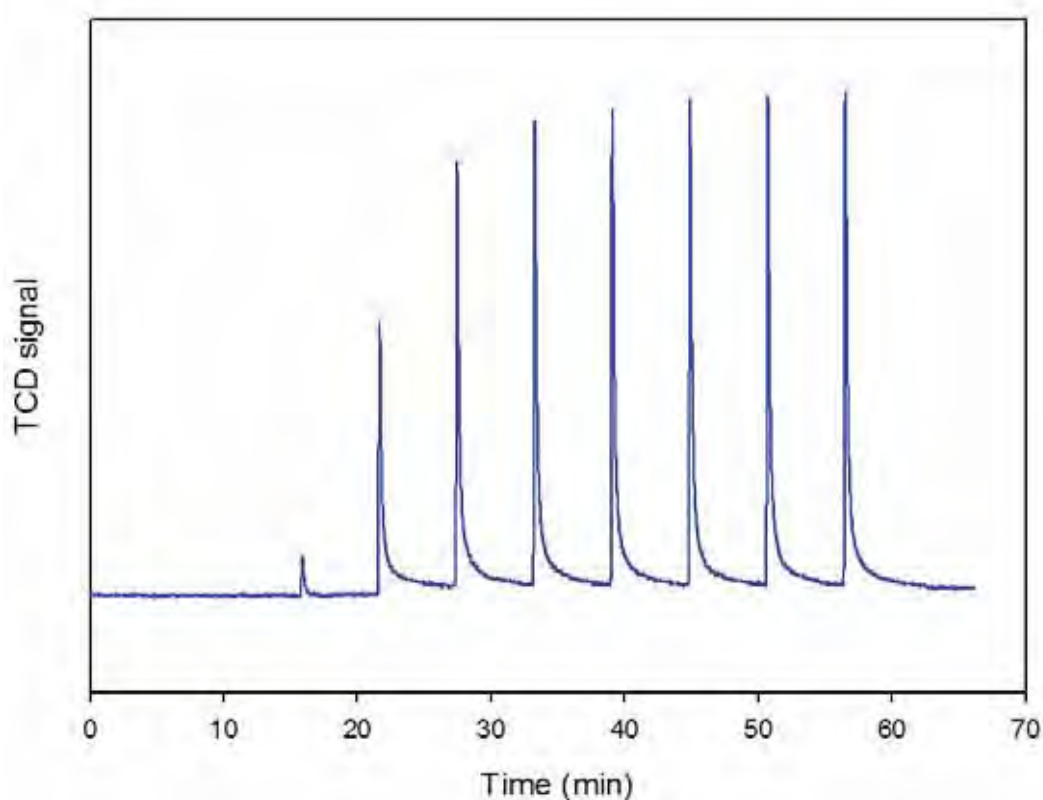


Figure 3.19 Typical pulse of hydrogen chemisorption profile

3.8.5. X-Ray Diffractogram (XRD)

X-ray diffractogram (XRD) measurement was performed using Philips X'pert MPD (available in Solid state and Elemental Analysis Unit in the University of New South Wales) at 45 kV, 40 mA, rate 0.2°min⁻¹(2θ) to identify various solid oxide phases in the catalyst. The catalyst sample of uniform size, 45 μm was placed into the holder (15 mm Ø). The samples

were scanned for 2θ angle between 5 to 85° . Based on Bragg's law, the inter-planar distance can be estimated using this equation [11]:

$$n\lambda = 2d \sin \theta \quad (3.11)$$

where,

n = integer determined by the order of reflection

λ = wavelength of incident radiation

d = spacing between the planes in the atomic lattice

θ = angle between the incident ray and the scattering planes

The X'Pert Pro software was used to identify the metallic oxide phases present. These results complemented the temperature-programmed runs (decomposition, reduction, and oxidation).

3.8.6. Scanning Electron Micrograph (SEM)

Scanning electron micrograph (SEM) using Phillips 505, Holland as shown in Figure 3.20, was used to investigate the morphology of the catalyst specimen. It is capable of producing high resolutions of SEM images by generating an electron beam with high intensity. The back-scattered electrons are emitted from an electron gun, then captured by detectors and images are produced. Catalyst sample was gold coated (~20nm thickness) using a modified Edwards E306A coater (Edward High Vacuum, Crawley, England) prior to the analysis. A range between 300 and 10 000 times magnification was used for the images captured, using ImageSlave v2.11 software.



Figure 3.20 Philip 505 Instrument for SEM measurement

3.9. Fischer-Tropsch Reaction

3.9.1. Catalyst activation

Prior to transferring the catalyst into the Parr slurry reactor, activation of catalyst was performed at 623 K. In order to avoid any undesirable vaporization of starting liquid medium and thermal degradation of paraffin oil, the activation was conducted *ex-situ* in a fixed bed reactor as shown in Figure 3.21.

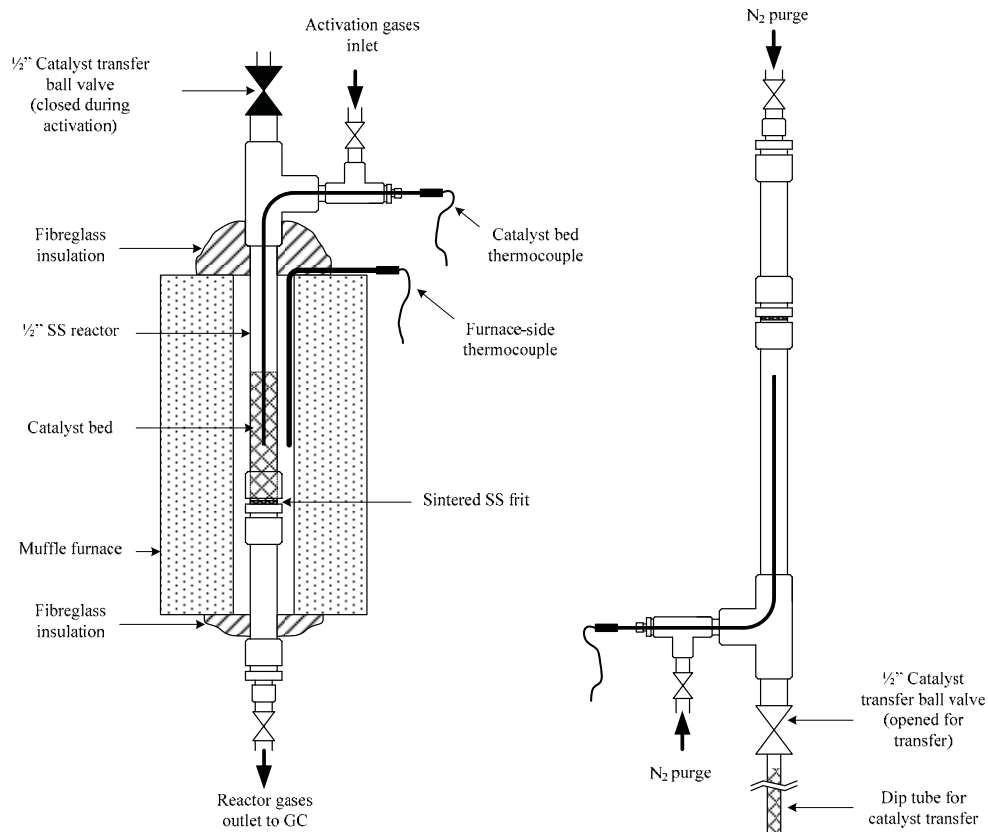


Figure 3.21 Catalyst activation in fixed bed reactor [12]

A desired temperature was achieved by controlling the furnace temperature as well as the reactor bed temperature via K-type thermocouples linked to a system of temperature controllers. The reactor was weighed before and after catalyst had been transferred to ensure an accurate amount of catalyst. A total of 10 g of catalyst was used with 5 g of unreduced catalyst charged per reactor. To prevent any possibility of catalyst deactivation during transfer into the Parr reactor, inert N_2 gas was used for the pneumatic transport.

3.9.2. Reactor characterization and ECT set-up

The experimental system as seen in Figure 3.22 consists of a gas manifold-station, an electrical capacitance tomography (ECT) module connected to the 2-litre Parr stainless steel reactor (ID = 100 mm) via a 12-electrode cylindrical basket sensor snugly fitted around the perimeter

of the vessel. The stainless steel electrode has a temperature-resistant coating to permit operation up to 553 K and pressure to 30 atm.

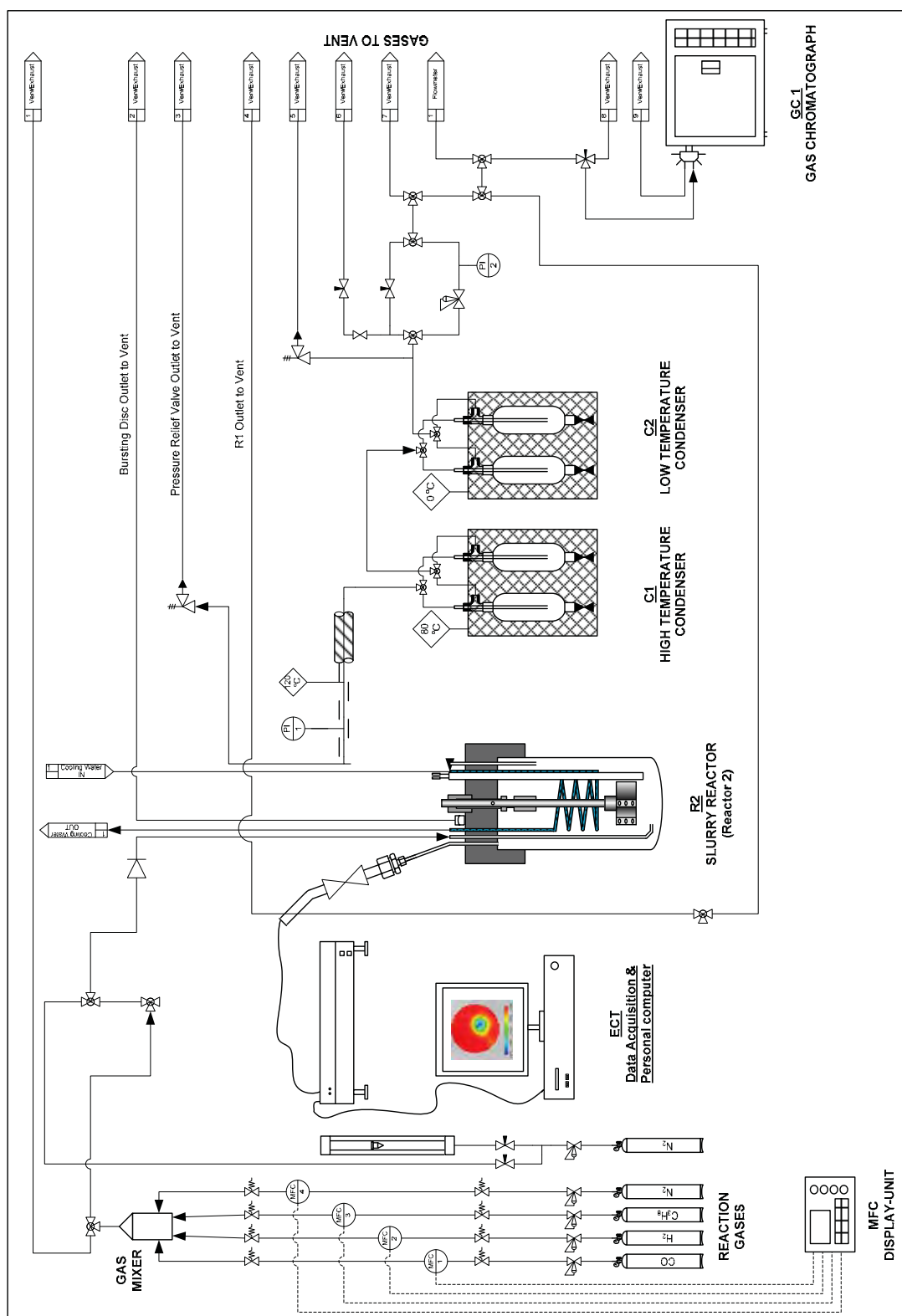


Figure 3.22. Experimental apparatus for the Fischer-Tropsch synthesis study.

The Parr reactor was mounted in a temperature-controlled electrical furnace and equipped with a gas-inducing stirrer as seen in Figure 3.22. The gas-inducing mixer was made of a hollow shaft with gas inlet port at the top (125 mm above the liquid surface) and a 4-blade flat impeller - each blade has 3 gas outlet ports -with a clearance of 60 mm from the reactor base. The final section is a product collection and analysis station consisting of two condensers placed downstream of the reactor (for C_{8+} hydrocarbons and water removal) and a Shimadzu gas chromatograph (model GC17A) for product composition determination. The activated catalyst is transferred under a N_2 blanket manually using a specially fabricated dip tube into the Parr reactor containing paraffin oil (boiling point 633 K) maintained at the reaction temperature prior to the FT runs.

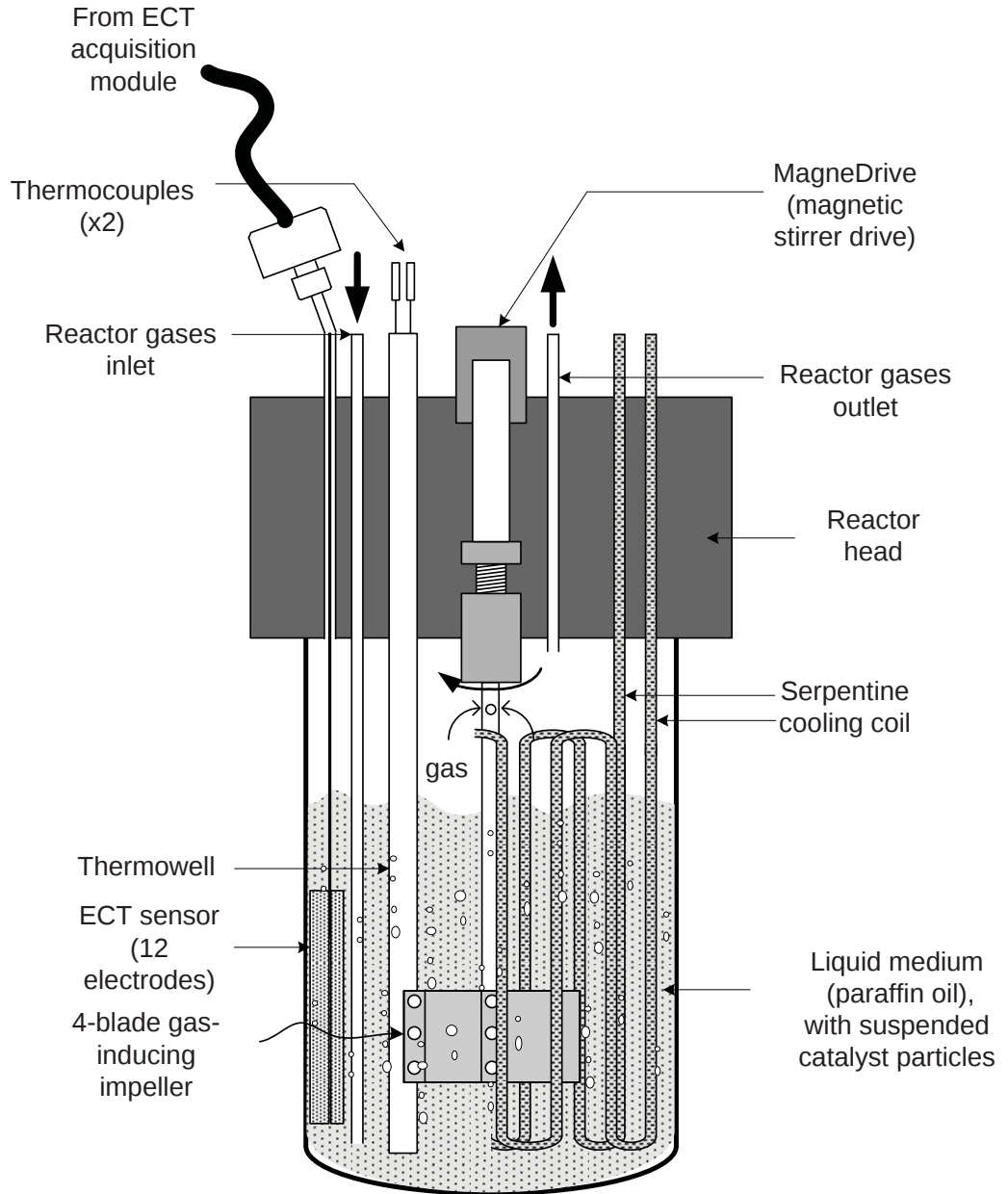


Figure 3.23 Parr reactor with ECT sensor

The minimum stirring speed required for gas induction through the gas inlet port on the shaft was estimated from the Sawant-Joshi equation [13] given by:

$$\frac{N_{cs}^2 D_I^2}{gh} \left(\frac{\mu}{\mu_{water}} \right)^{-0.11} = 0.21 \quad (3.12)$$

This correlation may be used to estimate the critical agitation speed, N_{cs} , where h is the impeller submersion depth, D_I = impeller diameter, μ is the liquid phase viscosity, μ_{water} is the viscosity of water, while g is the acceleration due to gravity. For the present stirred tank arrangement, $h = 56$ mm, $D_I = 50$ mm and the liquid phase was paraffin oil, $\mu/\mu_{water} = 1.93$ which gives $N_{cs} = 4.9$ rps (293 rpm). As a result of preliminary investigation of the effect of stirring speed on reaction rate, agitation rates greater than 300 rpm were chosen. Indeed, to avoid both external mass transport and pore diffusional limitations, a stirring speed of 1200 rpm with catalyst average particle size in the range 60-90 μm was used for all experiments.

The ECT sensor was connected to a central processing dual-modal M3000 (cf. Figure 3.3). Tomograms were recorded at 500 kHz over a 100-second interval at one frame per second to ensure excellent spatiotemporal resolution for each run. The reconstructed image during an experiment contained information about the cross-sectional distribution of electrical permittivity of the vessel contents within the measurement plane. Tomograms collected were analysed to obtain the cross-sectional average phase hold-up.

FT runs were carried out at total operating pressures between 1 to 21 atm and temperatures of 473 to 533 K as well as H_2 feed composition, y_{H_2} (0.2-0.9). Catalyst loading was kept constant at 10 gL^{-1} for all runs. The aqueous and high molecular weight liquid products were collected in cleaned and pre-weighed hot and cold traps located downstream of the Parr reactor. Two traps were connected in parallel (for both, hot and cold traps): one for normal/transient operation and the other for a mass balance period. Traps were checked for organic phase liquid products and re-weighed at the end of each run to account for in carbon balance. The uncondensed gases passed through the back-pressure regulator for analysis on the Shimadzu GC (model 17A) using a 30 m GS-Q capillary column. A bubble flowmeter was used to measure the non-condensable gas flow rate prior to analysis.

The dispersed phase hold-up, ε_D , was calculated using Maxwell equation (11) given as:

$$\varepsilon_D = \frac{2\varphi_C + \varphi_D - 2\varphi_M - \varphi_M \left(\frac{\varphi_D}{\varphi_C} \right)}{\varphi_M - \left(\frac{\varphi_D}{\varphi_C} \right) + 2(\varphi_C - \varphi_D)} \quad (3.13)$$

where φ_C is the permittivity of the continuous phase (liquid), φ_D is the permittivity of dispersed phase (gas and catalyst particle), and φ_M is the measured permittivity of the mixture obtained from pixel-averaged cross-sectional ECT data.

3.9.3. Product Analysis

The products that exited from the slurry reactor were analysed using a Shimadzu GC-17A gas chromatograph (GC). To ensure the accuracy of set pressure, injector split ratio and column flow velocity, the GC was equipped with electronic flow and pressure control. The GC comprised of both flame ionisation detector (FID) and thermal conductivity detector (TCD) with carrier gas of He used throughout. Sections of product lines after the pressure regulator were heated to avoid undesirable product condensation. The GC was also fitted with a 3-way metering needle valve capable of supplying approximately 10-20 ml min⁻¹ of products and a 6-port automated sampling valve (Valco Instruments Co. Inc.).

3.10. Computer Fluid Dynamics Modelling

The use of CFD within the context of the present problem is described below. CFD codes were structured around the numerical algorithms that tackle fluid flow problems. The code contains three main elements:

1. Pre-processor
2. Solver

3. Post-processor

3.10.1. Pre-Processor

The pre-processor creates the input of a flow problem to a CFD program by means of user-friendly interface i.e. GAMBIT version 2.4 and the input is transformed into a form suitable for use by the solver. For this purpose it is required to:

- a) Define the geometry of the computational domain or region of interest.
- b) Sub-divide the domain by means of grids.
- c) Define the fluid properties.

Specify appropriate boundary conditions at cells, which coincide with or touch the domain boundary. The solution to a problem is defined at nodes inside each cell. The number of cells governs the accuracy of a CFD solution. In general, larger the number of cells, better the solution accuracy. Optimal meshes are often non-uniform, finer in area where large variation occurs from point to point and coarser in the area with relatively low change. The pre-processor GAMBIT is used for grid generation. Three-dimensional (3D) grid was used with tetrahedral cells. Fine cells were used along the impeller region of the computational domain whereas coarser cells were adopted near the wall vessel. Over one million cells were used for this simulation to ensure high degree of accuracy.

3.10.2. Solver

Segregate solver used in this using control volume based method. Integration of the governing equation on the individual control volume to construct algebraic equation for the discrete dependent variables such as velocity, pressure, temperature, and conserved scalars. Linearisation of the discretised equation, thus the solution of the resultant linear equation

to yield updated values of the dependent variables. Solvers parameters are summarise in Table 3.3.

Table 3.3 Solver parameters

Parameter	Setting
Solver	3-D Segregated, Unsteady, Implicit
VOF scheme	Geo Reconstruct
Viscous model	k-epsilon
Operating pressure	101325 Pa
Water density	998.2 kg/m ³
Air density	1.225 kg/m ³
Pressure discretisation	Body force weighted
Pressure-velocity coupling	PISO
Momentum discretisation	Second order upwind

3.10.3. Post-Processor

FLUENT 6.3 packages are equipped with versatile visualization tools. These include: domain geometry and grid display, vector plots, line and shaded contour plots, 2D and 3D surface plots, particle tracking, view manipulation, colour postscript output, animation for the dynamic results display.

3.10.4. Convergence Criteria

Final convergence was decided by the way of a residual source criterion, which measures the departure from exactness for all the flow variables. The convergence criterion was set as less than 1×10^{-3} for the normalized total overall residue of all variables as shown in the Figure 3.24.

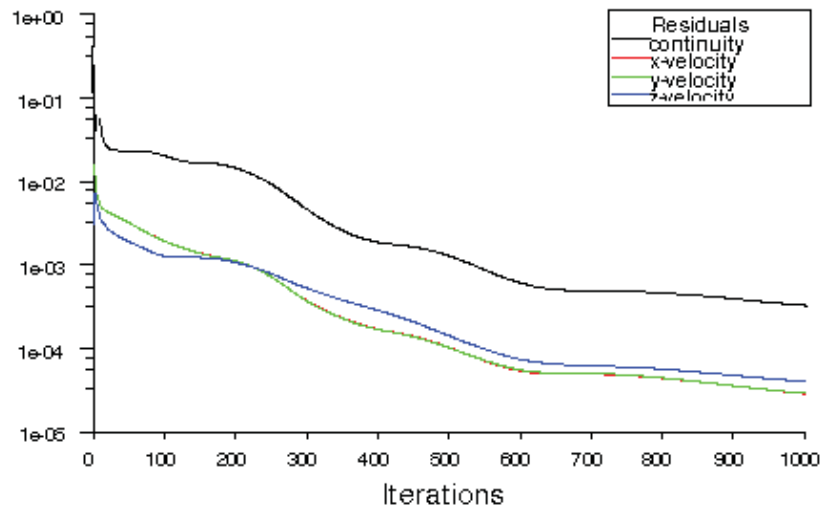


Figure 3.24 Convergence criteria set by overall residue of all variables

3.10.5. Time Dependence

FLUENT automatically refines the time step for the integration of the volume fraction equation, but this time step calculation can be modified using the Courant number. When FLUENT performs a time-dependent VOF calculation, the time step used for the volume fraction calculation will not be the same as the time step used for the rest of the transport equations. Time steps are refined in the VOF calculation automatically, based on the input for the maximum Courant Number allowed near the free surface. The Courant number is a dimensionless number that compares the time step in a calculation to the characteristic time of transit of a fluid element across a control volume viz.,

$$\text{Courant Number} = \frac{\Delta t}{\Delta x_{\text{cell}} / v_{\text{fluid}}} \quad (3.14)$$

I

Region near the fluid interface, FLUENT divides the volume of each cell by the sum of the outgoing fluxes. The resulting time represents the time it would take for the fluid to empty out of the cell. The smallest such time is used as the characteristic time of transit for a fluid element across a control volume, as described above. Based upon this time and the input for the maximum allowed Courant Number, a time step is computed for

use in the VOF calculation. The time step used for volume fraction calculation was different from the time step used for other variables and was calculated automatically in the code for the specified value of Courant number.

3.10.6. Pressure-Velocity Coupling

The application of continuity and momentum equations for a given domain of interest can solve any steady or unsteady flow problem. The velocity components can be updated using the momentum equations. However, the real difficulty in the calculation of the velocity fields lies in the unknown pressure field. The pressure gradients form a part of the source term in the momentum equation. The difficulty associated with the determination of pressure field has led to several methods of pressure-velocity coupling such as SIMPLE, SIMPLEC and PISO. SIMPLE, Semi Implicit Method for Pressure Linked Equations is the most basic pressure-velocity coupling scheme widely used. Two other methods are evolved with some modifications of the basic SIMPLE algorithm to achieve higher accuracy and faster convergence for complex problems. The solution procedure for this algorithm is that a pressure field is initially guessed and corresponding velocity field is computed using momentum equations over a time step. On substituting these fields in the continuity equation, a mass balance error arises, which is used to correct the pressure field. The above steps are repeated for many time steps or iterations, till converged solution is obtained. In this study, PISO is used as the Pressure-velocity coupling method because it is highly recommended for transient calculation with skewed mesh. PISO, The Pressure Implicit with Splitting Operators is a pressure velocity coupling scheme, part of the SIMPLE family algorithm. However, it is based on the higher degree of the approximate relation between the corrections pressure and velocity. One of the limitations of the SIMPLE algorithms is that new velocities and corresponding fluxes do not satisfy the momentum balance after the pressure-correction equation is solved. As a result, the calculation must be repeated until the balance is satisfied. To

improve the efficiency of this calculation, the PISO algorithm performs two additional corrections: neighbour correction and skewness correction.

3.11. Data treatment

All the experimental data in this study has been repeated at least twice to ensure reproducibility of the data (error=5-8%), with the exception of the FT slurry runs in GIST. It is impractical to repeat all the experimental runs for FT slurry reactor due to the long run time involved (over 36 h per run). However, to verify reliability of the results, the FT experiment at $T=498\text{ K}$, $P=21\text{ atm}$ and feed composition, $y_{H_2}=0.67$ was repeated and reproducibility error was found within 5%.

3.12. References

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4

■ Preliminary Work and System Characterisation

4.1. General consideration

The equipment used in this study was properly characterised prior to experimental runs to ensure the results are reliable and reproducible. In this chapter, a detailed description is provided of some preliminary work done in order to achieve the research objectives. This includes calibration of analytical equipment, catalyst characterisation, electrical process tomography calibration and Parr reactor characterisation. In addition, prior to the Fischer-Tropsch (FT) reaction study, experimental conditions were carefully laid out in order to generate meaningful results and avoid any possibility of mass and heat transfer inclusion in the reaction study.

4.2. Product Analysis

4.2.1. Gas Chromatography

In this study involving FT synthesis, the exit products in the gas form were analysed using gas chromatography (GC) equipment. The GC was equipped with both a thermal conductivity detector (TCD) and flame ionisation detector (FID). Hydrocarbon gases exiting the slurry reactor were measured by FID while unconverted reactants such as CO and H₂ could be measured by TCD. Methane could be measured by both TCD and FID. To avoid undesirable condensation of products leaving the reactor, the exit lines were insulated and heated at 373 K. The products leaving the reactor passed through hot and cold condensers including back pressure regulator (BPR) before being directed to the GC. Table 4.1 summarises the operating conditions of the GC's column.

Table 4.1 Gas chromatograph settings

Column	J&W Scientific
	30 m x 0.32 mm x 1 μ m
Total flow (ml min^{-1})	113
Column flow (ml min^{-1})	2.8
Sample loop temperature (K)	393
Detector temperature (K)	523
Carrier gas	Helium
Column velocity (cm s^{-1})	40
Split ratio	40
Oven temperature program	
Initial temperature (K)	313
Initial wait (min)	0
Step 1: rate (K min^{-1})	15
Step 1: temperature (K)	503
Step 1: wait (min)	10
Step 2: rate (K min^{-1})	-
Step2: temperature (K)	-
Step 2: wait (min)	-

4.2.2. GC calibration

Assuming the gaseous products entering the GC obey the ideal gas law, the total number of moles, n_T , is defined as

$$n_T = \frac{PV}{RT} \quad (4.1)$$

where,

P = effective pressure in the sample loop (atm)

T = GC operating temperature

V = sample loop size

R = universal gas constant

The total amount of gas entering a GC can be defined by P-V-T characteristic of the sample loop for the GC. The number of moles of component i , n_i , is proportional to the area of the corresponding peak for that component, as such

$$n_i = b_i' A_i \quad (4.2a)$$

where,

A_i = area of peak for species i

b_i' = a proportional constant of species i

Nonetheless, atmospheric fluctuations are bound to affect to amount of gas entering the GC, as well as other function of GC. Thus, to acknowledge this fact and compensate for the changing in GC response on day-to-day basis, a standard 1% CH₄ in Ar balance was analyses daily prior performing FT runs. At least three gas injections were performed and an average area was used. Thus, the Equation (4.2) can be redefined as:

$$n_i = b_i A_i' \quad (4.2b)$$

where,

b_i = the response factor for species i .

A_i' = The normalised peak area for species i .

The response factor for n-paraffins and i-olefins for C_1 - C_{12} were determined manually. C_1 - C_5 species were calibrated manually using standard gas containing known concentrations of paraffins in N_2 diluent, obtained from Coregas Australia. Multipoint calibration was performed by injecting several different dilutions of the calibration gas further diluted in N_2 . The response factor, b_i , was determined from the slope of the plot of n_i vs A_i for C_1 - C_5 calibration gas for both paraffins and olefins. Calibration of C_6 - C_{12} was carried out with the aid of liquid calibration standards from Alltech. The method of successive dilution was used to prepare several known concentrations diluted with CS_2 . Average area with three injections for each concentration was used. The response factors were found to be analogous to those of C_1 - C_5 species, and are listed in Table 4.2.

Table 4.2 Response factors for GC

Component	Response factor x 10 ³
Methane, CH ₄	10.6
Ethene, C ₂ H ₄	5.26048
Ethane, C ₂ H ₆	5.399115
Propene, C ₃ H ₆	3.836614
Propane, C ₃ H ₈	3.308034
Butene, C ₄ H ₈	2.80344
Butane, C ₄ H ₁₀	2.63997
Pentene, C ₅ H ₁₀	2.281456
Pentane, C ₅ H ₁₂	1.992272
Hexene, C ₆ H ₁₂	1.954991
Hexane, C ₆ H ₁₄	1.675232
Heptene, C ₇ H ₁₄	1.695976
Heptane, C ₇ H ₁₆	1.428209
Octene, C ₈ H ₁₆	1.499516
Octane, C ₈ H ₁₈	1.243873
Nonene, C ₉ H ₁₈	1.345205
Nonane, C ₉ H ₂₀	1.101129
Decene, C ₁₀ H ₂₀	1.220675
Decane, C ₁₀ H ₂₂	0.987379
Undecene, C ₁₁ H ₂₂	1.117985
Undecane, C ₁₁ H ₂₄	0.894636
Dodecene, C ₁₂ H ₂₄	1.031799
Dodecane, C ₁₂ H ₂₆	0.817597

A standard calibration gas containing 1% CH₄ in Ar as diluent was used to to compensate for possible daily variation of FID signals due to changes in gas flowrate, pressure and/or electronic noise. The peak area of all species were normalised against the peak area of this standard gas.

4.2.3. FT rate calculation

The reaction rate calculation without any recycle stream is given as [1],

$$r_i = \frac{y_i F}{m} \quad (4.3)$$

where,

r_i = reaction rate of species i

y_i = mole fraction of species i , in product stream

F = total molar feed flowrate (mol s^{-1})

m = mass of catalyst used (g)

4.3. Catalyst characterisation

Cobalt-based catalyst is the preferred choice of catalyst in the FTS industry due to its high activity, superior selectivity to higher hydrocarbons and low conversion to CO_2 when compared to iron catalysts [2, 3]. γ -alumina supported cobalt catalyst has received overwhelming attention in gas-to-liquid (GTL) technology due to its high attrition resistance and low water-gas-shift (WGS) reaction rates [4]. In this section, we investigate the temperament of γ -alumina supported cobalt catalyst using two-level factorial experimental design to explore the influence of the catalyst preparation conditions; calcination time, heating rate and impregnation pH. The main advantage of using two-level factorial design over the conventional technique i.e. multivariable process analysis is to reveal major trends and promising directions using a minimum number of runs in factor space [5]. Thus, the outcome of the results would be used in subsequent FT runs.

4.3.1. Catalyst preparation

Monometallic 10:90 Co/Al₂O₃ catalyst was prepared via impregnation method. The γ -alumina support with particle sizes between 60 and 90 μm was pre-treated at 673 K in air at 5 K min⁻¹ for 5 h to ensure thermal stability before impregnation with an aqueous cobalt nitrate hexahydrate solution obtained from Ajax chemicals and stirring for 3 h at controlled pH (5 M HNO₃ solution). Consequently, a two-level factorial experimental design was employed to investigate the influence of pH, calcination holding time and heating rate as shown in Table 4.3.

Table 4.3. Experimental plan according to a 2³ factorial design.

Catalyst Sample	pH	Holding time (h)	Heating rate (K min ⁻¹)
1	3.6	1	5
2	4.4	1	5
3	3.6	5	5
4	4.4	5	5
5	3.6	1	20
6	4.4	1	20
7	3.6	5	20
8	4.4	5	20

Subsequently, the impregnated slurry was dried in an oven for 20 h at 403 K. Heating rates of 5 and 20 K min⁻¹ were chosen because of the possibility of solid phase transformation reaction at lower heating rate and high formation rate of metal aluminate phase at higher heating rate [6]. High purity air at 55 ml min⁻¹ was used for calcination and TPO, while TPR was performed at the same rate with 50% H₂/N₂ mixture for 1 h up to 973 K. Compressed air at the same flow rate (55 ml min⁻¹) for 1 h and initial drying at a temperature of 403 K were incorporated in both calcination and reduction. However, during reduction step, argon gas was used instead. Calcination temperature was kept constant throughout this study at 673 K. Finally, polynomial regression models

were derived from intrinsic catalytic properties to suggest optimal preparation conditions for Fischer-Tropsch synthesis.

4.3.2. Physicochemical attributes

Based on the BET measurements shown in the Table 4.4, it is evident that the preparation conditions only imparted a slight change in total BET surface area, S_{BET} . However, Yates analysis reveals that pH exhibited a positive, statistically significant effect at 95% confidence level. Other key performance indices (KPI) played insignificant roles because calculated F values for these effects were lower than $F = 6.39$ (cf. Figure 4.6).

Table 4.4 Physicochemical properties of the catalyst sample

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	D_p (nm)	V_p (cm^3/g)	D (%)	D_m ($m^2 \cdot g^{-1}$ sample)	d (nm)
S0	205.1	12.0	0.6151	-	-	-
S1	185.2	11.3	0.5220	1.4203	0.9610	70.155
S2	179.7	11.6	0.5230	0.9180	0.6211	108.546
S3	170.8	11.1	0.4738	0.7168	0.4850	139.013
S4	172.7	11.5	0.4972	0.8974	0.6072	111.035
S5	183.0	11.3	0.5189	1.0998	0.7441	90.602
S6	185.3	11.6	0.5350	1.5062	1.0190	66.157
S7	170.5	11.4	0.4851	1.0036	0.6790	99.283
S8	176.5	11.5	0.5063	0.9064	0.6132	109.937

Table 4.5 Summary of ANOVA inferences for all effects (at 95% confidence level) on the physicochemical properties of the alumina-supported cobalt catalyst system.

Effect ID*							
Key Performance Index (KPI)	pH	t	pHt	β	$pH\beta$	$t\beta$	$pHt\beta$
S_{BET}	N	N(-)	N	N	N	N	N(-)

Average pore diameter	Y(+)	N(-)	N	N(-)	N(-)	N	N(-)
Average pore volume	N	N(-)	N	N	N	N	N(-)
Metal Dispersion (%)	N(-)	N(-)	N	N(-)	N	Y(-)	N(-)
Metal surface area	N(-)	N(-)	N	N(-)	N	N	N(-)
Metal particle diameter	N(-)	N	N(-)	N	N	N(-)	N

*Y=Yes – Effect is statistically SIGNIFICANT ; N= No – Effect is NOT statistically SIGNIFICANT

Table 4.6. Calculated F values for the response variables

Sample	Effect ID	S _{BET}	D _p	V _p	D (%)	D _m (m ² g ⁻¹)	d (nm)
S1	average						
S2	<i>pH</i>	0.423	6.412	2.244	0.290	0.339	1.106
S3	<i>t</i>	3.847	1.941	4.964	0.347	0.405	0.408
S4	<i>pHt</i>	1.000	0.412	1.000	0.857	1.000	1.000
S5	<i>β</i>	0.622	1.235	1.065	0.822	0.960	0.037
S6	<i>pHβ</i>	1.072	2.882	0.469	0.336	0.393	0.375
S7	<i>tβ</i>	0.009	1.471	0.418	0.420	0.490	1.241
S8	<i>pHtβ</i>	0.333	1.000	0.629	1.000	1.167	2.210

From TPO profiles as seen in Figure 4.1, decomposition of cobalt nitrate to the Co₃O₄ phase occurred at temperatures between 436 and 450 K, while the shoulder temperature between 484 and 523 K corresponds to the formation of CoAl₂O₄ phase, as similarly observed by other researchers [6, 7].

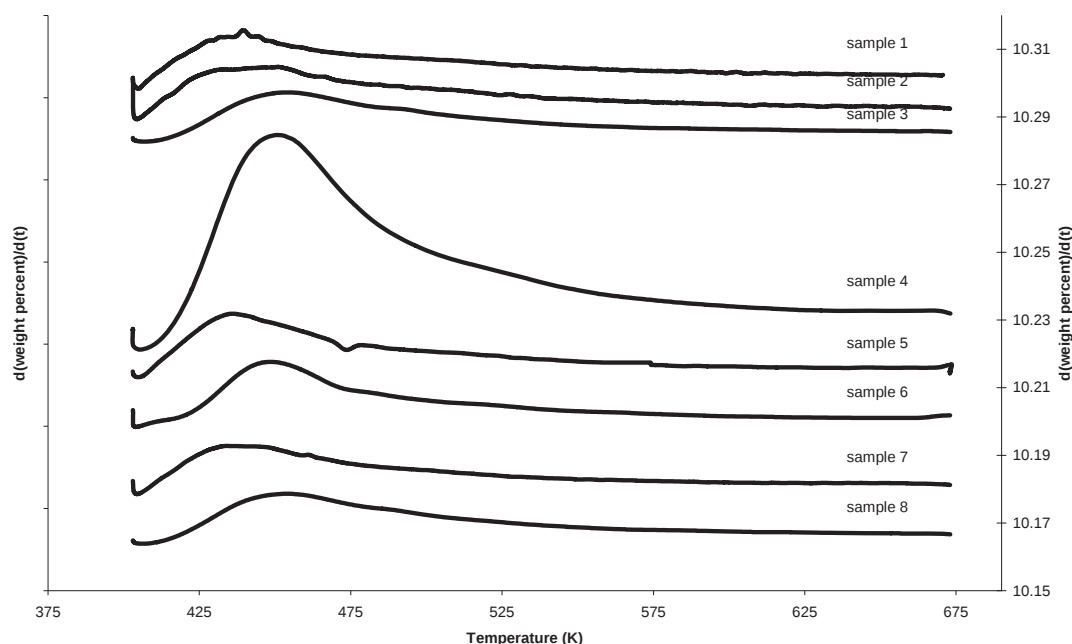


Figure 4.1 TPO spectra at various catalysts

TPR analysis confirmed that Co_3O_4 reduced in a two-step process from $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$. The temperature at which the reduction took place varied slightly depending on the catalyst preparation conditions i.e. 513-578 K and 667-720 K for the first peak and second peak respectively.

Samples 1 and 4 gave the highest cobalt dispersion but low crystallized metal particle size. These results contrast with samples 3 and 5 which showed the highest metal particle diameter but were low in cobalt dispersion percentage on the catalyst surface. However, there was no statistically significant evidence that these phenomena resulted from variations of catalyst preparation conditions. Thus, all subsequent runs followed sample 3 preparation conditions.

4.4. Electrical Process Tomography

A proper calibration technique is critical to ensuring results are reliable and produce less error.

4.4.1. ERT and ECT calibrations

ERT calibration involved two extreme calibration cases; low calibration in which the sensors were in the presence of air hence signal resistance to the sensor was low, and high calibration in which the sensors were in the presence of fully dispersed phase in the continuous phase where the signal resistance to the sensor was high. For ECT, low calibration was performed when the vessel was filled with material of lower permittivity (e.g. air for a gas/liquid 2-phase system) and high calibration was carried out when the vessel was filled with high permittivity material.

4.5. Fischer-Tropsch synthesis in a Slurry Reactor

4.5.1. Reactor characterisation

The appropriate stirring speed is critical to ensuring the solid (catalyst) is fully suspended and adequate gas dispersion can effectively enhance the ability of reactants dissolution in the liquid phase. Therefore, the choice to fit the slurry reactor with a gas-inducing impeller instead of a 6-bladed propeller was justified. The gas inducing impeller comprises of a stainless steel hollow impeller shaft with 5 mm gas inlet hole (at 230 mm from impeller end of the shaft) for gas headspace suction into the liquid phase via 3 gas dispersion (exit) ports (3.175 mm ID) located at the tip of each of the 4 blades of the impeller. Figure 4.2 shows the dimensions of the gas-inducing impeller used in this study. This impeller was fitted into a Parr reactor as depicted in Figure 4.3 with magnetic stirrer drive to ensure continuous rotation for longer runs typical of the FT reaction.

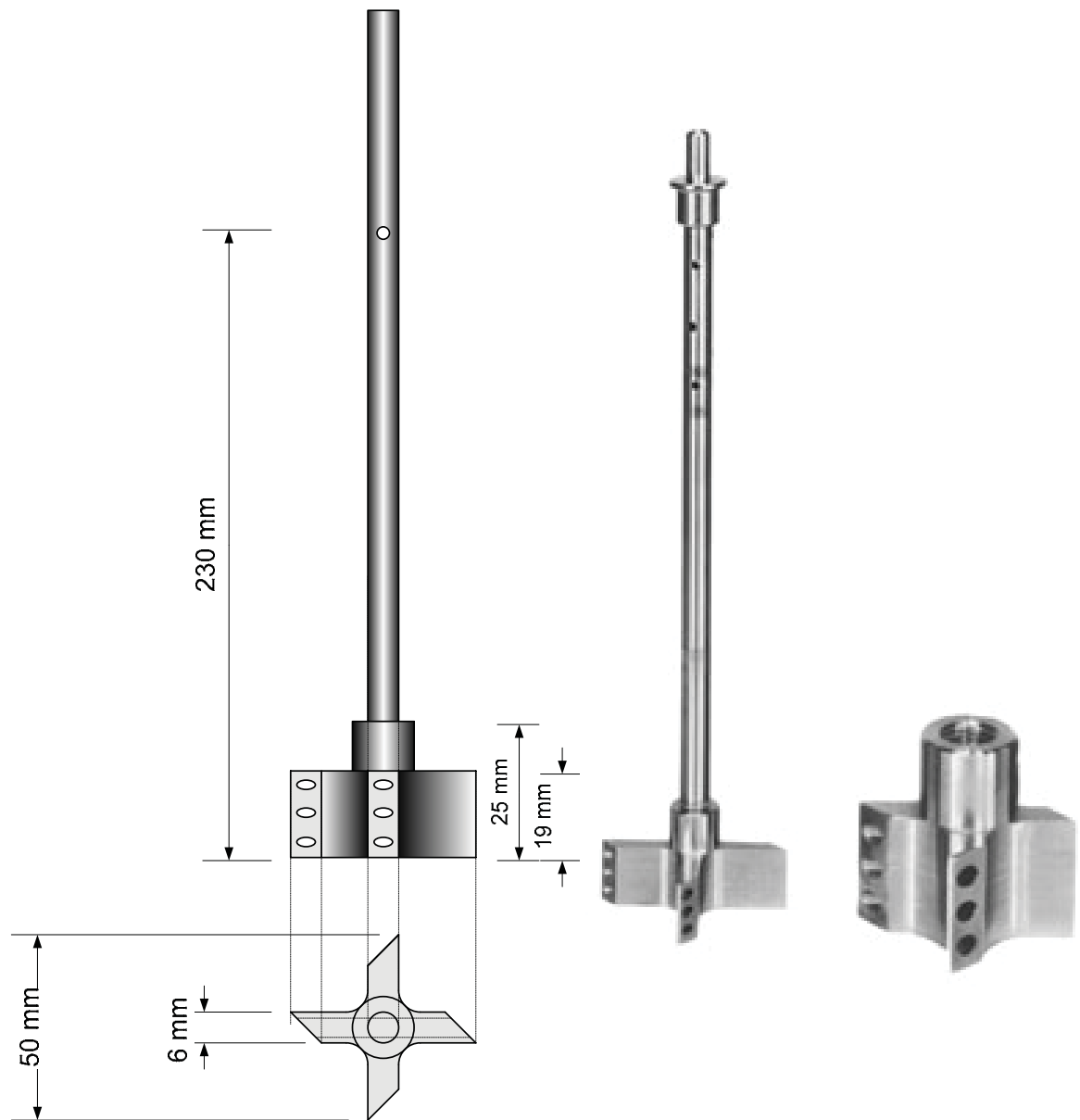


Figure 4.2 Schematic diagram of gas-inducing impeller

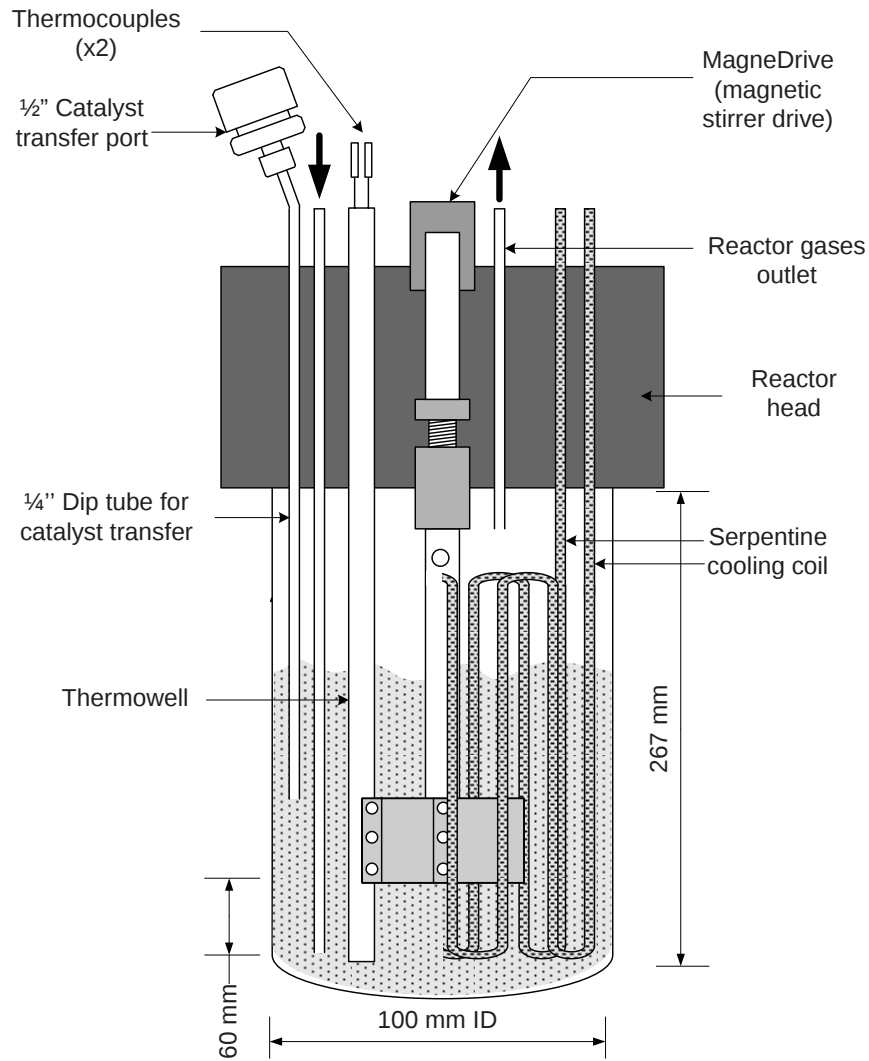


Figure 4.3 Schematic diagram of Parr reactor with gas-inducing impeller for FT synthesis

4.5.2. Critical impeller speed calculation

Gas flow through the gas-inducing impeller is based on the Bernoulli principle of differential pressure between the headspace (location 1) and the stirred blade orifice (location 2) given as

$$\frac{P_1}{\rho} + \frac{u_1^2}{2} + gh_1 = \frac{P_2}{\rho} + \frac{u_2^2}{2} + gh_2 \quad (4.4)$$

where,

P_1, P_2 = pressure at location 1 and 2

- u_1, u_2 = fluid velocity at location 1 and 2
- h_1, h_2 = static head at location 1 and 2
- ρ = density of the dispersed phase, in this case the gas phase
- g = gravitational acceleration, (9.81 m s⁻¹)

Based on this postulation, we adopted the correlation proposed by Sawant and Joshi [8] to determine critical impeller speed, N_{cs} for the gas-inducing impeller given as

$$\frac{N_{cs}^2 D_I^2}{gh} \left(\frac{\mu}{\mu_w} \right)^{-0.11} = 0.21 \quad (4.5)$$

Where,

- N_{cs} = stirrer rotational speed, rps (revolutions per second)
- D_I = diameter of impeller
- h = static head, height of liquid above the stirrer (0.036 m)
- μ = viscosity of paraffin oil at 503 K ($\mu = 5.91 \times 10^{-4}$ Pa.s)
- μ_{water} = viscosity of water at 298 K ($\mu_{water} = 8.90 \times 10^{-4}$ Pa.s)

Rearranging Equation (4.5) in the form of revolutions per minute (rpm) gives

$$N_{cs} = \frac{60}{D_I} \sqrt{0.21gh \left(\frac{\mu_{water}}{\mu} \right)^{-9.091}} \quad (4.6)$$

Equation (4.6) predicts the onset of gas induction at a stirring speed of 330 rpm. As a result, a preliminary investigation of the effect of stirring speed on reaction rate was done with agitation rate greater than 330

rpm. Indeed, to avoid both external mass transport and pore diffusional limitations, a stirring speed of 1200 rpm with catalyst average particle in the range 45-90 μm was used for all experiments. This experimental condition was later confirmed by the mass transfer limitation analysis elucidated in a subsequent subchapter.

4.5.3. Gas Induction Rate Calculation

Bernoulli equation can again be applied to estimate the gas flow rate, Q_G , through the orifice once the N_{cs} is obtained as

$$Q_G = A_{\text{orifice}} \sqrt{\left[\frac{\rho_L (1 - \varepsilon_G)}{\rho_G} + \varepsilon_G \right] \left[(\pi D_I N_s K)^2 + 2h_{f1} - 2gh \right] - 2hf_2} \quad (4.7)$$

where,

A_{orifice} = gas outlet orifice area

ε_G = gas phase hold-up

ρ_G = gas phase density

D_I = impeller diameter

N_s = impeller stirring speed (rps)

K = impeller speed loss coefficient

h_{f1} = energy loss in the turbulent field

h_{f2} = energy loss during gas flow through the impeller shaft from inlet to exit

For a relatively smooth hollow shaft, h_{f2} may be considered negligible while $gh \gg h_{f1}$. Consequently, at the critical impeller speed, N_{cs} where $Q_G = 0$, Equation (4.7) reduces to

$$(\pi D_I N_{cs} K)^2 = 2gh \quad (4.8)$$

or

$$K = \frac{\sqrt{2gh}}{\pi D_I N_{cs}} \quad (4.9)$$

Given that N_{cs} may be obtained from the Sawant-Joshi expression (cf. Equation 4.4) it is readily shown that

$$Q_g = A_{orifice}^T \sqrt{\left(\frac{\rho_l (1 - \varepsilon_g)}{\rho_g} + \varepsilon_g \right) \left(\left[\frac{N_s}{N_{sc}} \right]^2 - 1 \right) 2gh} \quad (4.10)$$

where $A_{orifice}^T$ is the total area for all orifices since there are 12 holes on the 4 impeller blades.

4.5.4. Reactor System Response

The response of the experimental system to a step change in gas phase composition (from pure nitrogen to argon) under typical FTS temperature and pressure provided the transport lag and characteristic time constant for the fluid phase mixing.

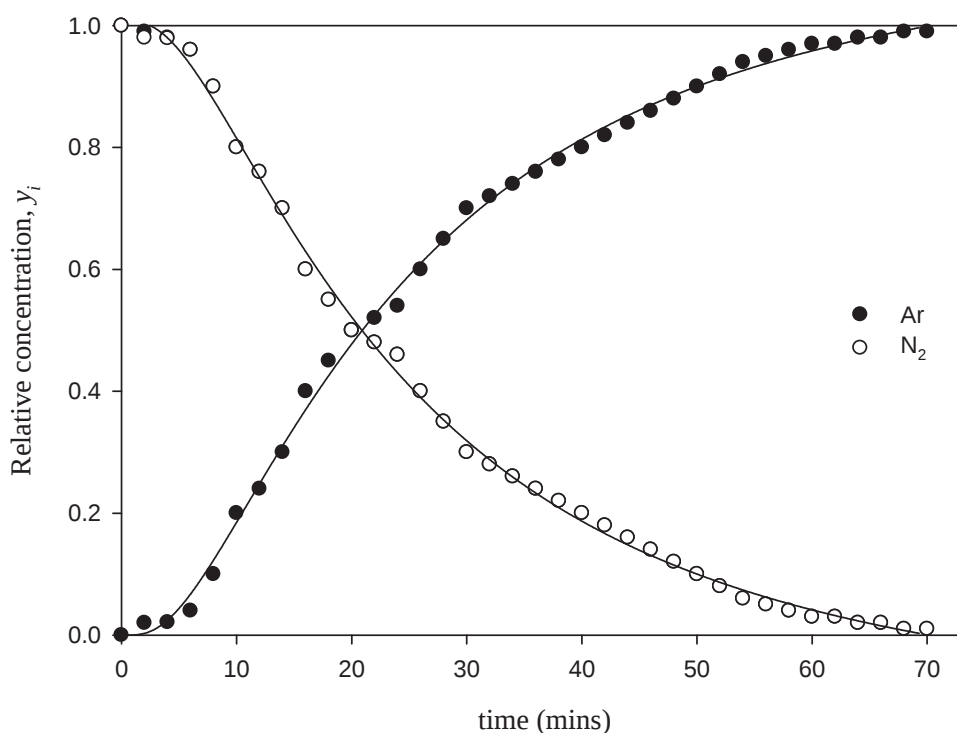


Figure 4.4 Experimental system response to a step change in feed gas composition (pure nitrogen to argon)

The data in Figure 4.4 were collected when the reactor was operated under identical conditions (temperature and pressure) to FT reaction but using pure Ar as the feed before an abrupt switch to pure N₂ stream. The GC was equipped with a FID and molecular sieve capillary column in order to detect the non-flammable stable gases. The overall volume of the slurry stirred tank assembly including gas mixer and condensers was significant. In addition the system was operated at high pressure. Therefore, hydrodynamics time delays must be present inherently within the system. Thus, there is a minimum time period after any changes to operating conditions to allow the system to equilibrate at a new set point. Thus, the hydrodynamics transient of the system was measured. The system response was carefully measured by carrying out the GC injection at two-minute intervals as seen in Figure 4.4. The system response seems to follow first order with time delay ($t_d=6$ minutes). This initial delay may have come from the significant length of stainless steel

tubing, condensers and gas mixer. The first order model can be expressed as:

$$y_i = \exp\left(-\frac{(t-t_d)}{\tau}\right) \text{ for Ar} \quad (4.11)$$
$$y_i = 1 - \exp\left(-\frac{(t-t_d)}{\tau}\right) \text{ for N}_2$$

Thus, the mixing first order time constant was found to be 26 minutes and time delay was 6 minutes, in agreement with response step change data in Figure 4.4.

4.5.5. Mass transfer limitation analysis

In a 3-phase slurry reactor, in particular involving a heterogenous catalytic reaction, 7 sequential steps interplay between reactant and catalyst phases as given below [9-11]:

1. Mass transfer of reactants from main flow to the external surface of the catalyst particle
2. Transport of the reactants by a diffusional process through the pores into the particle.
3. Adsorption of the reactants on the internal catalyst surface.
4. Chemical conversion in the adsorbed state.
5. Desorption of products.
6. Transport of products by a diffusional process through the pores of the particle to the surface.
7. Transport of products from the external surface of the catalyst particle to the bulk phase

Indeed, only steps 3, 4, and 5 truly represent the chemical kinetics of the system. The other steps (1, 2, 6, and 7) may substantially affect the overall reaction rate, while associated heat transfer processes may also be involved. Thus, preliminary experiments need to be conducted at conditions appropriate to ensure that only kinetic data is collected without the presence of transport resistances. In order to achieve this, preliminary runs at various catalyst loadings and stirring speeds were carried out in a stirred tank reactor equipped with gas-inducing impeller.

4.5.6. External mass transfer

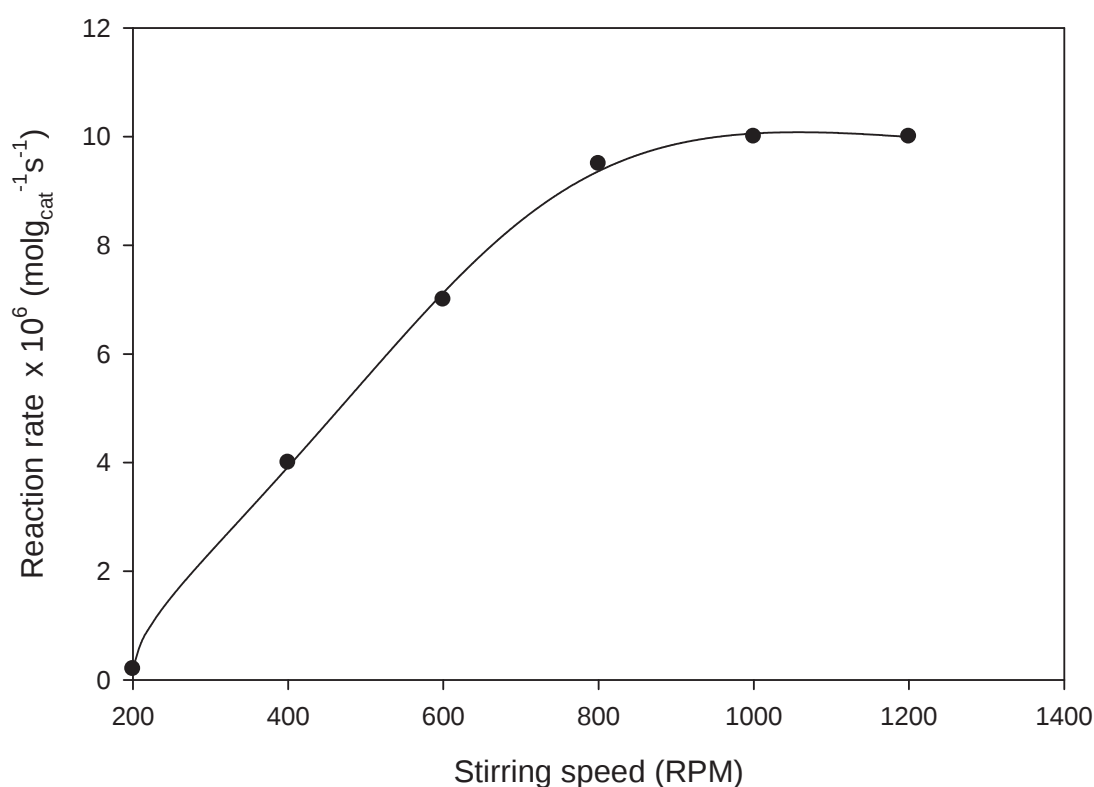


Figure 4.5 Rate of reaction as function of stirring speed, 498 K, 21 atm, H₂:CO=9:1

Figure 4.5 illustrates the effect of stirring speed on the reaction rate. It seems that the reaction rate became insensitive to the stirring speed above 800 rpm, implicating that the external mass transfer resistance may be neglected at stirring speeds beyond this threshold. Thus, a

stirring speed of 1200 rpm was employed in all subsequent FT synthesis runs.

4.5.7. Internal (Intra-particle) diffusion limitation

Internal or pore diffusion limitation can be deemed negligible if Hudgins 1968 [12] criterion is satisfied and given as;

$$\frac{r_{\text{exp}} d_p^2 |r'(C_0)n|}{D_{\text{eff}} r(C_0)} < 3 \quad (4.12)$$

where, the D_{eff} is the effective diffusivity of the primary reactant. It is confirmed that LHS of the Equation (4.12) has satisfied the criterion

$$\left(\frac{r_{\text{exp}} d_p^2 |r'(C_0)n|}{D_{\text{eff}} r(C_0)} = 2.98 \times 10^{-5} \right) \text{ for } n=3, \text{ and details of these calculations}$$

are provided in Appendix A7.

4.5.8. Catalyst loading criteria

The plot of reaction rate as function of catalyst loading as seen in Figure 4.6 suggests that the optimum loading for this system is around 10 g L⁻¹. Beyond this limit, increasing catalyst loading would not improve the reaction rate, therefore, a loading of 10 g L⁻¹ was used in all runs.

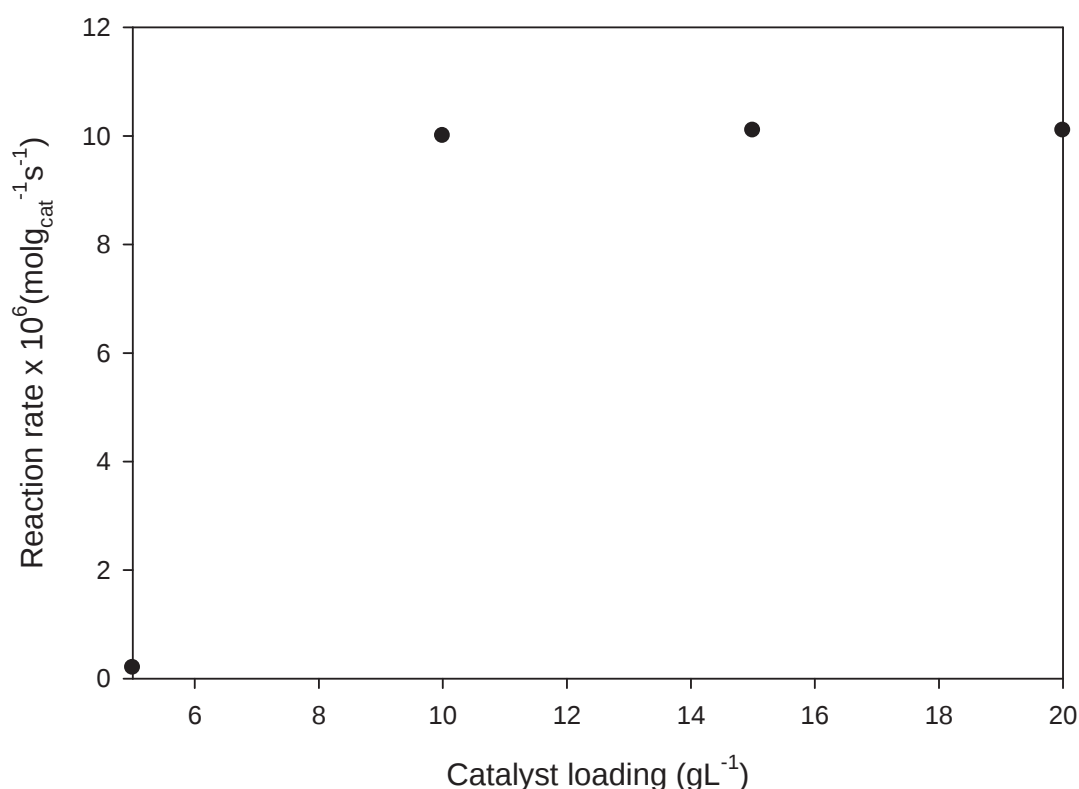


Figure 4.6 Reaction rate as function of catalyst loading, 498 K, 21 atm, H₂:CO=9:1

4.5.9. Blank test

This test was conducted to ensure there is no activity contribution other than by active metals (cobalt metal) in the catalyst. Blank test was prepared and tested without the presence of active catalyst (only alumina support) in similar operating conditions and procedures as with catalyst. The results indicated that the catalyst support as well as reactor material (stainless steel) were not active in the reaction.

4.6. References

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5 ■ Hydrodynamics and Mass Transfer in Gas-Liquid System

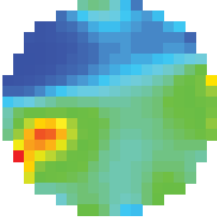
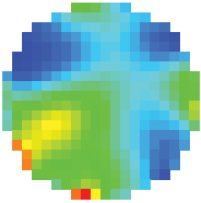
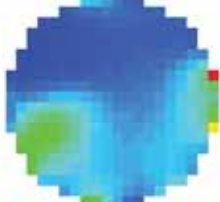
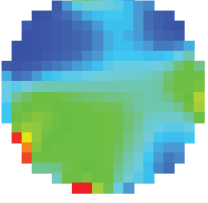
5.1. General Consideration

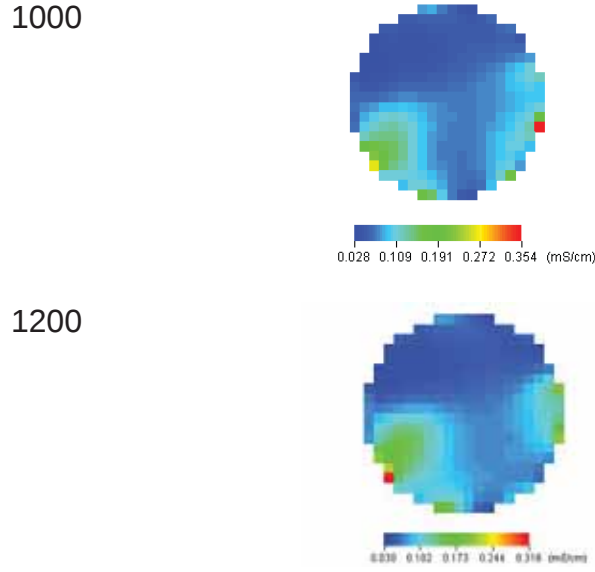
In this chapter, hydrodynamics of a gas-liquid system in a gas-inducing stirred tank reactor (GIST) has been studied both using electrical resistance tomography (ERT) and computational fluid dynamics (CFD) with particular emphasis on the gas volume fraction (hold-up). In a mass transfer study, three different types of reactor assembly were fabricated to investigate the efficacy of the gas-inducing impeller in comparison with conventional ones. Some materials presented in this chapter are excerpts from our publications, Abdullah *et al.* [1], in Chemical Engineering Science, Abdullah *et al.* [2], presented at the 5th International Symposium of Design, Operation and Control of Chemical Processes, and Abdullah *et al.* [3], to be submitted to Journal of Chemical Technology and Biotechnology.

5.2. Global analysis for the gas phase hold-up

The primary data from tomographic images were stored in terms of conductivity values. From this data, time-averaged pixel images were generated by the conductivity variation with spatial co-ordinates, as shown in Table 5.1.

Table 5.1 Tomographic images at different stirring speeds

Stirring speed (rpm)	Tomographic images
200	 0.026 0.067 0.109 0.150 0.191 (mS/cm)
400	 0.029 0.059 0.090 0.121 0.151 (mS/cm)
600	 0.029 0.101 0.173 0.244 0.315 (mS/cm)
800	 0.030 0.070 0.109 0.149 0.189 (mS/cm)



Qualitatively the blue colour intensity increases with stirring speed, implying that at higher stirring speed gas occupied more space due to the increase in formation and break up of air bubbles from the gas-inducing impeller. Hence, conductivity decreased with increasing stirring speed.

The dispersed phase hold-up, ε_D , can be determined using the Maxwell relation (cf. Equation (3.2) in chapter 3). If the dispersed phase is a non-conductive material, such as air, the expression may be further simplified to:

$$\varepsilon_G = \frac{2\sigma_1 - 2\sigma_m}{2\sigma_1 + 2\sigma_m} \quad (5.1)$$

Figure 5.1 depicts the increase of gas phase hold-up with impeller Reynolds number, Re_I and tends to plateau beyond $Re_I = 6.25 \times 10^4$. It is interesting to observe that the gas phase hold-up, ε_G , can be reasonably captured by 3-parameter Chapman-Richards model given by

$$\varepsilon_G = \varepsilon_{G,\max} \left[1 - \exp(-\tau_{gpp} Re_I) \right]^{\gamma_G} \quad (5.2)$$

where,

$\varepsilon_{G,max}$	= gas phase hold-up for infinitely fast stirring (maturity)
τ_{gpp}	= non-dimensional gas phase mixing time constant (growth)
γ_G	= exponent related to the gas bubbles clustering activity (birth)

The parameters estimate based on non-linear regression analysis as tabulated in Table 5.2 represent the curve in Figure 5.1.

Table 5.2 Parameters estimate from Equation (5.2) for global ε_G distribution

Parameter	$\varepsilon_{G,max}$	$\tau_{gpp} \times 10^5$	γ_G
	0.068±0.000	6.0±0.015	2.473±0.006

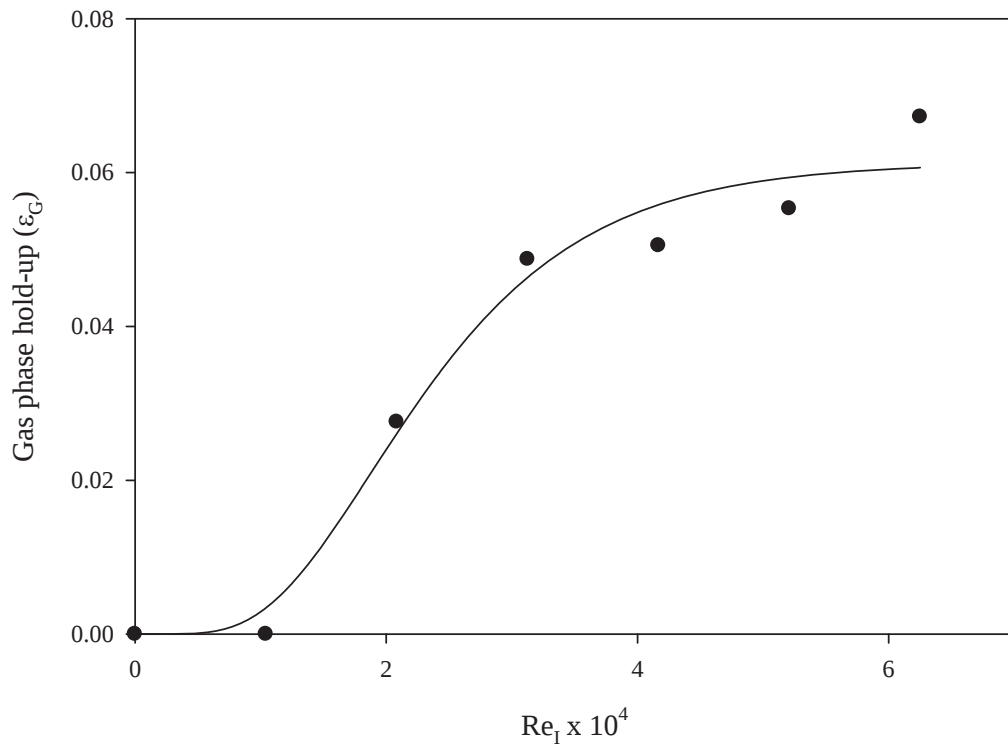


Figure 5.1 The effect of impeller Reynolds number, Re_I , on gas phase hold-up.

This behaviour is expected since the maximum gas flow rate through the orifice (fixed diameter) is determined by the head-space pressure (e.g. atmospheric) for a given liquid depth and further increase in gas suction will be capped once the speed corresponding to this maximum has been attained. In particular, the data for the gas-liquid runs revealed that gas flow into the liquid phase did not commence until a stirring speed just above 200 rpm ($Re_I = 10417$) was used. This suggests that the critical agitation speed for gas induction, N_{CS} , must be at least 200 rpm. The critical stirring speed, N_{CS} , given by Sawant and Joshi [4] in this system (air-water system) was estimated as the $N_{CS} = 3.883$ rps or 233 rpm ($Re_I = 1.2 \times 10^4$) which is consistent with the visible lack of liquid phase aeration for the runs conducted at impeller rotational speed up to 200 rpm in the set of gas-liquid experiments [1].

5.3. Local analysis of gas hold-up distribution

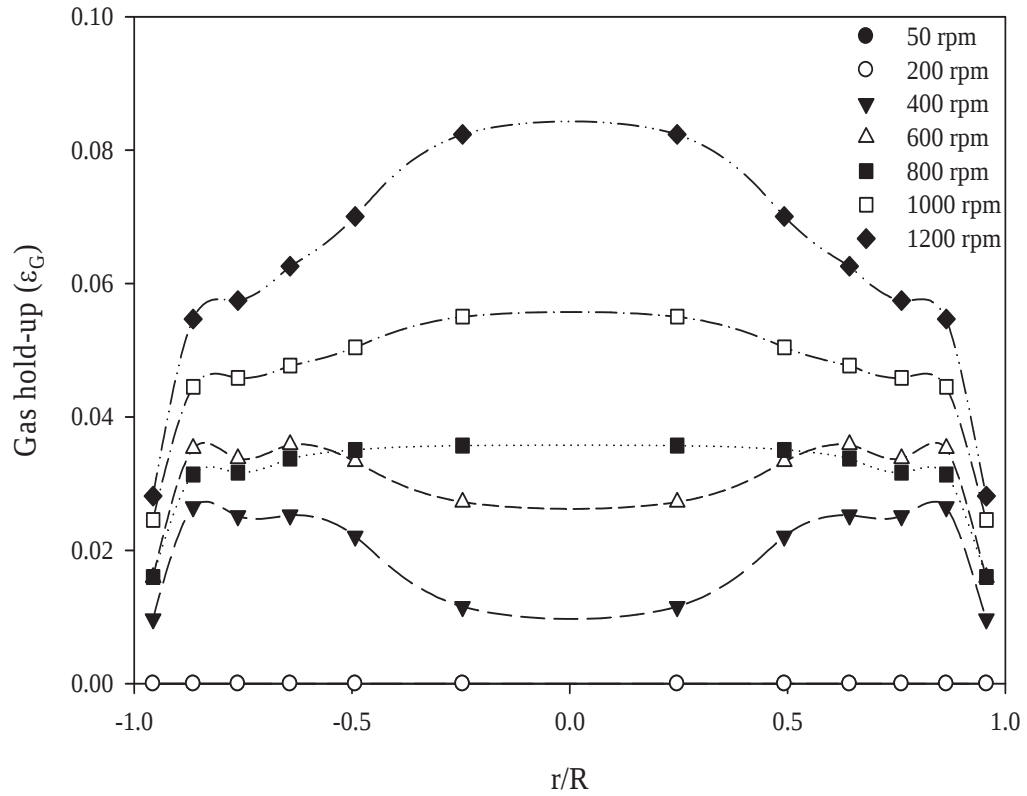


Figure 5.2 Radial distribution of gas phase hold-up in stirred tank reactor

The profiles reveal the parabolic nature of the dispersed phase hold-up with respect to radial distance. As may be seen from Figure 5.2, at rotational speed below 800 rpm ($Re_t = 4.17 \times 10^4$), the gas phase hold-up passed through a minimum at the centre ($r/R = 0$) but above this crossover speed, the profiles have a maximum at the centre.

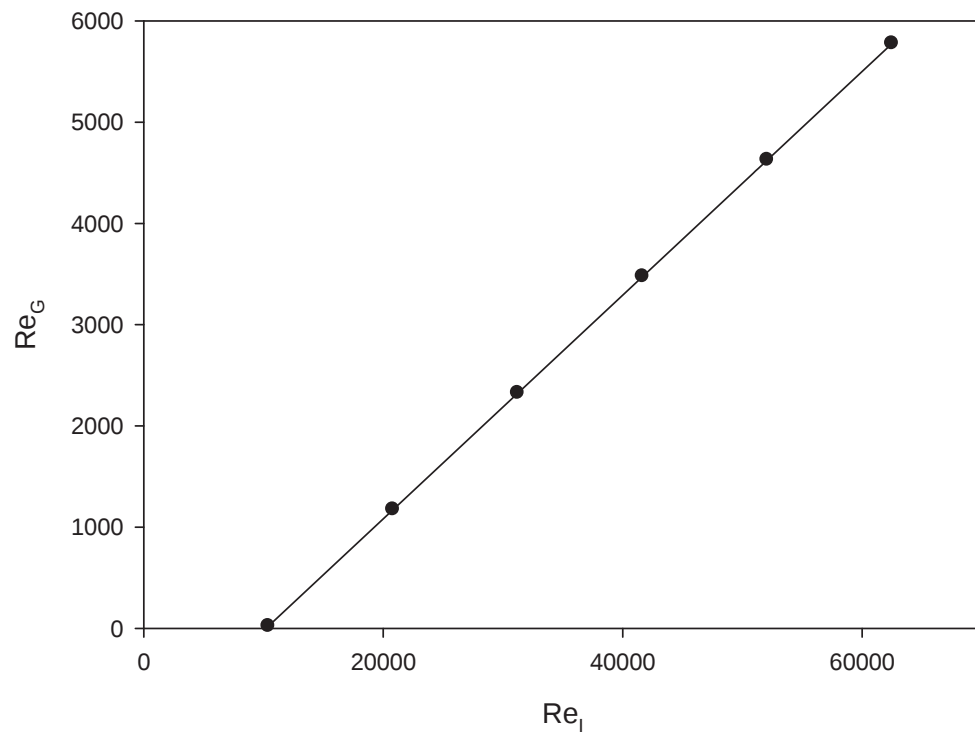


Figure 5.3 Gas Reynolds number (Re_G) as a function of impeller Reynolds number (Re_I)

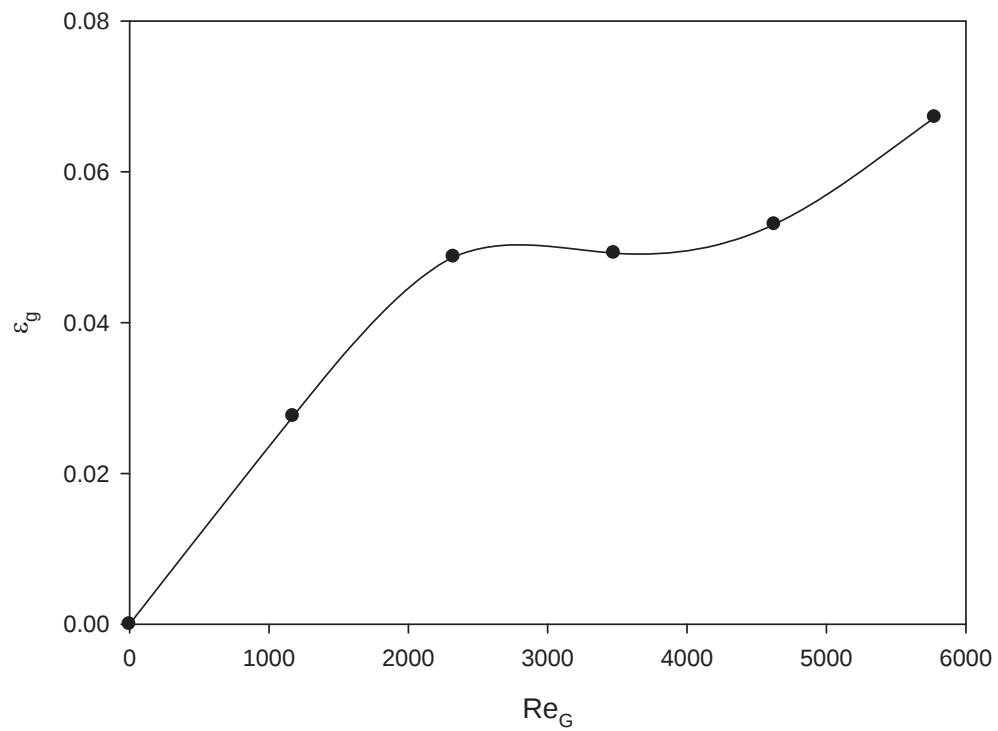


Figure 5.4 Gas phase hold-up (ϵ_g) as a function of Gas Reynolds number (Re_G)

Interestingly to note that at this stirring speed, it corresponds to gas flow ($Re_G \approx 3.5 \times 10^3$) in the transition stage to churn-turbulent flow. Gas phase hold-up passes through a minimum at the centre at gas flow ($Re_G < 2500$; $Re_l < 3.1 \times 10^4$) as shown in Figure 5.4 in laminar region. In this region, the gas flow was due to a predominant radial flow as it emerged from gas orifices and relatively low (rise) gas velocity causing a high gas concentration in the annular space between the baffle and impeller blade. Nonetheless, at high impeller speed (> 800 rpm), the liquid phase pushed towards the vessel wall with the gas phase displaced inwards and concentrated in the vicinity of the shaft as a result of vortex effects. Thus, this explains the maximum concentration of gas phase hold-up observed in this condition. However, in all cases, behind the baffle ($0.86 \leq r/R \leq 1.0$), the gas hold-up dropped abruptly may be due to presence of boundary layer in this region.

5.4. Computational Fluid Dynamics Modelling

5.4.1. Reactor geometry

Figure 5.5 illustrates the GAMBIT meshing representation of the stirred tank reactor with gas-inducing impeller. The vessel specifications are provided in Table 5.3. Each of the blades consists of three orifice ports (3.175 mm diameter) through which gas was dispersed into the liquid phase. Unsteady-state 3-D simulation was performed at stirring speeds between 200-1200 rpm in the stirred tank reactor using FLUENT 6.3 with geometry created using GAMBIT 2.4. Specifications used in this simulation were pre-collected from the experimental runs performed earlier in our laboratory.

Table 5.3: Stirred tank reactor specifications and dimensions.

Specification	Value
Vessel diameter	100 mm
Vessel height	277 mm
Liquid height	127.3 mm
No of blades	4
Impeller height above the vessel bottom	90 mm
Impeller diameter	50 mm

The governing differential equations were solved using the finite control volume technique for the entire vessel. A Volume of Flow (VOF) method coupled with discrete phase model (DPM) was employed to simulate the behaviour of the gas-liquid solid system in the stirred tank reactor. Liquid was considered as the continuous phase and gas bubbles the dispersed phase. A multiple reference frame (MRF) approach was used for the simulation on the impeller rotation, with the vessel divided into two zones. This method reduced the computation time by an order of magnitude and has been successfully employed by others [5-7]. The rotating domain was positioned at $r = 52$ mm and $87 \text{ mm} \leq z \leq 124 \text{ mm}$. Tetrahedral elements were used for meshing the entire geometry. Mesh independent study has been performed using two different grid sizes i.e 1 mm^2 and 0.01 mm^2 . The results for finer grid size (0.01 mm^2) only gave <5% improvement as compared to coarser grid size (1.0 mm^2). Thus, for subsequent simulation runs, the grid size of 1.0 mm^2 would be used.

All governing equations were discretised using second-order upwind differencing and first order implicit scheme for time integration. A high quality mesh (skewness < 0.8) with over one million grid elements has been employed throughout the computational domain as depicted in Figure 5.5. Unsteady-state simulations were then carried out for a flow

time of 10 s with initial time step of 10^{-5} s followed by a gradual increase to 10^{-2} s.

Electrical resistance tomography (ERT) was employed for verifying the data obtained from CFD. The stirrer shaft was a stainless steel pipe (ID = 5 mm), while the impeller head was made of brass. The gas inlet port on the shaft was a 5 mm hole located at 6.5 mm above the liquid surface. To minimise fluid vortex formation and promote mixing, the vessel was equipped with baffles in the form of 8 PVC rods as shown in Figure 5.5.

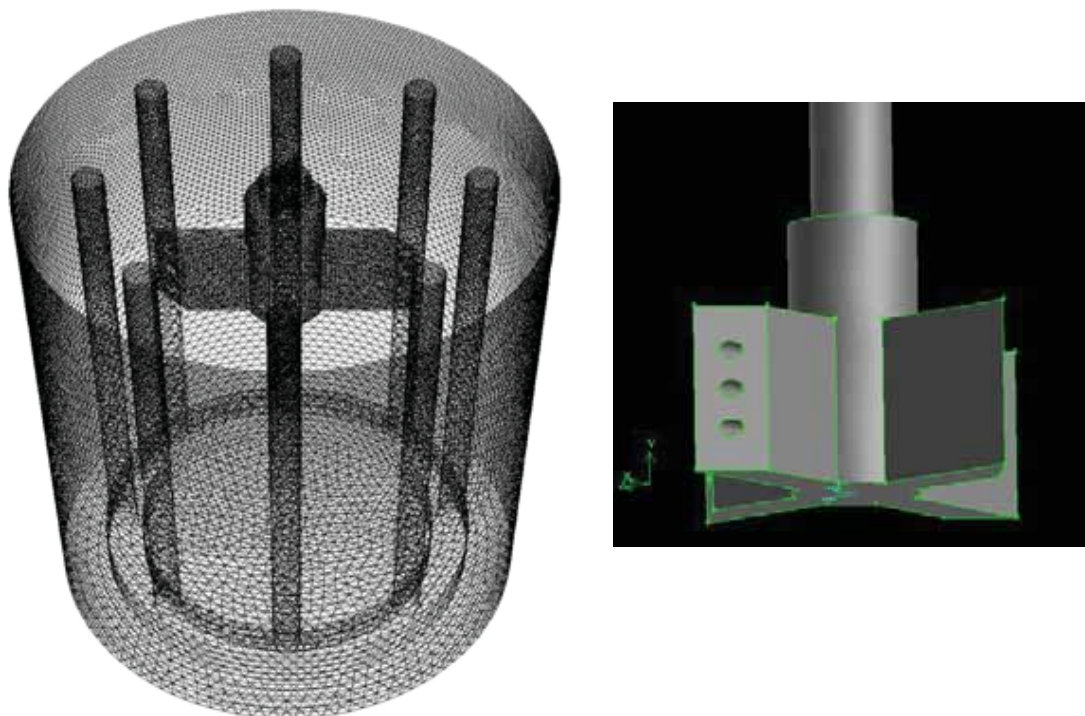


Figure 5.5: Finite volume grid for stirred tank reactor with gas-inducing impeller

The ERT sensor located 55 mm above the vessel bottom was a 16-electrode cylindrical basket that snugly fitted to the vessel interior. Data collection was done via a dual tomography unit, M3000 supplied by Industrial Tomography Systems (Manchester, UK). Image reconstruction utilized a non-iterative algorithm based on linear back projection method for real-time imaging at one frame per second. In addition, the Maxwell relationship (cf. Equation 3.2)) was used to determine global gas hold-up from the volume-averaged conductivity data.

5.4.2. Governing equations for two-phase system

Modelling of the gas-liquid system was carried out using VOF model, where all the phases involved were modelled by local, instantaneous conservation equations for mass and momentum. The volume average continuity equation for the k^{th} phase is given by [7]:

$$\frac{\partial(\varepsilon_k \rho_k)}{\partial t} + \nabla \cdot (\varepsilon_k \rho_k \langle U_k \rangle) = 0 \quad (5.3)$$

where ρ_k is the density, ε_k is the volume fraction, and U_k is the velocity vector of k^{th} phase. The corresponding momentum equation is given as

$$\begin{aligned} & \frac{\partial(\varepsilon_k \rho_k \langle U_k \rangle)}{\partial t} + \nabla \cdot (\varepsilon_k \rho_k \langle U_k \rangle \langle U_k \rangle) \\ &= -\varepsilon_k \nabla p + \nabla \cdot \left(\varepsilon_k \mu_{\text{eff},k} \left\{ \nabla \langle U_k \rangle + (\nabla \langle U_k \rangle)^T \right\} \right) + \varepsilon_k \rho_k g - F_k \end{aligned} \quad (5.4)$$

where p is the static pressure, μ_{eff} is the effective viscosity, g is an acceleration due to gravity, and F_k represents the inter-phase momentum transfer force.

The interactions between the gas and liquid phase were accounted for via momentum exchange mechanisms such as drag, lift and added mass force. However, only the contribution of drag force was considered in this study [8, 9]. The drag coefficient exerted by the gas phase on the liquid phase is the important parameter to be considered in the CFD modelling. A correlation of the Brucato drag model [10] was used:

$$\frac{C_{DAvg}}{C_{D,0}} = 1 - 8.76 \times 10^{-4} \left(\frac{d_p}{\lambda} \right)^3 \quad (5.5)$$

and

$$C_{D,0} = \max \left\{ \left(\frac{2.667 E_0}{E_0 + 4} \right) \left(\frac{24}{Re_b} (1 + 0.15 Re_b^{0.687}) \right) \right\} \quad (5.6)$$

where C_{DAvg} is the averaged drag coefficient, $C_{D,0}$ is the drag coefficient in the stationary liquid, λ is the Kolmogoroff scale of turbulence and d_p is the bubble diameter. The correlation developed by Sawant and Joshi [11] (cf. Equation 3.11) permitted the estimation of the critical impeller speed (for which gas recirculation through the liquid phase commenced) and was in fact, corroborated by preliminary experimental data in this study.

5.4.3. Bubble break-up and coalescence model

In FLUET, the bubble break-up and coalescence model are based on the conservation of bubble number density equation and can be written as;

$$\frac{\partial n}{\partial t} + \nabla \cdot (n \mathbf{U}_G) = k_{br} n - k_{co} n^2 + \phi_{in} \quad (5.7)$$

where ϕ_{in} is the gas source at orifices blade. Thus, the break-up term is first order and coalescence term is second order. The terms k_{br} and k_{co} are defined as follows:

$$k_{br} = C_{br} (1 - \varepsilon_2) \left(\frac{k_\varepsilon}{d^2} \right)^{1/3} \exp \left(\frac{we_c}{We} \right), \quad We \geq we_c; \quad k_{br} = 0, \quad We < We_c \quad (5.8)$$

and

$$k_{co} = C_{co} (1 - \varepsilon_2) k_\varepsilon^{1/3} d^{7/3} \exp(-C_2 \sqrt{We}) \exp \left(-k_{co} \frac{d^3}{\varepsilon} \right) \quad (5.9)$$

where k_ε is the energy dissipation rate per unit mass. When Weber number, We , exceeding We_c , the coalescence and break-up are competing with each other. Nonetheless, the coalescence term becomes insignificant at high We . For this model to be included in FLUENT, the equation for bubble number density needs to be in scalar variables. Thus, additional variable Θ is introduced as follows;

$$\frac{\partial \rho_G \varepsilon_G \Theta}{\partial t} + \nabla \cdot (\rho_G \varepsilon_G \Theta \mathbf{U}_G) = \varepsilon_G S_G \quad (5.10)$$

and modified bubble number density, n' , is given as:

$$n' = \frac{n}{\varepsilon_G} \quad (5.11)$$

In this study, the compressibility of the gas is considered insignificant since the hydrostatic pressure was not large. Therefore, n' is simply reciprocal of the characteristic local bubble volume,

$$n' = \frac{1}{\frac{\pi}{6} d_B^3} \quad (5.12)$$

Hence, Equation (5.10) becomes;

$$\frac{\partial \rho_G \varepsilon_G n'}{\partial t} + \nabla \cdot (\rho_G \varepsilon_G n' \mathbf{U}_G) = \rho_G \varepsilon_G (k_{br} n' - \varepsilon_G k_{co} n'^2) + \varepsilon_G S_i \quad (5.13)$$

and

Source term, S_i , is given by;

$$S_i = \rho_G (u_s A_T) \left[\frac{1}{\frac{\pi}{6} d_0^3} \right] \quad (5.14)$$

where,

d_0 = initial bubble size

u_s = superficial velocity

A_T = Total area of the orifices on impeller blade

5.4.4. Gas phase hold-up calculation

The transient profiles of the gas phase hold-up at different stirring speeds are shown in Figure 5.6 where it is evident that gas phase hold-up increased with time for a given impeller speed until a final steady-state value was reached. Indeed, the gas phase hold-up value, ε_G , also increased with stirring speed suggesting that the gas recirculation rate through the fixed volume liquid phase improved with stirring.

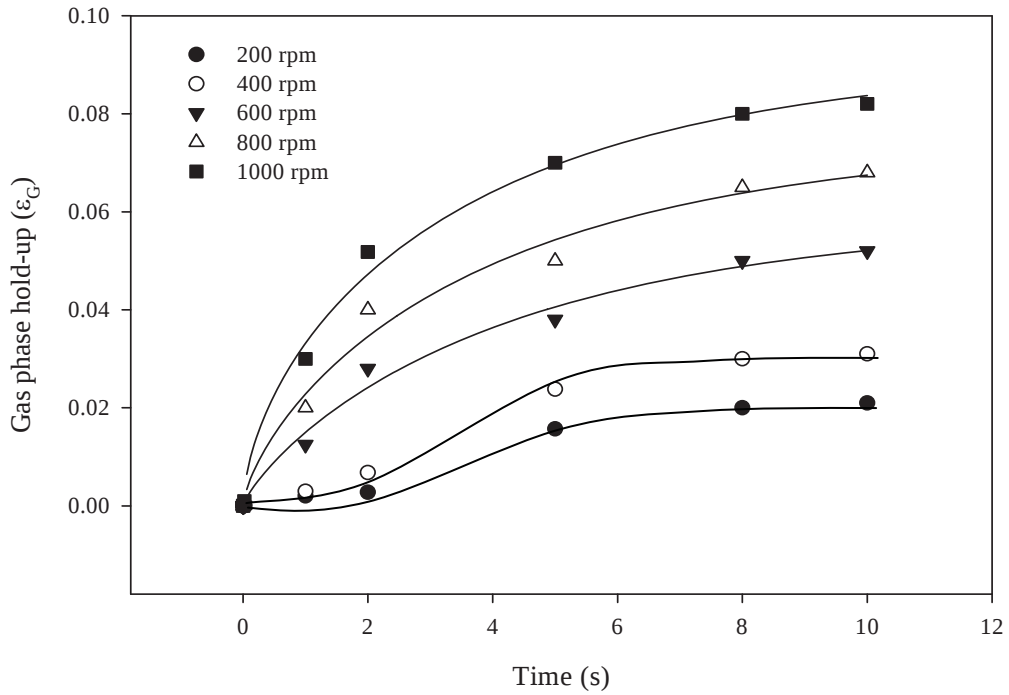


Figure 5.6 Transient profile for gas phase hold-up at different stirring rates

We have previously shown that the gas recirculation rate, Q_G , through the liquid phase for the gas-inducing impeller increases with stirring speed (after N_{cs} has been breached) and is given by [12];

$$Q_G = A_{orifice}^T \sqrt{\left(\frac{\rho_L (1 - \varepsilon_G)}{\rho_G} + \varepsilon_G \right) \left(\left[\frac{N_s}{N_{cs}} \right]^2 - 1 \right) 2gh} \quad (5.15)$$

Whilst the gas hold-up at impeller speeds greater than 600 rpm rose almost exponentially to its steady-state value, the behaviour at slow stirring rate is a sigmoid, characterized by an initial slow rise followed by a relatively rapid rise before attaining the final plateau. It would therefore seem that the step responsible for the initial slow rise was probably short-circuited with increased stirring rate. The hydrodynamics of gas flow through the liquid phase after exiting the impeller orifices involves both bubble break-up and coalescence [8, 13]. Additionally, as the initial gas bubbles emerged out of the orifice, they were subjected to both radial and axial momentum forces culminating in surface evolution into the headspace above the liquid from where gas was sucked in again (via the inlet port) down through the hollow shaft and back into the liquid phase. A combination of these independent mechanisms within the liquid phase was responsible for the observed gas hold-up dynamics. As a result of these considerations, and given that the minimum speed employed in this study (200 rpm) located gas-liquid mixing in the turbulent region ($Re_i = NsD_i^2\rho_L/\mu_L > 10^4$), the transient profiles may be described by a common Laguerre equation, viz;

$$\varepsilon_G(t) = AL_2(t) + BL_1(t) + CL_0(t) \quad (5.16)$$

where $L_i(t)$ is the Laguerre polynomial of order i with A , B and C as stirring speed-dependent coefficients. From a functional analysis perspective, Equation (5.16) captures the essential features of bubble population dynamics in the liquid phase related to birth, growth and death especially because of the exponential characteristics of these fundamental processes even though the detailed physics governing these primary mechanisms is not fully understood [13, 14]. Since $L_i(t)$ is an orthogonal polynomial in the sense;

$$\int_0^\infty e^{-t} L_j(t) L_k(t) dt = 0 \quad j \neq k \text{ but } j, k \in i \quad (5.17)$$

Then, $L_i(t)$ represents the independent primary phenomena underlying the hydrodynamic processes. Furthermore, Equation (5.17) satisfies the time domain $[0 \leq t \leq \infty]$ where e^{-t} is the weighting function. Regression of the data across time and stirring speed, N_s (rps), yields estimates in Table 5.2. Consequently, Equation (5.5) written as;

$$\varepsilon_G(t) = 1.6 \times 10^{-3} e^{0.1661N_s} L_0(t) - 2.2 \times 10^{-3} e^{0.1238N_s} L_1(t) - 7.0 \times 10^{-5} e^{0.1913N_s} L_2(t) \quad N_s \geq N_{sc} \quad (5.18)$$

where $L_0(t) = 1$; $L_1(t) = 1-t$ and $L_2(t) = t^2 - 4t + 2$. The orthogonal functions, $L_0(t)$, $L_1(t)$ and $L_2(t)$ relate to the production (birth), bubble coalescence and bubble break-up processes respectively.

Table 5.4: Parameter estimates for Equation (5.16)

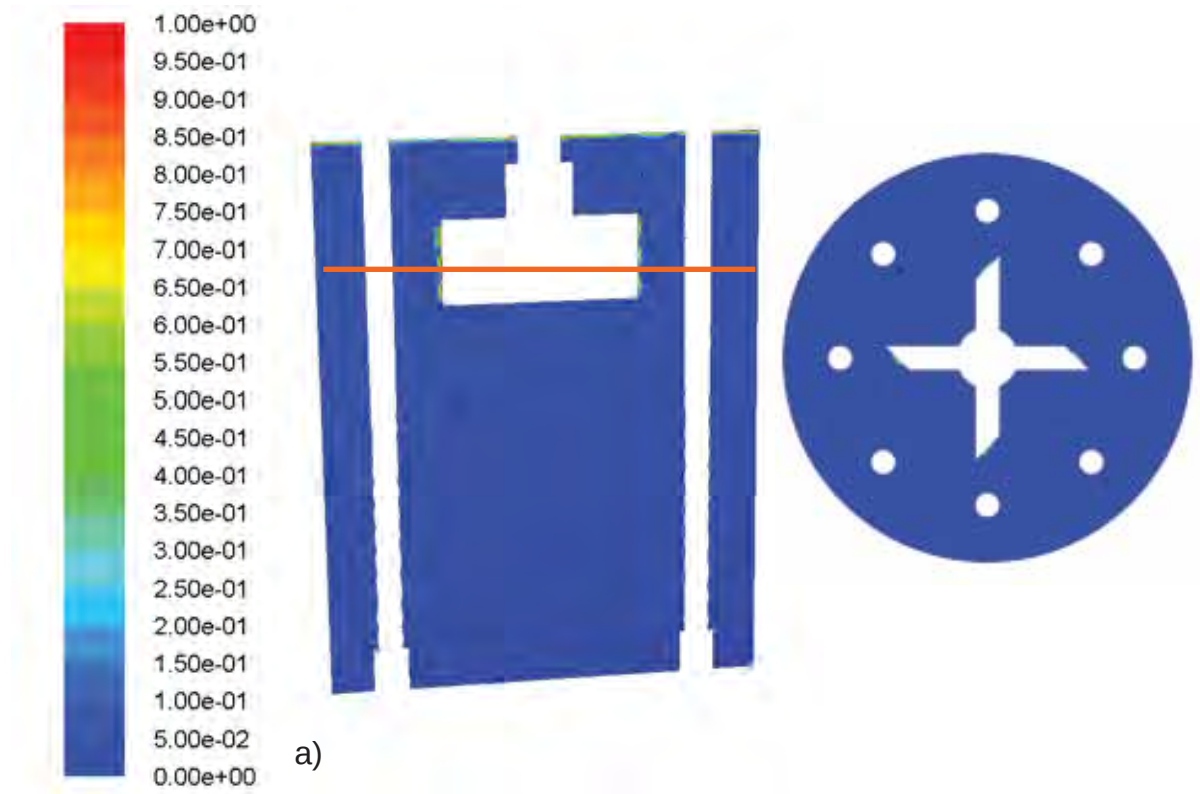
$N_s(\text{rps})$	A	B	C
3.33	-0.0001±0.0000	-0.0032±0.0000	0.0027±0.0000
6.67	-0.0003±0.0000	-0.0046±0.0000	0.0043±0.0000
10.00	-0.0006±0.0000	-0.0089±0.0001	0.0113±0.0002
13.33	-0.0009±0.0000	-0.0117±0.0001	0.0162±0.0002
16.67	-0.0014±0.0000	-0.0158±0.0002	0.0223±0.0002

Analysis of Equation (5.18) suggests that the time to attain steady-state, t_{ss} , is given by;

$$t_{ss} \geq 2 + 15.71e^{-0.0675N_s} \quad \text{for } N_s \geq N_{cs} \quad (5.19)$$

which provides estimates between 7 to 14 seconds over the range of stirring speed examined and hence, justifies the use of 10 seconds for our computational time although a period of 8 seconds has been most commonly used in different studies [15]. Figure 5.7 shows the contour of gas phase hold-up at different times. The onset of gas dispersed into the liquid starts around 0.2 s. The dispersion of gas bubbles from the orifice ports commences when the reduction in pressure at this region (on the

impeller blade) is sufficient to overcome the static pressure above the liquid level. This phenomenon has been discussed in Rielly *et al.* [16] and Deshmukh *et al.* [17]. Moreover, the flow pattern in Figure 5.8 (CFD image of the rotating impeller) also reveals that the gas accumulated behind the impeller by forming gas cavities. This behaviour has been previously observed by Murthy *et al.*, [15, 18] using different types of gas-inducing impeller design. Consequently, the immediate vicinity of the stirrer shaft experienced a high gas hold-up.



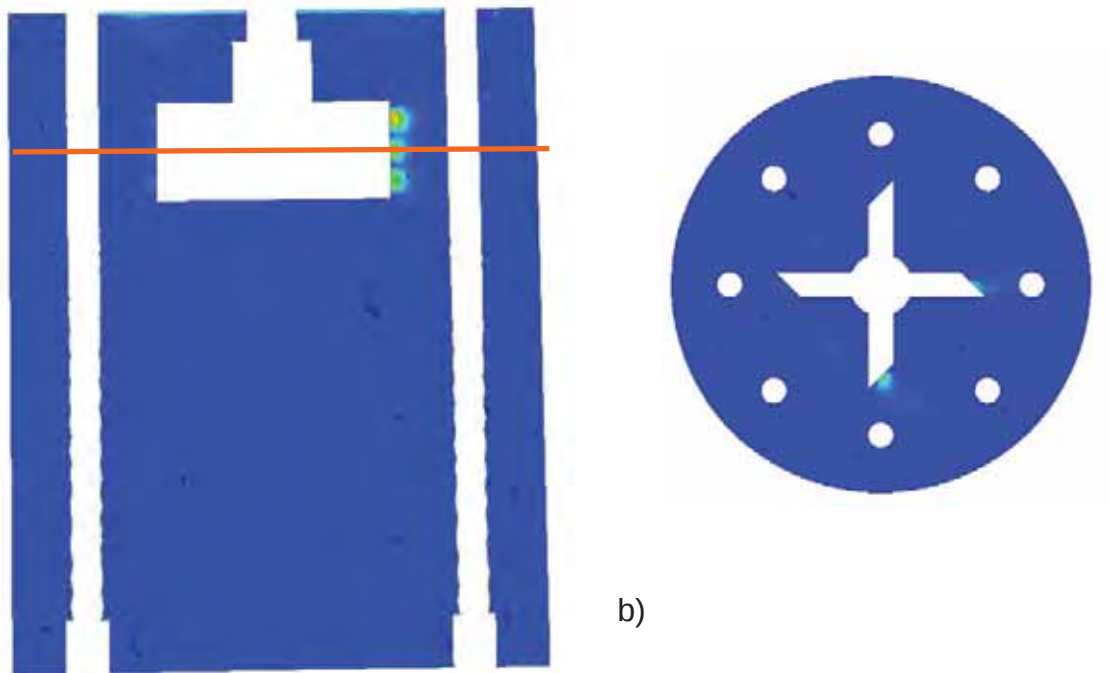


Figure 5.7 Contour of gas phase hold-up at 400 rpm at different time a) 0.01 s b) 0.2 s

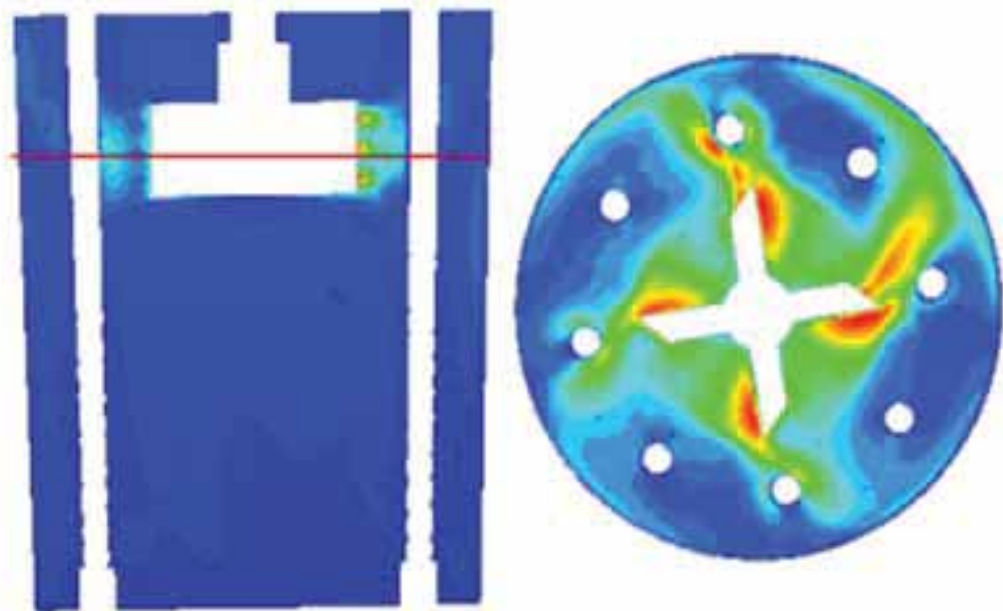


Figure 5.8 Contour of gas phase hold-up at 400 rpm at 10 s

5.4.5. Effect of stirring speed

The effect of stirring speed on the steady-state global (averaged ERT data over the cross-sectional plane) gas phase hold-up is illustrated in Figure 5.9. It is apparent from this plot that CFD results are in reasonable agreement with the tomographic measurements. The gas phase hold-up at steady state condition ($t=10$ s), ε_G is adequately captured by;

$$\varepsilon_G = \varepsilon_{G,\max} (1 - \exp[-\tau_{br} N_s]) \quad (5.20)$$

where

$\varepsilon_{G,\max}$ = gas phase hold-up at infinite stirring speed

τ_{br} = bubble rise time, minute

N_s = stirring speed, rpm

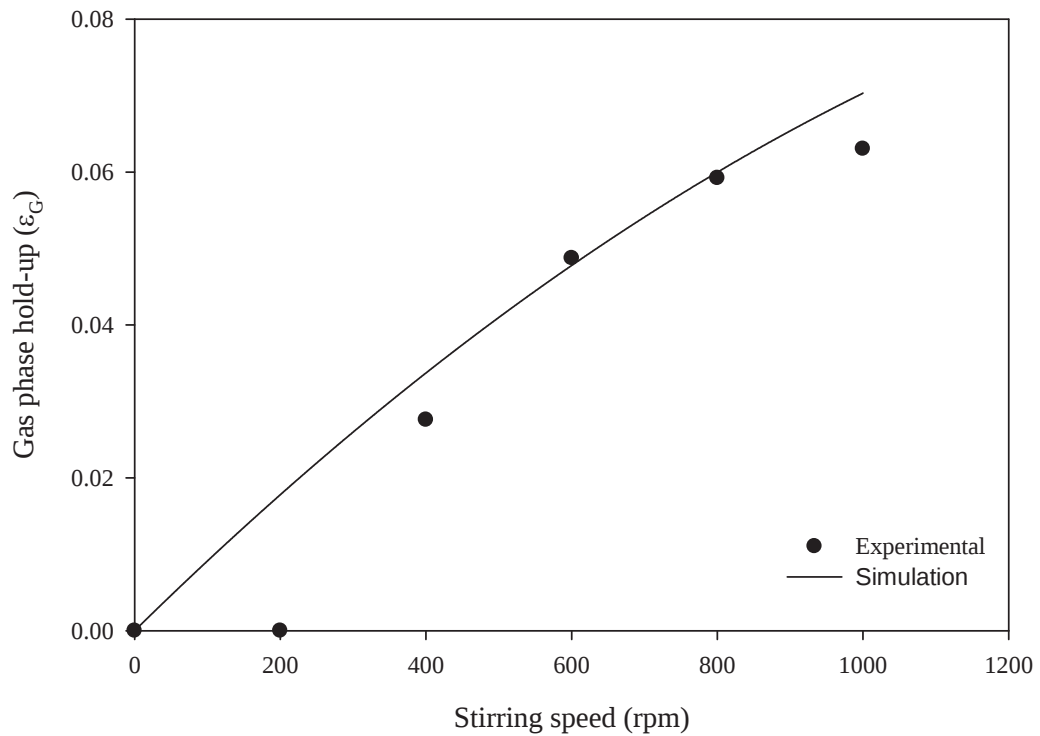


Figure 5.9 Influence of stirring speed on steady-state global gas phase hold-up

and τ_{br} is equal to 10^{-3} mins. The parity plot in Figure 5.10 shows a reasonably good agreement was obtained between experimental and

simulated values with an exception at 200 rpm. At lower stirring speed, CFD fails to predict the gas-phase hold-up that may have contributed from the simplified drag coefficient used in this study and exclusion of mass and lift forces in momentum equations.

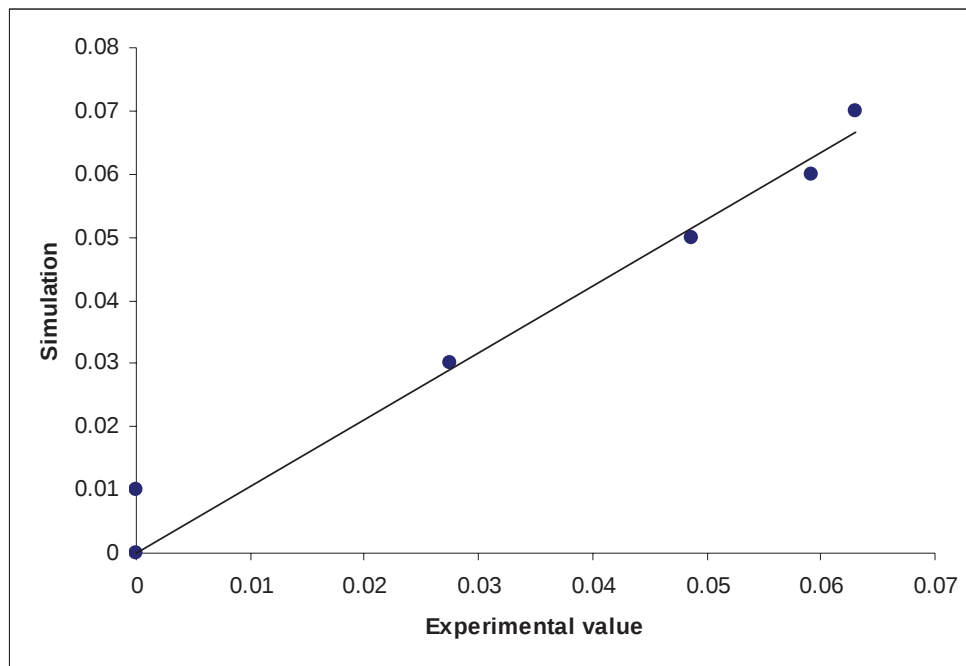


Figure 5.10 Parity plot

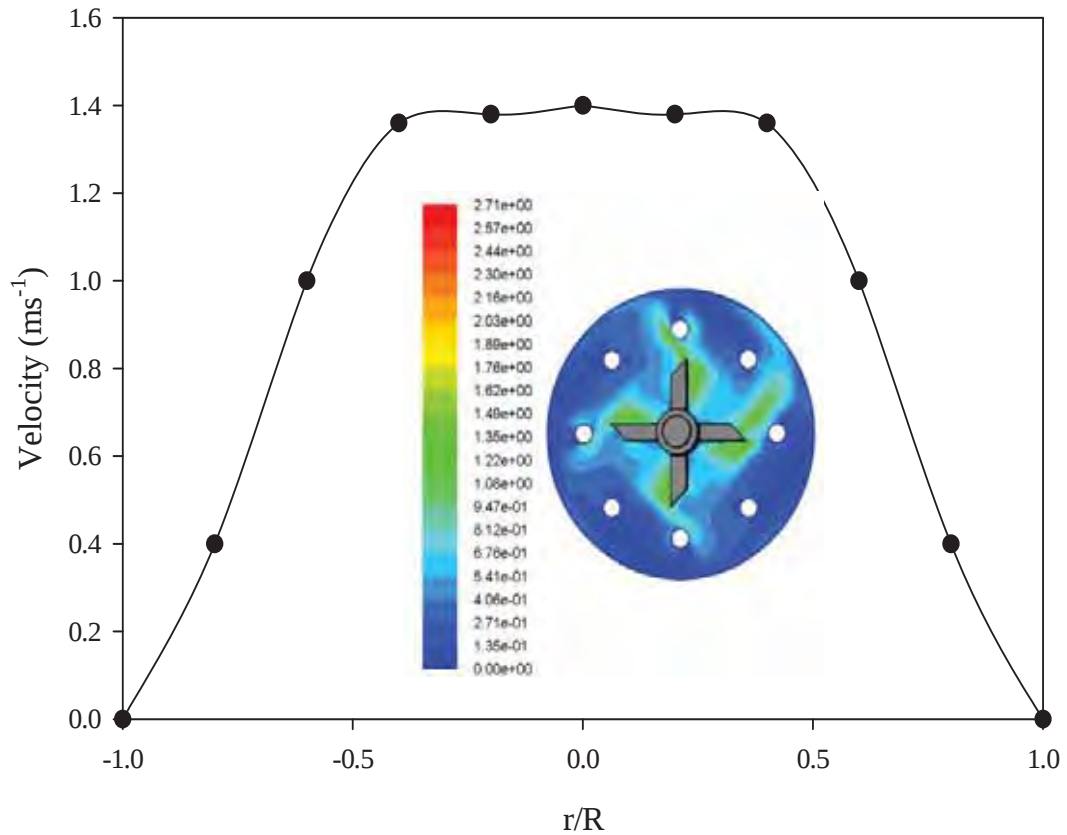


Figure 5.11 Velocity profile at 400 rpm (8 s)

The radial velocity profile shows a maximum at the centre ($r/R=0$), was almost constant within the impeller region ($0 \leq r/R < 0.5$) and dropped rapidly towards the tank wall as seen in Figure 5.11.

Figure 5.12 shows the vector flow field at the impeller rotational speed of 400 rpm. It can be seen the impeller pumps the liquid in an outward direction (radially) before a vertical rise and ultimately returning downwards along the wall. Murthy et al. [18] have reported a similar liquid flow field using a self-inducing impeller but different design. This velocity profile also confirms the gas flow direction as postulated earlier in previous chapter (chapter 3).

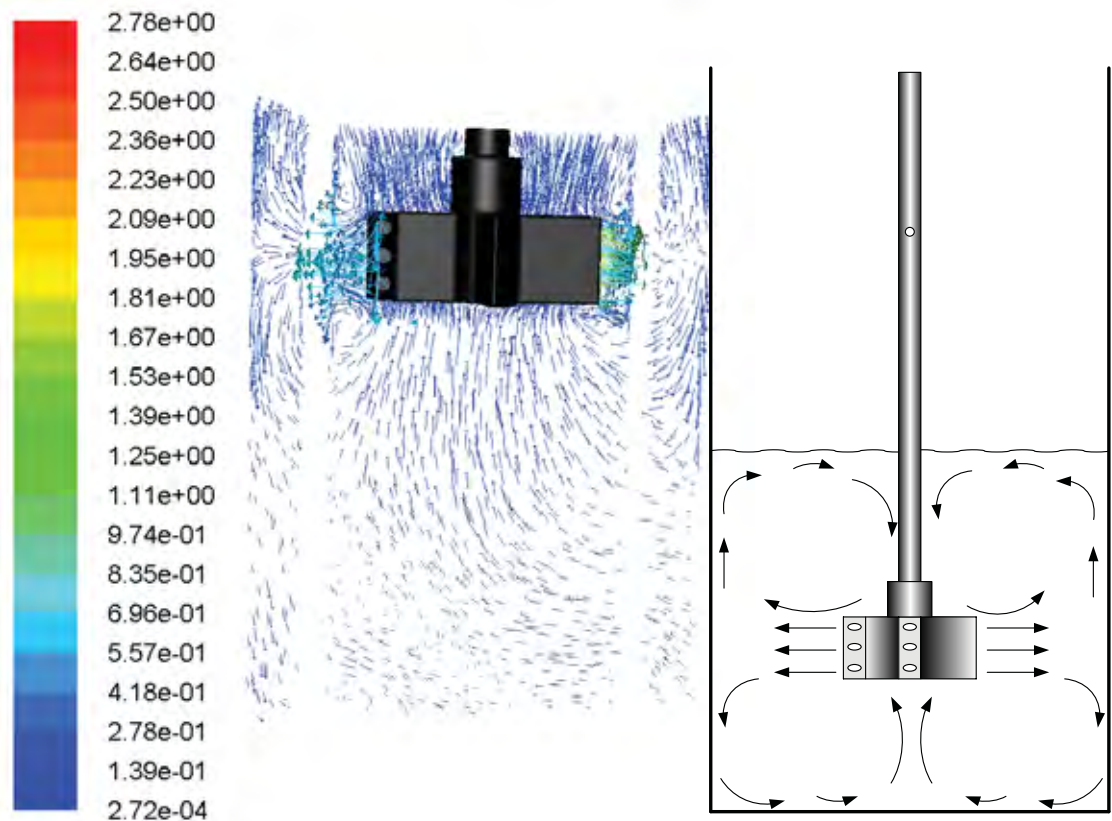


Figure 5.12 Velocity flow field for liquid phase at stirring speed of 400 RPM (2.9s)

The presence of high velocity contour in a region of orifices indicating the gas starts to commence at this speed as shown in Figure 5.3. This agrees with the calculation $N_{cs}=232$ rpm.

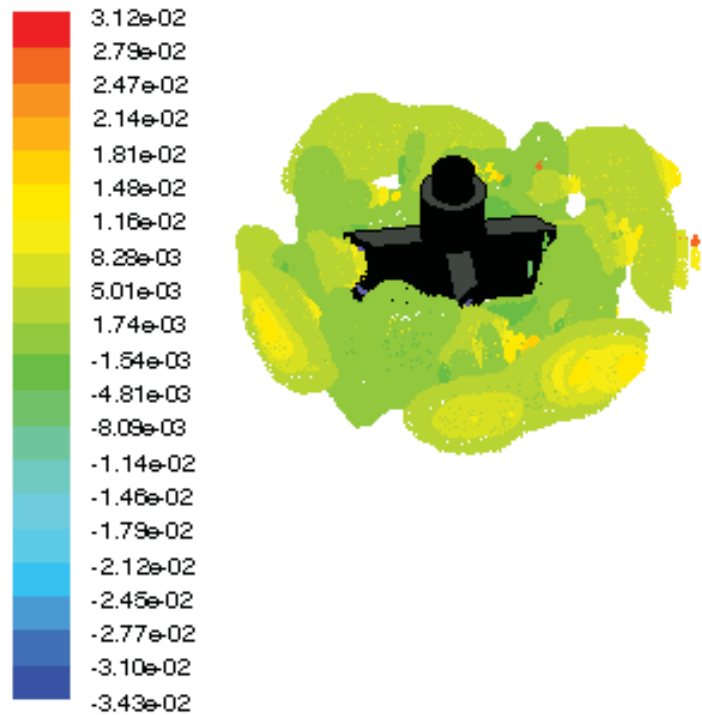


Figure 5.13 Velocity contour within the tank vessel at stirring speed of 200 rpm

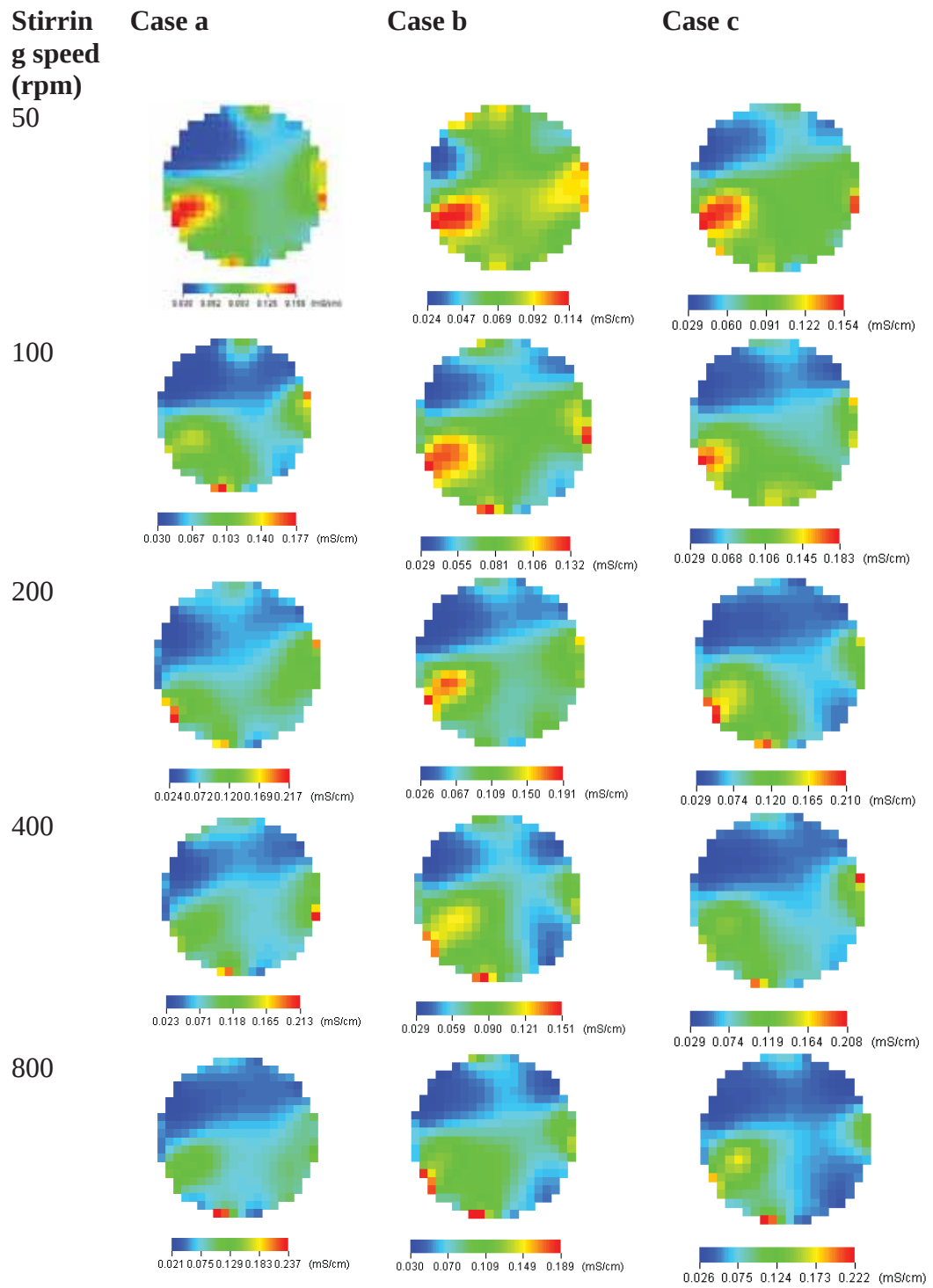
5.5. Gas-liquid Mass Transfer

In this particular section, three different types of reactor assembly were investigated namely;

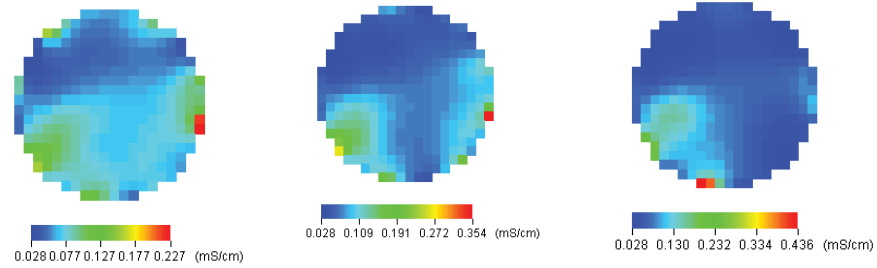
- Conventional (non-gas inducing impeller) stirrer with external gas-sparging. The standard impeller design was the exact replica of the gas-inducing impeller.
- Gas-induced impeller in the absence of external air-sparging and,
- Combined gas-inducing impeller with external gas-sparging.

5.5.1. Tomographic images

Table 5.5: Tomographic images at different stirring speeds



1200



The tomograms shown in Table 5.5 indicate a variation in the hue of the pixels across the vessel diameter (where the two extremes of the colour spectrum, blue and red, represent low and high mixture conductivity respectively). These time-averaged pixel conductivity distributions provide the dispersed phase (gas bubbles) distribution in the radial direction. The red-coloured regions covering the left hand corner in case (a) turned to a mixture of blue and green-coloured pixels which denote a decrease in mixture conductivity as conventional impeller speed increases. Case (b) and (c) followed a similar trend to case (a) with a larger decrease in mixture conductivity. At a stirring speed of 1200 rpm, the tomogram for case (c) exhibited a high intensity blue colour, suggesting a heavy spread of small gas bubbles arising from the shear force of the impeller blades causing bubble break-up across the radial plane. This may be attributed to the superior performance of the gas-inducing impeller over external air-sparging at high speeds.

5.5.2. Gas phase volume fraction

The gas phase hold-up, ε_G , was obtained from electrical conductivity values using the Maxwell relation, [19] as given in chapter 3 (cf. equation 3.2)

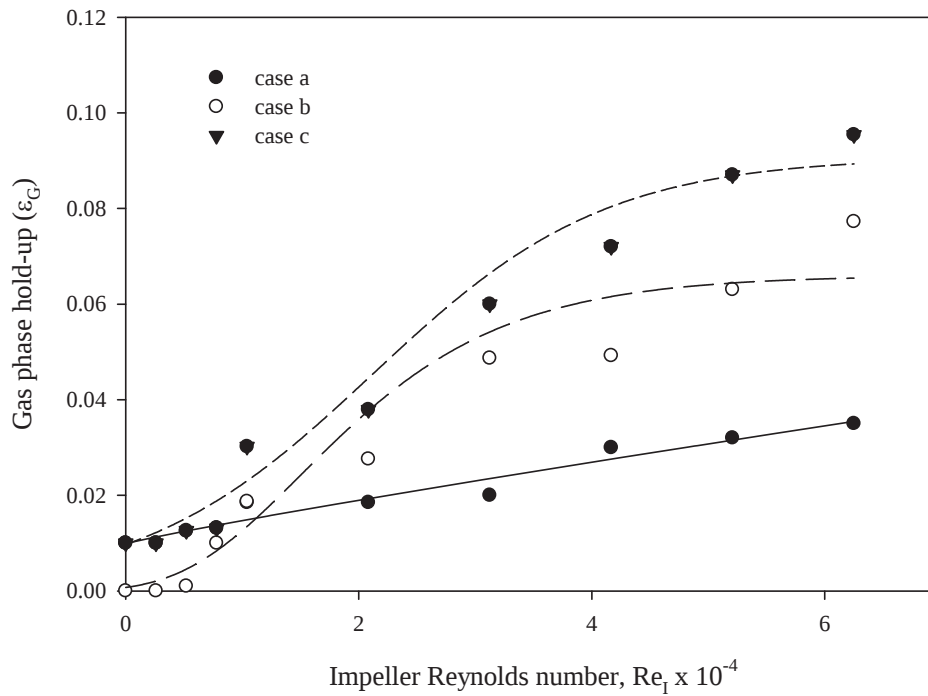


Figure 5.14. Gas phase hold-up as function of impeller Reynolds number

Figure 5.14 shows the global phase hold-up variation with increasing agitation rate (Re_I). It is evident that cases (a and c) gave a positive intercept on the y-axis while case (b) – stirring with gas-induced impeller but in the absence of external gas sparging - revealed an initial delay in gas flow through the liquid phase until an impeller Reynolds number of about, $Re_I=10^4$ corresponding to a stirring speed, $N_{CS}=200$ rpm, followed by a rapid rise.

The critical speed, N_{CS} , for gas effusion from the impeller gas exit ports is a characteristic of the gas-inducing stirrer operation and is given by Equation 4.5 (cf. Chapter 4) [4] and yields, $N_{CS}=232$ rpm. However, in all three cases, it is apparent that the gas hold-up cannot continue to rise indefinitely with increasing Re_I but must reach a maximum plateau dictated by the fixed gas flow rate through the liquid phase at which point the liquid phase would contain uniformly distributed fine bubbles corresponding to a maximum phase hold-up. Indeed, case c also displayed a similar induction period albeit at a non-zero gas phase hold-up equivalent to the constant external gas flow rate.

In order to accommodate the features in gas hold-up for all cases, the general Chapman-Richards equation given as;

$$\varepsilon_G = \varepsilon_{G,0} + \varepsilon_{G,\max} \left[\left(1 - \exp(-\tau_{gl} \text{Re}_l) \right) \right]^c \quad (5.21)$$

was used to describe the data in Figure 5.14 where $\varepsilon_{G,0}$ is the initial gas phase hold up when there is no stirring, $\varepsilon_{G,\max}$ is the maximum gas phase hold-up at infinite stirring, and τ_{gl} is the dimensionless mixing time constant for the particular mode of operation and c is an empirical constant.

Nonlinear regression analysis of the data provided the parameter estimates displayed on Table 5.6. The associated parity plot in Figure 5.15 illustrates the good agreement between the experimental values and model prediction.

Table 5.6: Parameter values for Equation (5.21)

Reactor type	$\varepsilon_{G,0}$	$\varepsilon_{G,max}$	$\tau_{gl} \times 10^6 (-)$	c
Case a	0.00102±0.0000	0.1441±0.0029	3.1210±0.0471	1.000±0.015
Case b	0.00000±0.0000	0.1574±0.0024	10.8021±0.1632	1.000±0.015
Case c	0.01020±0.0002	0.2326±0.0035	8.0202±0.1212	1.000±0.010

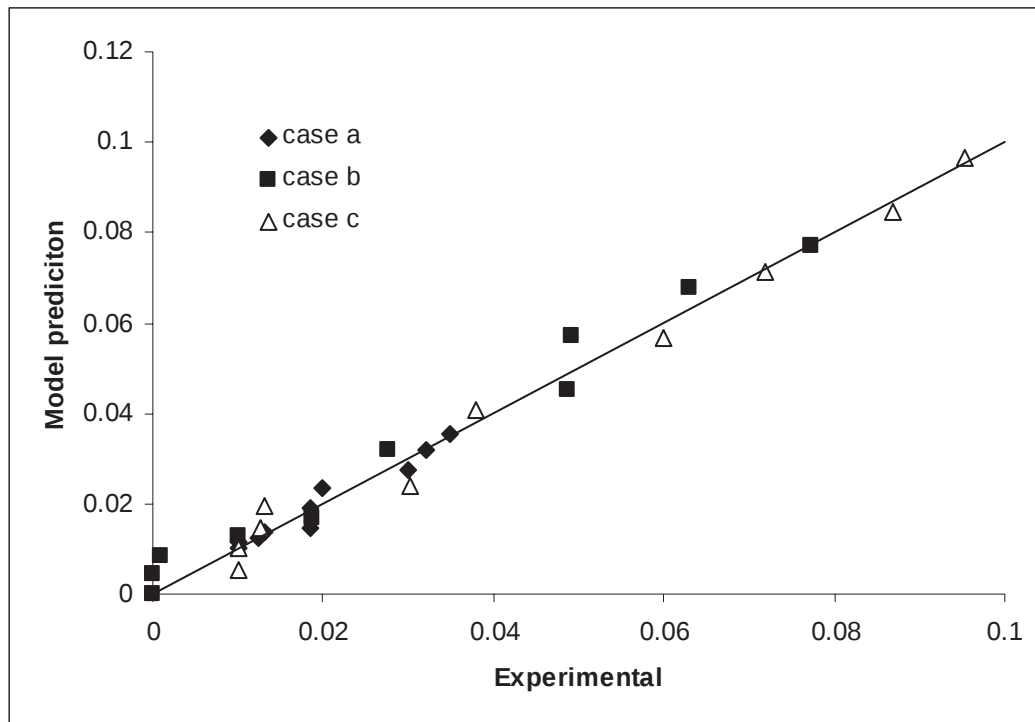


Figure 5.15. Parity plot for gas phase hold-up (Equation 5.21)

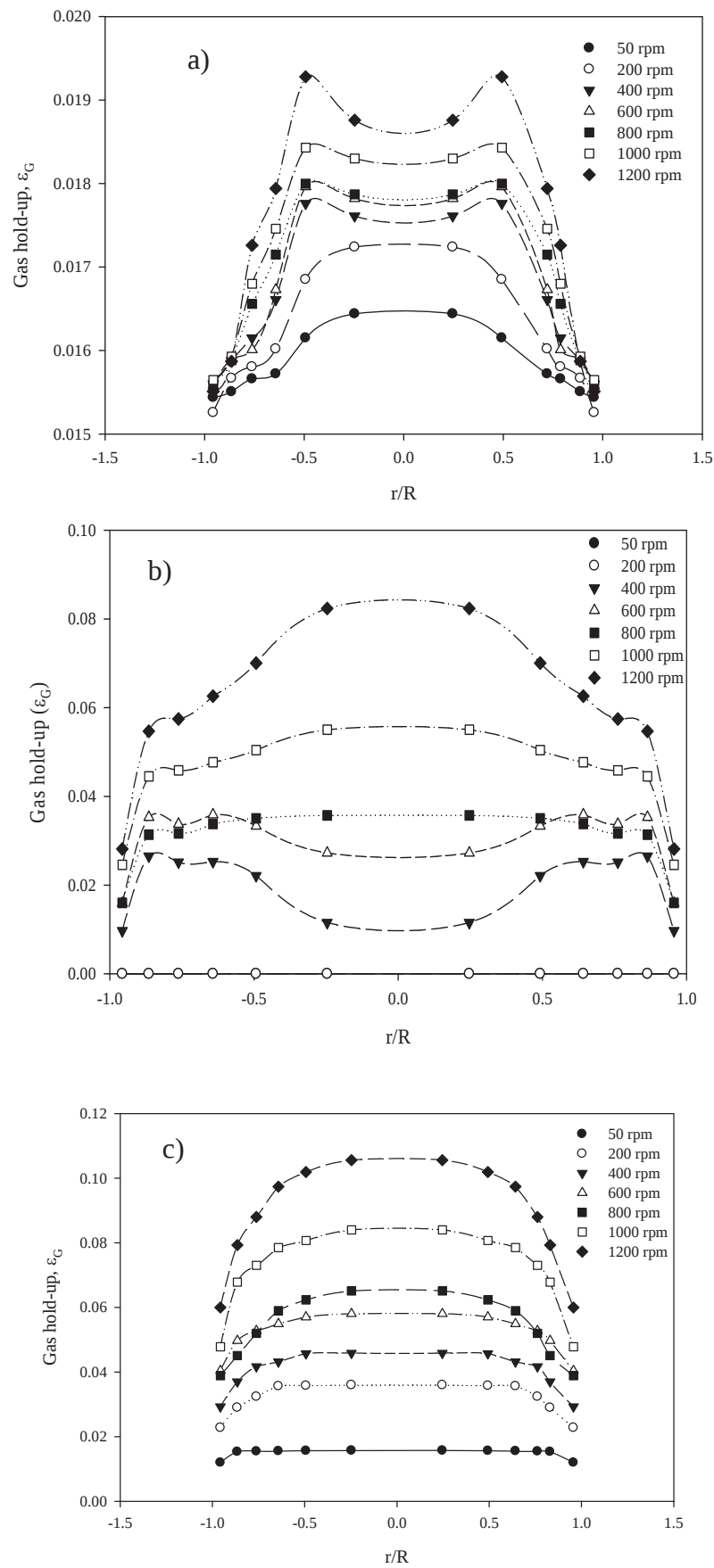


Figure 5.16. Radial profiles of gas phase hold-up for case (a), (b) and (c)

Figure 5.16 (a-c) shows the radial gas hold-up distribution for the 3 cases considered. When the conventional impeller was used without external upward gas sparging (case a), the gas hold-up went through a minimum at the shaft ($r/R=0$) and rose to a maximum just before the PVC baffle behind which it rapidly decreased to near zero values close to the vessel wall. However, at agitation speeds greater than 200 rpm, the gas hold-up profile had a maximum at the centre before it decreased to almost zero near the wall as expected. It would seem that once the critical Taylor number ($Ta=1700$ equivalent to $Re_l=10.8 \times 10^4$) has been exceeded, the radial gas hold-up profile distribution changes from having maximum to minimum at the centre. This switch from maximum to minimum in the radial hold-up profile suggests that the gas flow in the liquid phase changed from predominantly laminar radial to axial flow. The relevant Taylor number, Ta' , is given as

$$Ta' = \omega r_m^{\frac{1}{2}} b^{\frac{3}{2}} \frac{\rho_c r_r}{\mu_c r_s} \quad (5.22)$$

where

ω = angular velocity in radians s^{-1}

r_r = radii of the rotor (impeller)

r_s = radii of the stator (stirred vessel)

r_m = mean radius of the annulus, $(r_s + r_r)/2$, cm\

b = annular width, $r_s - r_r$, cm

ρ_c = density of continuous phase

μ_c = viscosity of the continuous phase

For a stirred tank, the critical Ta value of 1700 indicates the onset of vortex effects and equation (5.22) yields a stirring rate of 3.55 rps (213

rpm) for the vessel geometry employed in this work. Incidentally, the switch from a maximum profile to a minimum radial hold-up distribution occurred between the runs at 200 and 400 rpm as seen in Fig. 5.12a. It would seem that, for case a, the upward laminar flow of gas through the liquid phase was not significantly affected at low stirring speeds (<200 rpm) and hence, the maximum (or plateau) in the gas hold-up around the stirrer shaft. However, as the spinning action of the impeller increased, the gas bubbles were displaced away from the centre as a result of increased centrifugal forces leading to a reduction in the gas hold-up at the centre but an increase with radial distance. However, the hold-up attained its maximum value at or near the impeller radius and decreased rapidly thereafter towards the vessel wall.

An opposite behaviour was observed for case (b). At impeller speeds below about 600 rpm, gas flow was predominantly laminar radial flow within the annulus where upward vertical motion is provided largely through buoyancy effects. The net result is a high gas hold-up in the annular space between the impeller and vessel radius with a minimum at the shaft. However, as Ta' exceeds 1700 (i.e. 800 rpm) the vortex effect sets in and the gas is pushed towards the vessel centre (shaft) upon emergence from the orifice impeller gas ports. This causes a maximum gas hold-up at the shaft and the magnitude of maximum increased with agitation rate. Finally, for case (c) due to combined effects of the gas entrainment impeller and sparger, the gas hold-up has a maximum in the shaft region regardless of the speed. The gas hold-up dropped gradually behind the PVC baffle and closer to the tank wall ($0.86 \leq r/R \leq 1.0$). The global and radial gas hold-up profiles have good agreement with the sequence of tomograms for each case as stirring speeds increase from the laminar mixing regime to the churn-turbulent mixing regime.

5.5.3. Influence of agitation rate on bubble size

The mean bubble size variation with impeller Re_i is shown in Figure 5.17. It is evident from the behaviour that the bubble size was larger at low Re_i

and nearly constant up to about $Re_l = 1.5 \times 10^4$. However, as Re_l increased beyond 2×10^4 , the bubble size dropped quite sharply with Re_l before finally levelling out at about 2 mm for $Re_l \geq 4.5 \times 10^4$. The finer bubbles observed at stirring speeds > 200 rpm may have contributed to the shearing force that resulted from the impeller blade. The quality of bubble size distribution was estimated from the variance, σ , in individual bubble size for each impeller speed and given by

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (d_i - \bar{d})^2}{N - 1}} \quad (5.23)$$

where the degree of the gas mixing homogeneity is given by $1 - \sigma$. Figure 5.17 also shows that the degree of gas homogeneity within the liquid phase as a function of Re_l is a sigmoid.

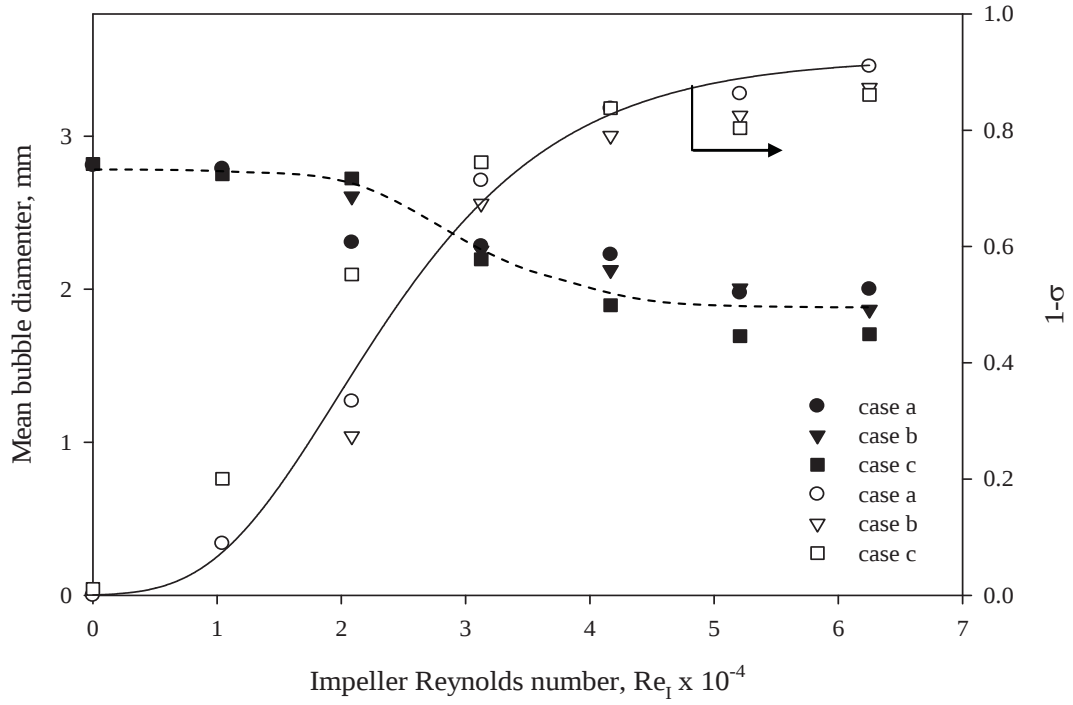
Three regions are identifiable in this behaviour corresponding to

the laminar zone where $0 \leq 1 - \sigma \leq 0.2$

the transition region with $0.2 \leq 1 - \sigma \leq 0.8$

the homogenous region where $1 - \sigma \geq 0.8$

These three zones practically coincide with earlier delineations of the bubble size characteristics. In the laminar and homogenous zones, the mean bubble size is essentially constant although the bubbles are relatively fine in the homogenous regime. This analysis is particularly instructive since it shows that only in the turbulent zone do we reasonably have bubbles that are small and uniformly distributed.


 Figure 5.17. Mean bubble size as a function of stirring speed, Re_I

5.5.4. Sauter mean bubble diameter and gas-liquid interfacial area.

Sauter mean bubble diameter, d_{32} is one of the important variables affecting the performance of mass transfer and can be calculated using the expression;

$$d_{32} = \frac{\sum_i^N n_i d_i^3}{\sum_i^N n_i d_i^2} \quad (5.24)$$

Figure 5.18 shows the Sauter bubble diameter, d_{32} decreases with the agitation rate for all cases. This behaviour appears to be attributed to higher probability of bubble-breakup with increasing stirring speed while coalescence within the bubbles did not occur instantaneously due to the low aspect ratio of this study ($H/D < 3.0$). Among others, bubble breakup

and coalescent rates control bubble size distribution in a gas-liquid mixing system. The decrease in Sauter mean bubble size with Re_i until a limiting low value is attained at $Re_i > 4 \times 10^4$ indicates that the probability of bubble break-up exceeded bubble coalescence as the impeller speed increased. However, at $Re_i > 4.5 \times 10^4$, it would seem that the bubbles are sufficiently fine that bubble break-up probability was essentially the same as that for bubble coalescence especially given the low aspect ratio ($H/D < 3$) for the vessel thus the Sauter mean bubble diameter reached its lowest value. It would seem that the behaviour of the Sauter mean bubble size is not influenced by the type of gas induction but more by the vessel geometry and impeller characteristics (shape, diameter, etc.)

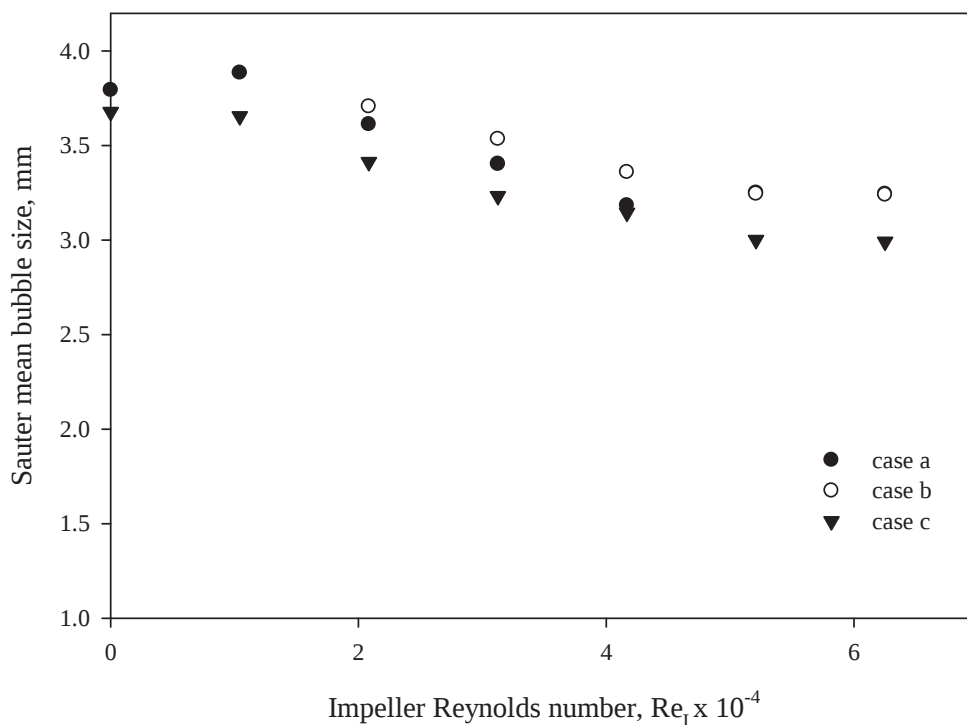


Figure 5.18. Sauter bubble diameter as a function of impeller Reynolds number, Re_i

Gas-liquid interfacial area per unit volume, a , can be obtained from Sauter mean bubble diameter and gas phase hold-up as;

$$a = \frac{6\varepsilon_G}{d_{32}} \quad (5.25)$$

Figure 5.19 shows that initially the specific interfacial area barely changed with Re_i until a critical impeller speed ($Re_i \approx 3 \times 10^4$), where there was a sudden rise in its value. Although speed beyond 1200 rpm was not used, it seems almost certain that the specific interfacial area must attain a finite maximum value which will remain invariant with further increase in agitation speed. Thus, the present S-curve model is very well fitted with a 3-parameter Chapman–Richards model given as;

$$a = a_{\max} \left[(1 - \exp(-bRe_i)) \right]^\delta \quad (5.26)$$

where $a_{\max}$ is the maximum of specific interfacial area at infinite stirring speed, b is the empirical constant related to impeller Reynolds number and δ is a non-dimensional constant. The interfacial area values for cases (b) and (c) were generally higher than in case (a) where only external sparging through the bottom gas distributor occurred. This would suggest that the finer bubbles generated by the gas-inducing impeller have a significant contribution to the high bubble interfacial area. The lower value for case (a) is indicative of larger bubbles produced from the 10 mm sintered stainless steel plate. Interfacial area, a , increased with impeller Reynolds number albeit gradually up to $Re_i = 3.2 \times 10^4$. The sudden increase after this value indicates the bubbles breaking up at a much faster rate than coalescence as was observed during the runs.

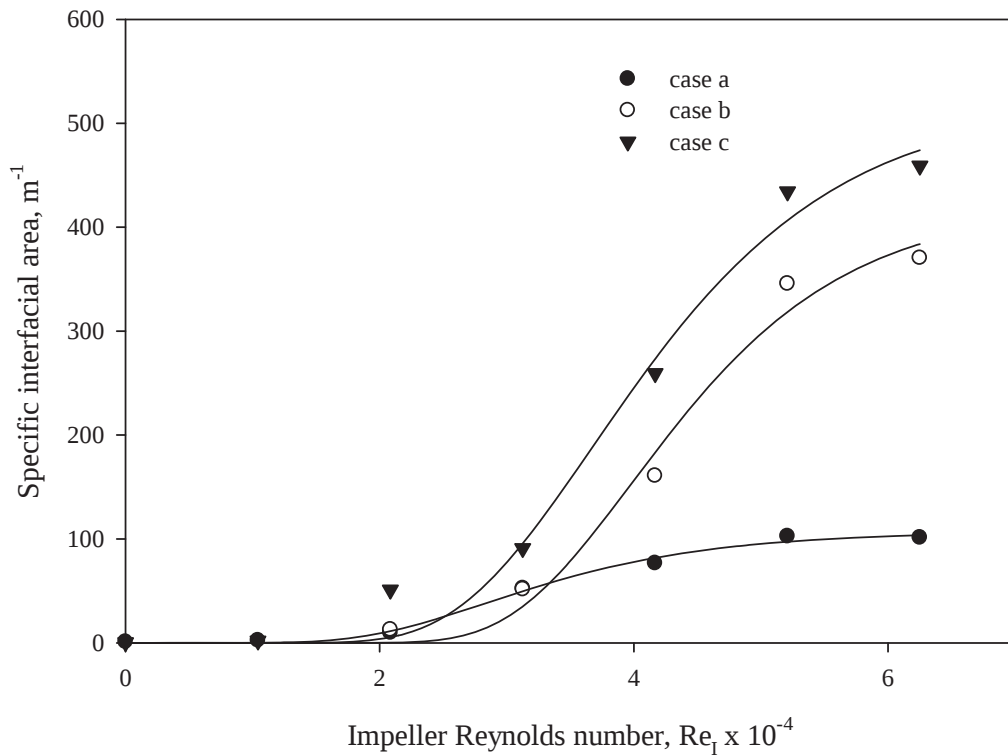


Figure 5.19. Specific interfacial area as a function of impeller Reynolds number, Re_i

5.5.5. Volumetric mass transfer coefficient, $k_L a$

Figure 5.20a illustrates the dependence of the volumetric mass transfer coefficient, $k_L a$, on Re_i . Although a sigmoidal relationship is implicated in all 3 cases, the shape of the curves for cases (b) and (c) where the gas-inducing impeller was used are different to that of case (a) – stirring with the conventional impeller. Curves for (b) & (c) are parallel. This is a reflection of the difference in gas-liquid mass transfer mechanism (or physical rate – controlling step) between the gas-inducing stirrer and the standard type. The increase in $k_L a$ – values for case (c) is clearly due to additional contribution from the externally-sparged gas. However, as previously indicated case (c) is not merely the linear combination of cases (a) and (b). The nonlinear change in mixing characteristics is reflected in both gas hold-up and the volumetric mass transfer dependency on Re_i and design over its standard counterpart. Importantly, in view of the similarity in the interfacial area, dependency on

finer bubbles alone is not the determinant of high mass transfer rates. Indeed, as seen in Figure 5.20b, the relationship between k_L (intrinsic mass transfer velocity) and impeller Reynolds number, the k_L values are almost constant with Re_i . The Calderbank and Moo-Yong [20] correlation shows a similar pattern for different bubble sizes, given as

$$k_L = 0.31 \left(\frac{\Delta P \mu_c g}{\rho_c^2} \right)^{1/3} N_{Sc}^{-2/3} \quad (5.27)$$

The above correlation is only applicable to rigid spherical bubbles. However, for bubbles that do not behave as rigid spheres, Calderbank and Moo-Yong [21] proposed a new correlation given as

$$k_L = 0.42 \left(\frac{\Delta P \mu_c g}{\rho_c^2} \right)^{1/3} N_{Sc}^{-1/2} \quad (5.28)$$

Sardeing et al ([22] found that the Equations (5.27) and (5.28) are applicable for bubble sizes of <1.5 mm and >3.5 mm respectively.

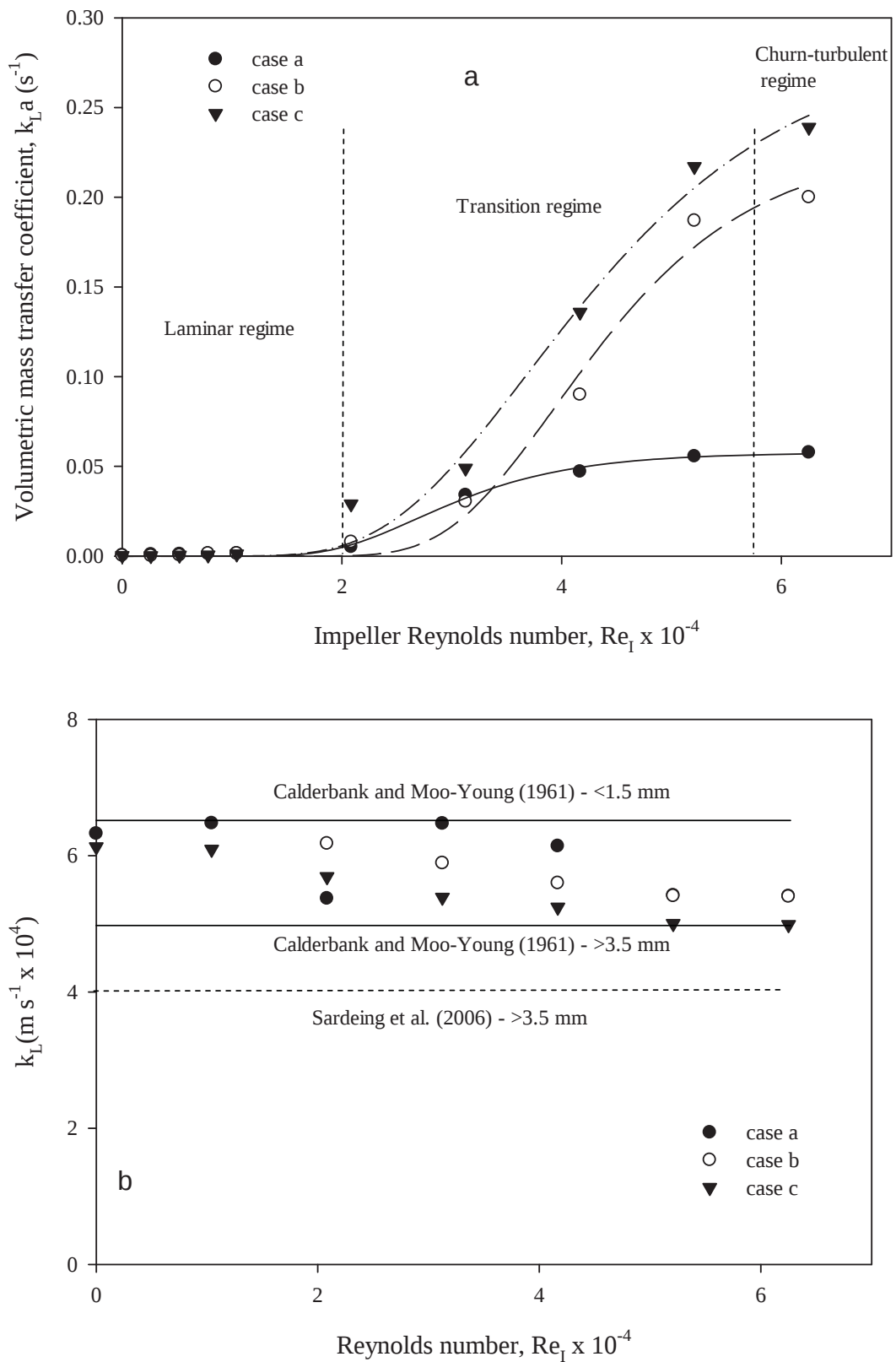


Figure 5.20 a) Volumetric mass transfer coefficient, $k_L a$ as function of Re_i b) Liquid side mass transfer coefficient, k_L , as function of Re_i .

As the stirring speed, N_s , increased, the $k_L a$ values approached an asymptotic value at rotational speed greater than 1200 rpm ($Re_I = 6.2 \times 10^5$). The sigmoidal nature of these curves indicates that three possible regimes were experienced during the multiphase mixing. It appears that negligible $k_L a$ values in the laminar region prevailed for impeller speeds lower than about 400 rpm ($Re_I < 2.1 \times 10^4$). In this regime, it appears that no or insufficient gas was dispersed into the liquid. However, as stirring rate increased beyond 400 rpm, gas starts to disperse through the orifice and $k_L a$ values increase gradually to attain the maximum at $Re_I > 6 \times 10^5$.

Equation (5.29) describes the sigmoidal behaviour where $k_{La_{max}}$ is the mass transfer coefficient at infinite stirring and Re_I is the impeller Reynolds number, τ is dimensionless gas-liquid transfer time constant and γ is a bubble-liquid interface factor.

$$k_L a = k_{La_{max}} (1 - \exp[-\tau Re_I])^\gamma \quad (5.29)$$

The constant values for the parameters in Equation (5.29) are reported in Table 5.7.

Table 5.7: Constant values for Equation (5.29)

Reactor type	$k_{La_{max}} (s^{-1})$	$\tau \times 10^4 (-)$	γ
Case (a)	0.0576±0.0009	1.0±0.015	30.0±0.453
Case (b)	0.2293±0.0023	0.9±0.009	50.0±0.502
Case (c)	0.2874±0.0014	0.7±0.004	14.7±0.074

A similar trend has been reported by Hichri et al [23] and Dietrich et al [24] in a slurry reactor using self-gas-inducing impellers but with different

designs. The parity plot in Figure 5.21 shows the model predicted is in good agreement with experimental data.

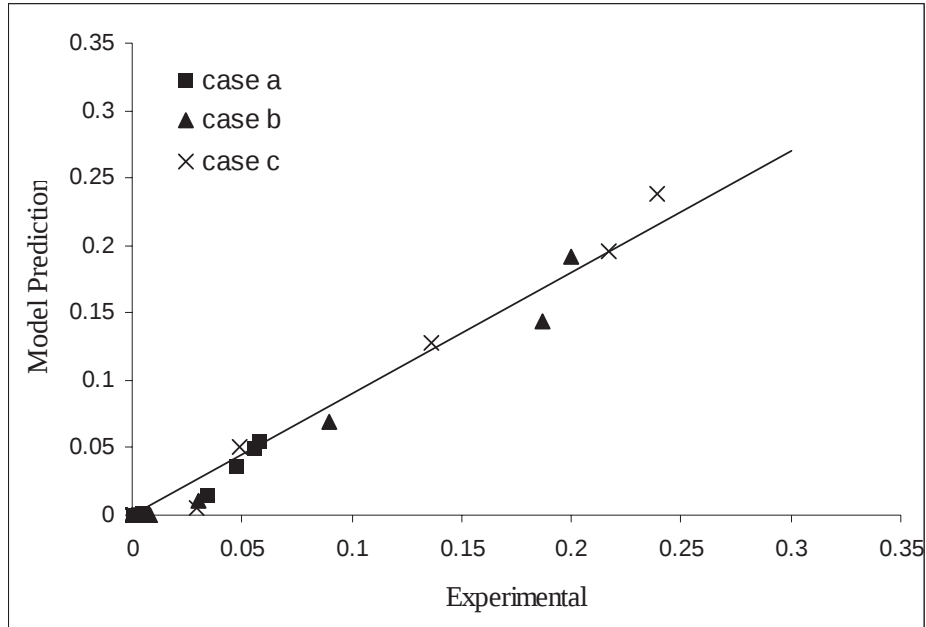


Figure 5.21. Parity plot for volumetric mass transfer coefficient, k_La (Equation 5.29)

Sauter mean bubble diameter-based Sherwood number, Sh_{Sauter} , defined as

$$S_{h_{Sauter}} = \frac{k_L d_{32}}{D_{AB}} \quad (5.30)$$

where,

k_L = liquid side mass transfer coefficient

d_{32} = Sauter mean bubble diameter

D_{AB} = Diffusivity of gas in liquid

was correlated with impeller Reynolds number, Re_i as seen in Figure 5.22.

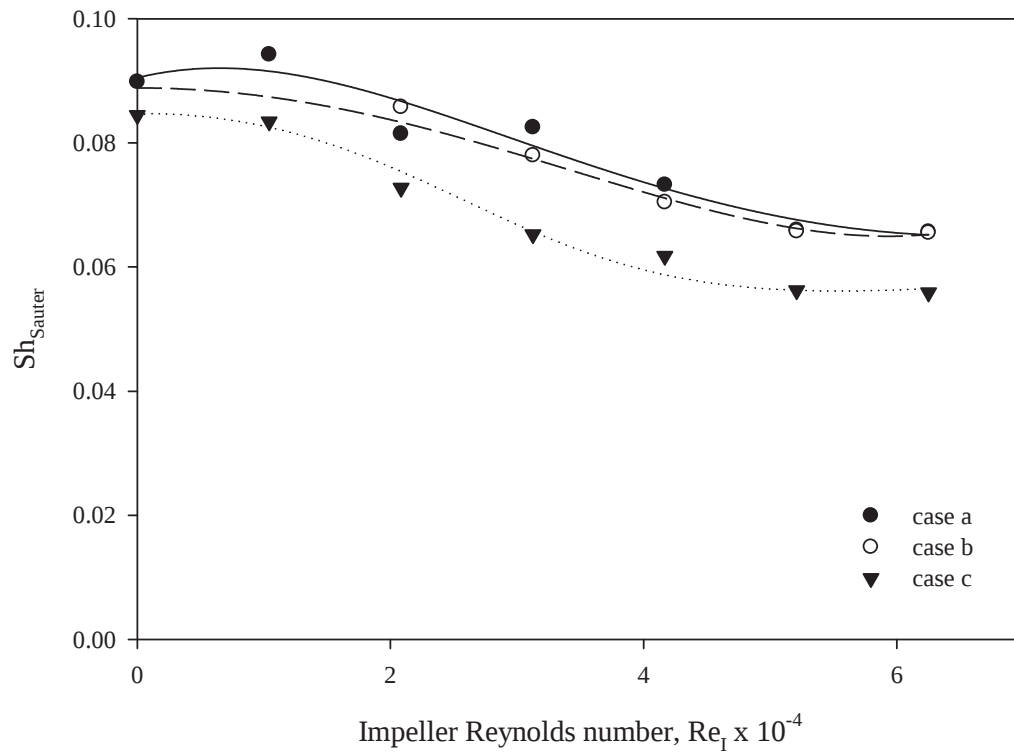


Figure 5.22 Sauter based Sherwood number as function of impeller Reynolds number

A number of proposed correlations in the open literature were compared with the experimental data for a similar range of operating conditions as seen in Figure 5.23. It shows that the existing study gave a better prediction over the same range of impeller Reynolds number in particular at low Re_I ($Re_I < 10^4$). Judat [25] and Kavic and Heidel [26] gave a lower prediction of $k_L a$ at high impeller Reynolds number ($Re_I > 5.5 \times 10^4$).

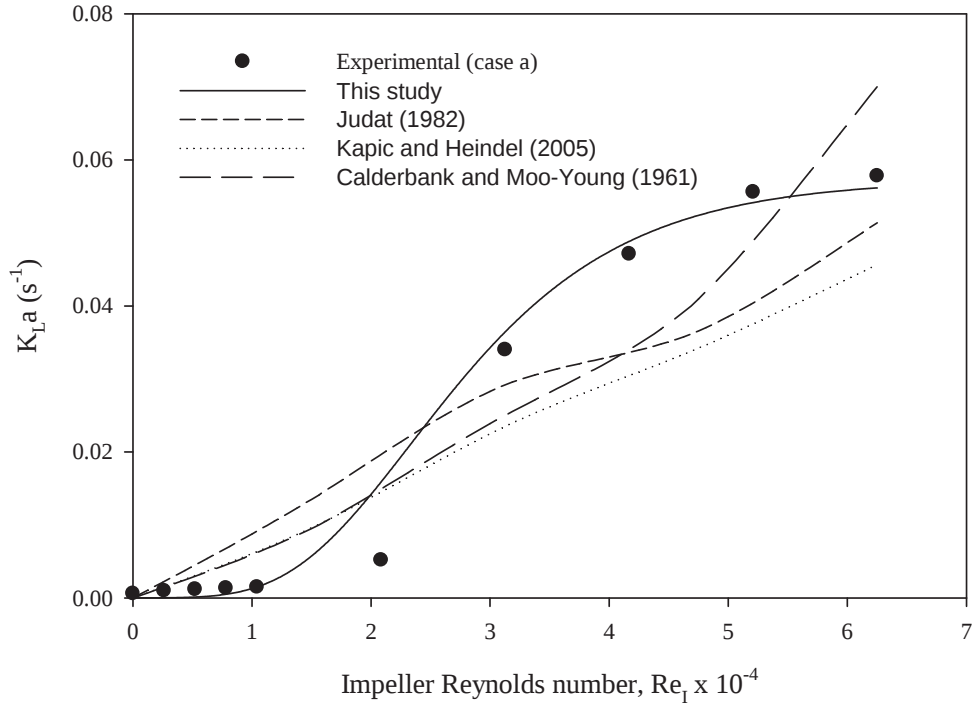


Figure 5.23 Comparison of correlations against the experimental data. The data were correlated based on these parameters: $D_T=100$ mm, $D_I=50$ mm, $\rho_L=1\text{gcm}^{-3}$, $\mu_L=8\times 10^{-3}\text{gcm}^{-1}\text{s}^{-1}$.

The mass transfer coefficients are furthermore influenced by the gas hold-up behaviour obtained by the tomographic data and dependent on the energy consumption by mechanical agitation of the gas-inducing and the non-gas-inducing impellers.

5.6. Power Analysis

The amount of energy consumed by the impeller can also affect the efficiency of mass transfer. The gas-liquid mixing in the tank was carried out using a Heidolph motor (model RZR 2102) equipped with a torque display for the chosen rotational speed, N_s . The power input, P , in a reactor with a gas-inducing impeller is given by [27] ,

$$P = \rho_l W N_s \left(\frac{D_I}{2} \right)^4 \left[C_{DO}^* - C_{DY}^* \left(1 - \frac{1}{\Phi Fr} \right)^3 \right] + 2\pi N_s T \quad (5.31)$$

where W is the impeller width, C_{DO}^* and C_{DY}^* are the impeller drag coefficients in the gas-liquid dispersion conveying and central zone estimated as 1.0, Φ , the vortexing constant is 1.7 [28] and Fr is the Froude number based on impeller submergence depth.

For a conventional impeller with no gas involvement, P_0 is calculated from the expression:

$$P_0 = N_{P0} \rho_l N_s^3 D_I^5 \quad (5.32)$$

where $N_{P0}=4$ for a standard 4-blade impeller [29].

The mass transfer is plotted as a function of the dimensionless combination of power consumption and the global gas hold-up as shown in Figure 5.24 and this relationship is adequately captured by Equation (5.33) as given by;

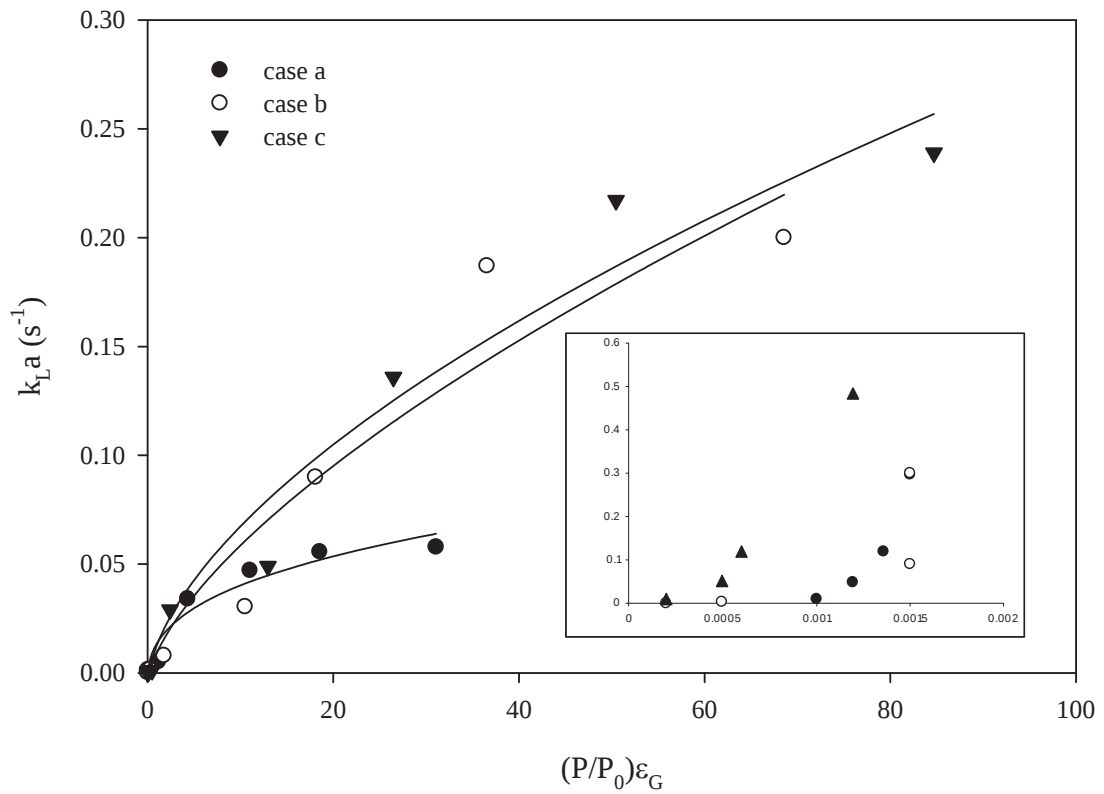
$$k_L a = k_L a_0 + \alpha \left(\frac{P}{P_0} \varepsilon_G \right)^\beta \quad (5.33)$$

Where,

$k_L a_0$ = initial volumetric mass transfer coefficient

α = net bubble collision frequency (s^{-1}) for the three cases

β = gas-inducing enhancement factor

Figure 5.24. $k_L a$ as function of dimensionless $(P/P_0)\epsilon_G$

Parameter β represents the advantage of the gas-inducing impeller system over the mechanically agitated setup. For example, the difference in mixing efficiency between case (a) and case (b) was 34%. This shows that the gas-inducing impeller allowing recirculation of gas from the headspace back into the liquid is an attractive alternative since it provided better mass transfer of oxygen in water compared to the conventional gas-sparged stirred tank reactor. However, these advantages only come into effect after 200 rpm, the critical rotational speed, N_{cs} , where gas begins to flow from the headspace into the bulk liquid phase. Similar results were obtained by Dietrich et al. [24] for 2000 Wm^{-3} power consumption.

Table 5.8. Estimate parameter values for equation (5.33)

Case	$k_L a_0 \times 10^3 (\text{s}^{-1})$	$\alpha \times 10^2 (\text{s}^{-1})$	β
Case (a)	1.0±0.020	1.24±0.012	0.48±0.0048
Case (b)	1.0±0.015	1.16±0.017	0.69±0.0104
Case (c)	1.0±0.010	1.51±0.023	0.69±0.0069

5.7. Conclusions

Mixing intensity affects both the gas hold-up and mass transfer coefficient in stirred tank reactors. The gas phase hold-up radial profiles in the gas-liquid system went through a minimum at the shaft ($r=0$) for $Re_l < 4.2 \times 10^4$ while the curves exhibited a maximum at the same location for $Re_l > 4.2 \times 10^4$. The radial gas phase hold-up distribution was practically flat between $0 \leq r/R \leq 0.86$ at $Re_l = 4.2 \times 10^4$. As expected, the gas phase hold-up plummeted to nearly zero value at the wall (behind the baffle) due to the formation of a relatively unperturbed liquid layer. Vorticity in the gas-liquid system was responsible for the switch from a minimum to a maximum radial gas hold-up profile between 600 and 800 rpm. This experimental observation was consistent with the requirement from Taylor number analysis. Gas hold-up and mass transfer coefficient in the gas-liquid system studied achieved a sigmoidal increase with increasing Re_l . The three types of gas-liquid mixing systems showed that even though in case (c), the added effect of the gas-inducing impeller combined with external gas sparging gave the highest gas hold-up and mass transfer coefficient compared to cases (a) and (b), the 9% increase in mass transfer relative to case (b) proved that from an economical standpoint, case (b) with gas-inducing impeller can achieve efficient and sufficient mass transfer with no added expenses of oxygen and air gas cylinders which are large consumable equipment liabilities. The use of a gas-inducing impeller reduced the amount of power consumption providing a higher and more suitable mass transfer in the reactor vessel than that of the conventional 4-blade impeller. The upward

parabolic trends at higher speeds for the GIST enabled successful classification of the mixing regimes associated with the gas-liquid system; laminar, transition and churn-turbulent mixing regime, indicating the existence of a radial transport gradient. Mean bubble size decreased gradually with stirring speed. CFD simulation predicts gas phase hold-up in reasonably good agreement with experimental measurement i.e. ERT. The gas phase hold-up is highly concentrated near the impeller zone. As expected, low gas hold-up was found behind the baffle possibly due to the presence of the baffle itself, as an obstacle for the gas bubble to pass through. The existence of a boundary layer near the vessel wall may have contributed to low gas fraction in this region. Favourable comparisons between CFD and tomographic data were established thus justifying the usefulness of an unsteady-state 3D CFD model for scale-up and optimization purposes, especially for industrial related applications. Overall, the combination of qualitative and quantitative analyses of ERT along with dissolved oxygen concentration permitted an insightful analysis of the self-gas inducing impeller as a superior mixing technology for industrial applications involving gas-liquid operations.

5.8. References

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6 ■ Hydrodynamics and Mass Transfer in Gas-liquid-solid System

6.1. General Consideration

Multiphase stirred vessels are commonly employed in the process industries for a variety of operations including pharmaceutical production, metallurgical processing, polymerisation and petrochemicals manufacturing [1-3]. In many cases, the liquid represents the continuous phase while the gas and solid phases constitute the disperse phase. Thus, the stirred tank performance strongly depends on the mixing efficiency of the gas-liquid and solid-liquid phases. This is especially important in catalytic processes where product yield and selectivity are key economic indicators. Superior mixing characteristics are often sought by maintaining turbulent conditions in the vessel (impeller Reynolds number, $Re_i > 10^4$), employment of multi-level impellers, baffle incorporation and other enhancement devices [4].

In this chapter, we present an ERT and ECT analysis of gas-liquid-solid mixing in a gas-inducing stirred tank reactor (GIST). Existing design correlations are based on information collected from intrusive techniques such as direct residence-time distribution measurements [5, 6] and in many cases, applicable to a narrow range of operating variables. Specifically, the goals of this investigation were to obtain tomographically-guided correlations for solid- and gas- phase hold-ups as a function of stirring speed, solid loading and particle size over sufficiently wide range to cover most practical conditions. Moreover, we

provide an expression for the spatial variation of the local phase hold-up within the mixed tank since this will be necessary in subsequent reactor analysis (cf. chapter 7). Some materials presented in this chapter are excerpted from our publication in Abdullah *et al.* [7], in Chemical Engineering Science.

6.2. Preliminary study

Dispersed phases in this study are gas (air) and alumina particles while continuous phase is water. Accidentally, both of dispersed phases are non-conductive materials and ERT only measures the single non-conductive phase due to its inability to differentiate between two phases with low conductivities (i.e. gas bubbles and solid particles), two independent preliminary studies were carried out namely;

Set 1 runs using:

- a. conventional stirrer (non-gas inducing) followed by similar runs with,
- b. gas-inducing impeller with identical geometry and,

Set 2 runs - differential pressure measurements at various rotational speeds across the tank using both types of stirrers. The schematic diagram for pressure measurement experiments is illustrated in Figure 6.1.

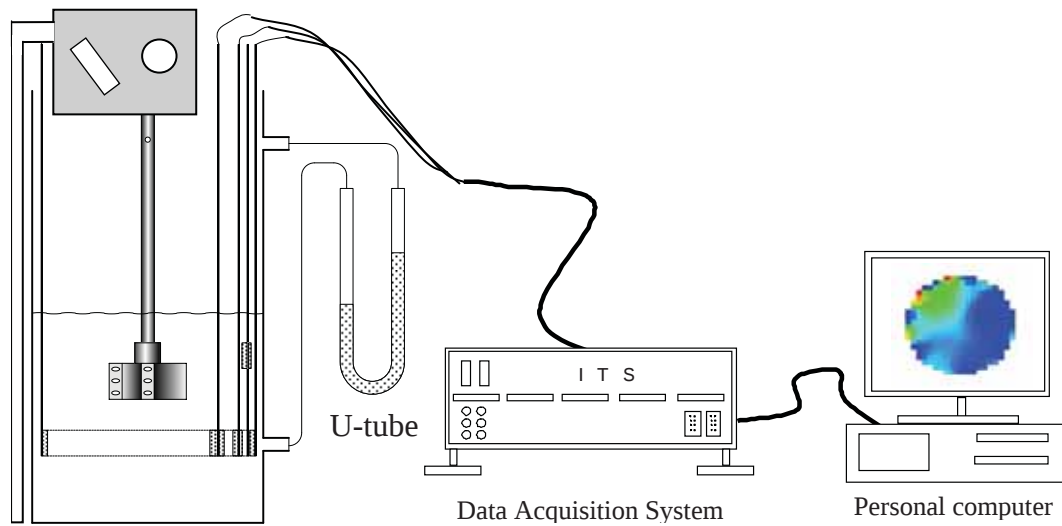
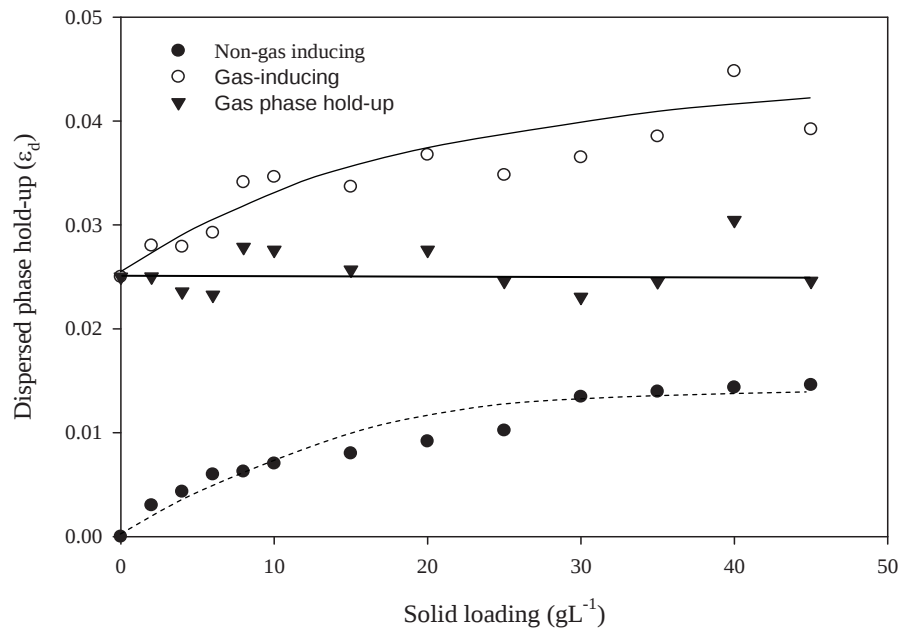


Figure 6.1. Experimental setup for pressure-based method

The purpose of set 1 runs is to permit the extraction of separate solid and gas phase hold-ups from ERT data while set 2 runs provide an independent avenue to corroborate ERT-based dispersed phase hold-up data with energy balance equation estimates.



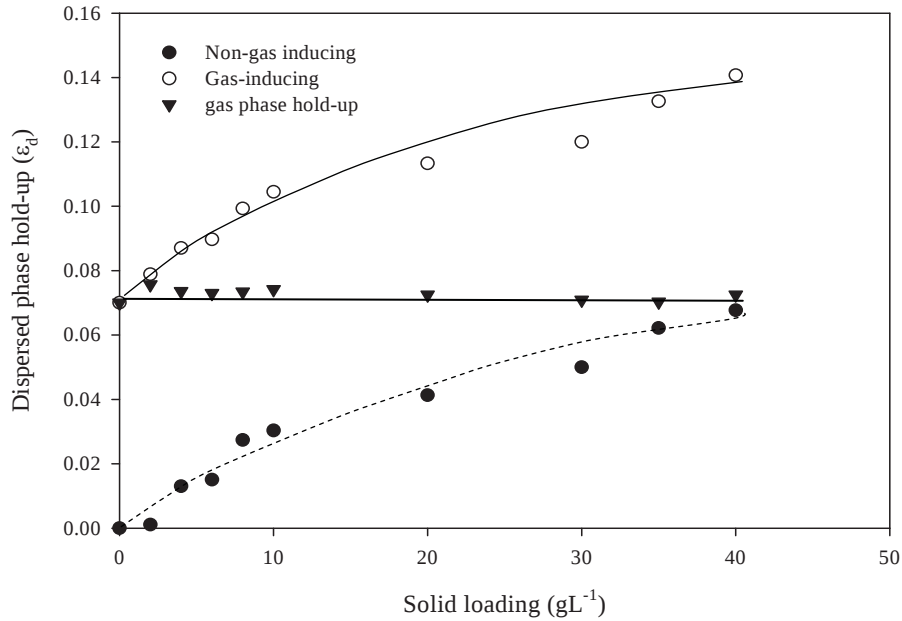


Figure 6.2 The effect of alumina loading for non-gas and gas-inducing impellers at
a) $Re_i = 2.1 \times 10^4$ and b) $Re_i = 6.25 \times 10^4$

Figure 6.2 (a & b) show the effect of solid loading on dispersed phase hold-up under conditions for both gas-inducing and conventional (non-gas inducing) stirrers. The latter corresponds to the situation for Set 1a runs where the system is fundamentally a liquid-solid mixture while the gas-inducing impeller represents the gas-liquid-solid system (Set 1b runs). Although the ERT technique does not discriminate between gas bubbles and solid particles in the phase hold-up, ϵ_d , measurements, these preliminary data suggest that the ϵ_d for the 3-phase system ($\epsilon_{d_{3-phase}}$ - open circle) and the 2-phase counterpart ($\epsilon_{d_{2-phase}}$ - closed circle) exhibited a constant difference over the range of solid loading, w , investigated at the two representative Re_i values (2.1×10^4 and 6.25×10^4). These constant differences (0.025 and 0.061) are the gas phase hold-up values, ϵ_G , and indeed, are nearly identical to the dispersed phase volume fractions obtained in Figure 6.3 for the case with zero solid loading at each of the Re_i values employed. Consequently, the dispersed phase hold-up, ϵ_d , may be written in terms of its constituent parts as:

$$\varepsilon_d = \varepsilon_g + \varepsilon_s \quad (6.1)$$

where $\varepsilon_{s,}$ is the solid phase hold-up. Equation (6.1) was subsequently used to compute the $\varepsilon_{s,}$ values for various solid loadings at different Re_i in Figure 6.3. The overall dispersed phase hold-up within the stirred tank at any given impeller speed was obtained from Equation (3.2) (refer to chapter 3). Figure 6.3 shows that for both gas-liquid and gas-liquid-solid systems, the gas phase hold-up increased with impeller Reynolds number, Re_i , and appears to approach a plateau at rotational speed greater than 1200 rpm ($Re_i=6.25 \times 10^4$).

6.3. Global analysis of dispersed phase hold-up

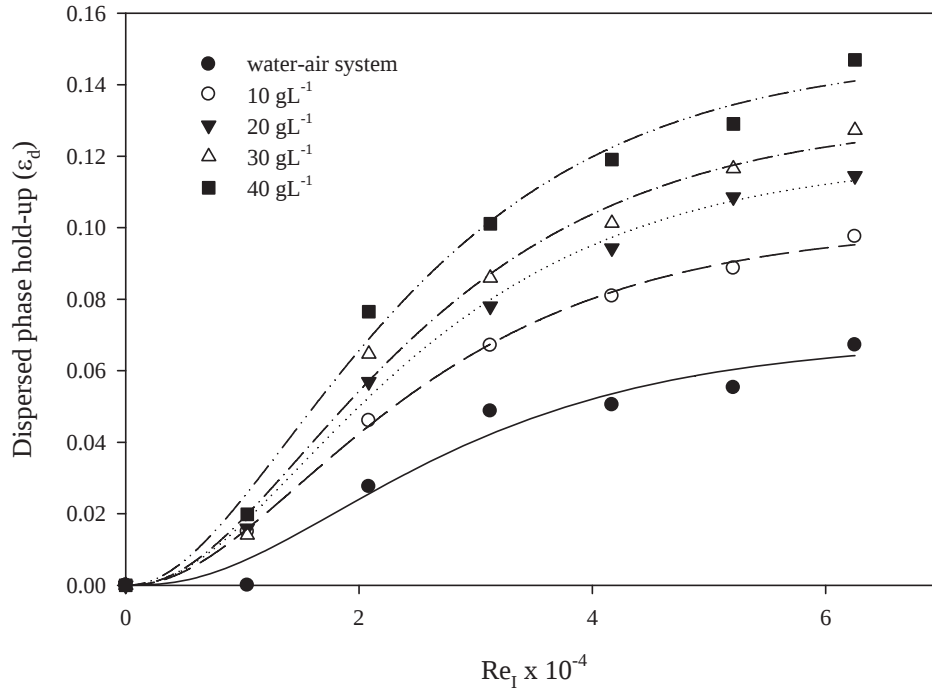


Figure 6.3 The effect of impeller Reynolds number, Re_i , on dispersed holdup at various alumina loadings. Experimental data points are indicated by the open or closed symbols while the continuous or dashed curves represent the correlation (Equation (6.2)) prediction

Figure 6.3 ascribes a sigmoidal relationship between the dispersed phase hold-up and the impeller Reynolds number, Re_i . Due to the complex physics underlying the gas-liquid-solid particles interaction in a multiphase stirred system, a low-parameter mechanistically-based model is rarely possible. As a result, the literature is replete with various nonlinear and power-law models [5, 8-10]. Additional insights into the mixing processes may, however, be secured, if the behaviour is described in terms of a model with parameters that capture or represent key distinctive features of the operation. It is in this respect that we employed the Chapman-Richards growth *3-parameter* model to describe the dependency of dispersed phase hold-up on Re_i in view of the similarities in the macroscopic steps implicated between natural

ecological systems [11, 12] and the dispersed phase hold-up evolution in a gas-inducing liquid-solid mixing tank, namely; *birth* (bubbles and solid particles initiation into the liquid medium), *growth* (bubble-particle propagation and dispersion) and finally, *maturity* (attainment of maximum gas volume fraction and solid particles homogeneity). Thus, the pertinent Chapman-Richards 3-parameter equation for the sigmoidal dispersed phase hold-up is:

$$\varepsilon_d = \varepsilon_{d,\max} \left[1 - \exp(-\tau_{dpp} \text{Re}_l) \right]^\gamma \quad (6.2)$$

where ε_d is the overall dispersed phase hold-up in the tank, and the Chapman-Richards parameters are; γ , which is an exponent related to the alumina particle and/or gas bubbles clustering activity (birth), τ_{dpp} , a non-dimensional dispersed phase mixing time constant (growth) and $\varepsilon_{d,\max}$, the dispersed phase hold-up for infinitely fast stirring (maturity). Parameter estimation based on non-linear regression analysis of the data gave dimensionless time constant, $\tau_{dpp} = 6.0 \times 10^{-5}$ for these curves. However, both γ and $\varepsilon_{d,\max}$ are functions of w as seen in Table 6.1.

Table 6.1 Parameters estimates from Equation (6.2) for global dispersed phase hold-up distribution.

Parameter	0 g	10 g	20 g	30 g	40 g
$\varepsilon_{d,\max}$	0.068±0.00	0.101±0.00	0.120±0.00	0.131±0.00	0.148±0.00
	0	1	1	2	4
γ	2.473±0.00	2.423±0.02	2.445±0.02	2.466±0.03	2.286±0.05
	6	7	1	8	6
$\tau_{dpp} \times 10^5$	6±0.015	6±0.066	6±0.051	6±0.088	6±0.146

$\varepsilon_{d,\max}$ has a linear dependency on w given by;

$$\varepsilon_{d,\max} = 0.068 + 0.0022w \quad (6.3)$$

The behaviour of γ with increasing w (solid loading) appears to be nonlinear due to the multiple dispersed entities (bubble-bubble, bubble-particle and particle-particle) interactions. In fact, γ is a *hybrid* clustering activity parameter for both gas bubbles and solid particles where additional insights may be gained if the dispersed phase hold-up is decoupled into the constituent, gas and solid phase hold-ups.

Moreover, data from Set 2 runs (pressure measurements) were also used to corroborate the ERT results using the independent expression provided in [13] for ε_s , viz;

$$\varepsilon_s = \frac{1}{\rho_s} \left(\frac{\Delta P}{g\Delta z} - \varepsilon_l \rho_l \right) \quad (6.4)$$

The results depicted in Figure 6.4 show good agreement between ERT and manometric estimates at two typical solid loadings.

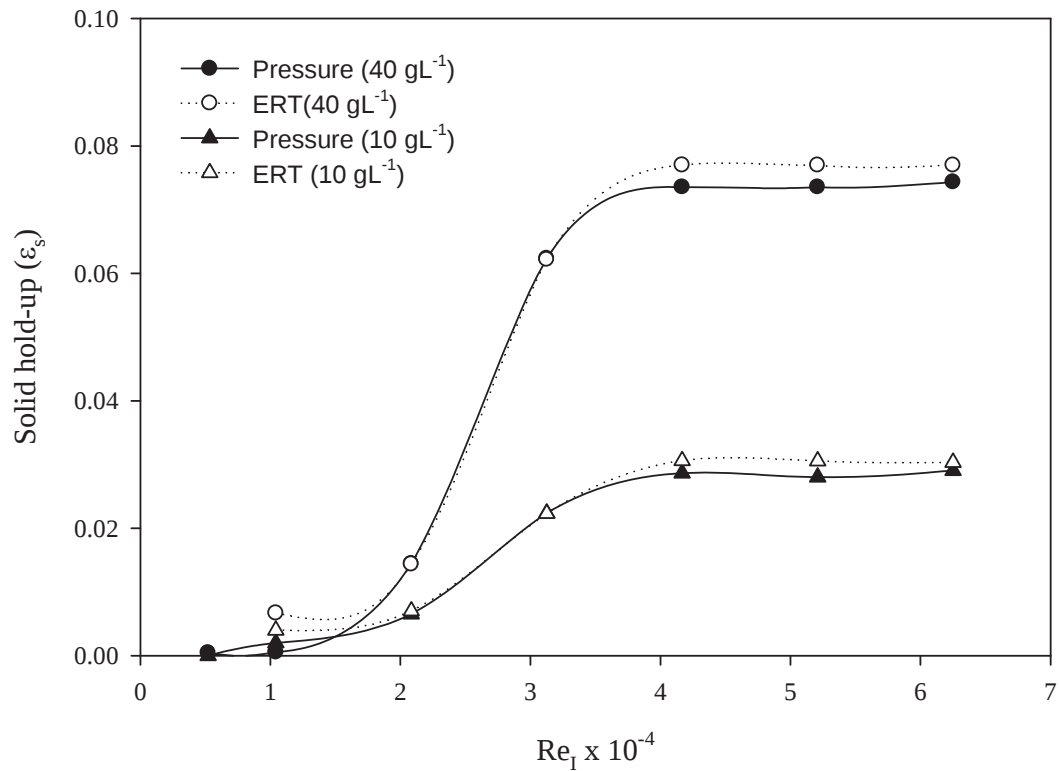


Figure 6.4 Solid phase hold-up distribution for different measuring methods.

6.3.1. Solid phase hold-up analysis

Using data from the gas-liquid runs and the corresponding data from the gas-liquid-solid runs, the solid phase hold-up values were plotted as a function of Re_l as illustrated in

Figure 6.5.

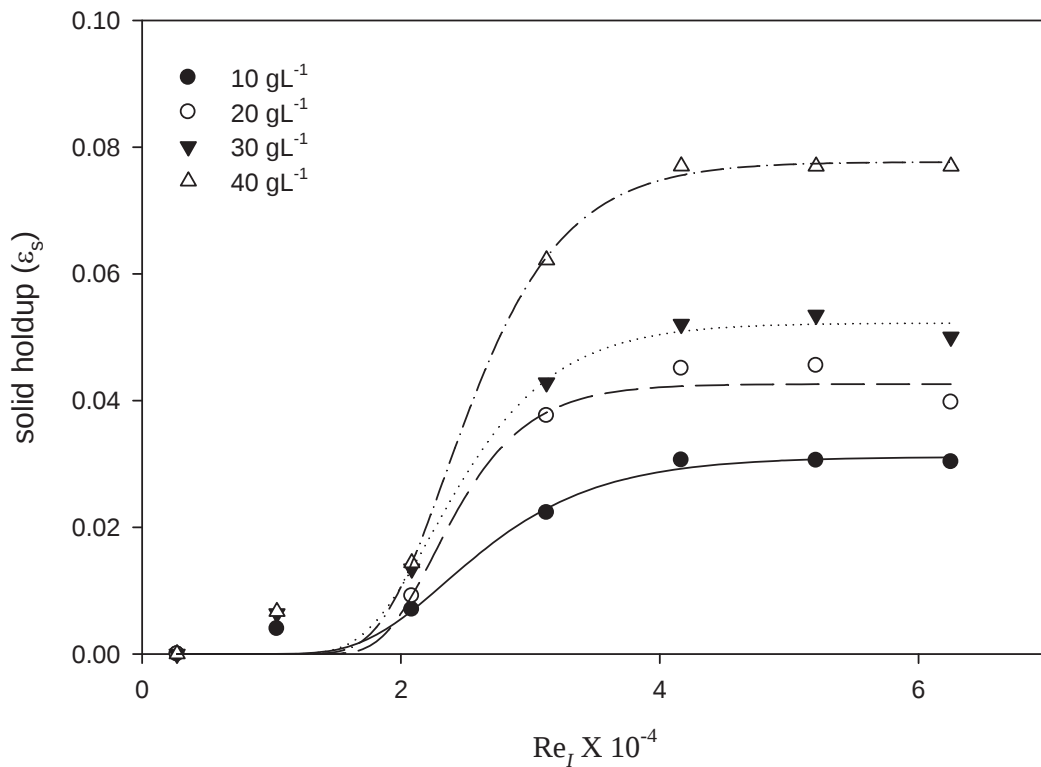


Figure 6.5 Solid phase hold-up (ϵ_s) for different solid loadings as a function of Re_l . Experimental data points are indicated by the open or closed symbols while the continuous or dashed curves represent the correlation (Equation (6.5)) prediction.

The sigmoidal nature of these curves indicates that three possible solid suspension regimes were experienced during the multiphase mixing. It appears that an incomplete solid suspension prevailed for $Re_l < 20800$ but not below N_{js} (≈ 52 rpm). In this regime, all solid particles have not been lifted off the tank bottom due to a distribution in solid particle size and the initial resistance presented by inter-particle cohesive forces in the bulk solid phase. However, as Re_l increased beyond 2.08×10^4 , all alumina particles were displaced into the liquid phase with the extent of dispersion increasing with impeller speed. This region, referred to as off-bottom suspension [14] attained its upper limit at about $Re_l = 4.2 \times 10^4$ such that rotational speed in excess of the latter resulted in no significant improvement in solid phase hold-up and hence, the existence of a homogeneous solid suspension. As may be expected, the solid phase

hold-up in this third and final regime is dependent upon the initial amount of solid added to the liquid phase. Non-linear regression of the data in Figure 6.5 to Equation (6.5) – the solid phase hold-up equivalent of Equation (6.2), i.e.

$$\varepsilon_s = \varepsilon_{s,\max} \left[1 - \exp(-\tau_{spp} \text{Re}_l) \right]^\gamma \quad (6.5)$$

gave values for τ_{spp} (the solid phase dimensionless time constant) as 2×10^{-4} where, γ , is now specifically assigned to the alumina particle clustering activity in the liquid phase. Nonetheless, both γ and $\varepsilon_{s,\max}$ (the maximum solid phase hold-up) are functions of the solid loading, w . Specifically, the power law expression;

$$\varepsilon_{s,\max} = \frac{w^{\frac{1}{m}}}{M_p} \quad (6.6)$$

was obtained, where m is the minimum number of particles to initiate solid cluster formation in the continuous liquid phase and M_p is the effective number of particles in a stable colloid per unit volume of solution. Estimates of m and M_p were obtained as 1.48 and 166 respectively. The dependency of γ on w may be given by the relation;

$$\gamma = \gamma_0 \exp\left(\frac{-k}{w}\right) \quad (6.7)$$

where γ_0 , the dimensionless clustering frequency for alumina particle in water was estimated as 88.78 and k , the alumina colloid formation constant was obtained as 1.32.

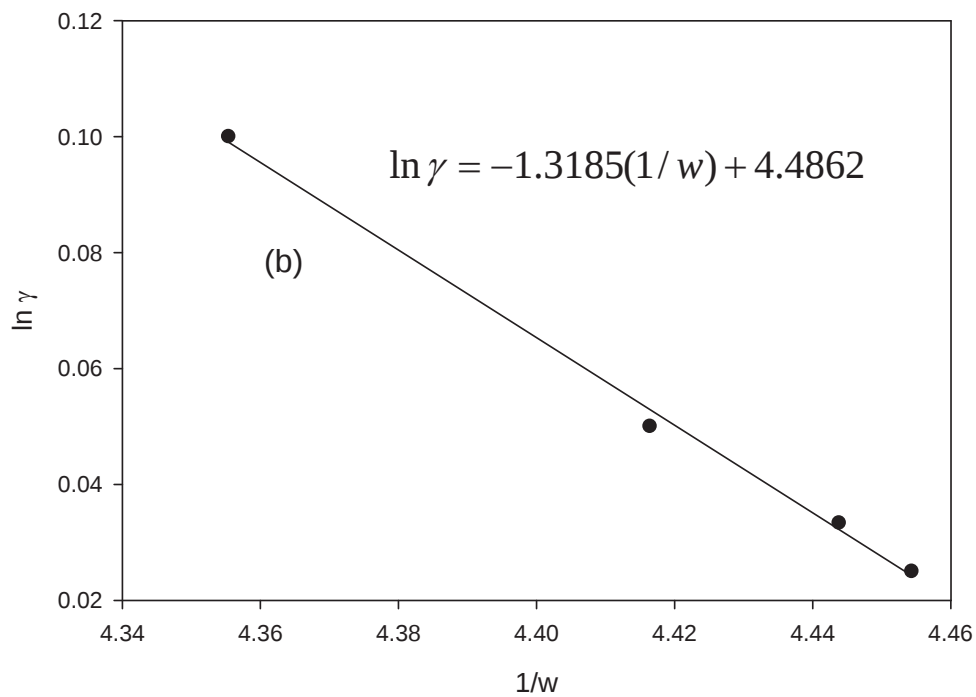
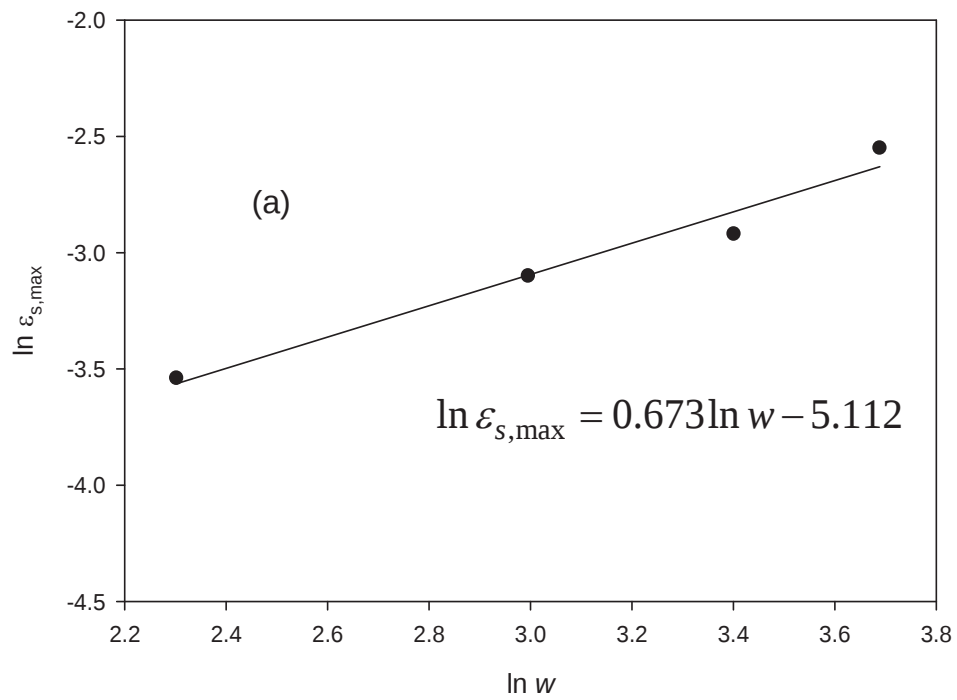


Figure 6.6 Fit of the experimental data to correlations provided by a) Equation (6.6) and b) Equation (6.7) respectively

Figure 6.6 (a & b) demonstrates the excellent agreement between Equations (6.6) and (6.7) and the experimental data. Superior mixing in

systems with a gas-inducing impeller is due to improved radial and axial solid dispersion [15] occasioned by the gas motion through the liquid phase. Since the mixing was carried out in all cases in the turbulent regime, the Prandtl mixing length may be deemed constant for the stirring speeds used in this study. As a result, the frequency of collision between the dispersed phase particles (gas bubbles and/or alumina entities) is the reciprocal of the characteristic time constant. From our estimates, it is evident that the particle-particle collision frequency was higher in the gas-liquid-solid system than in the liquid-solid system. As may be expected, the dimensionless particle-particle collision frequency in the solid-liquid system was 5×10^3 compared to 1.67×10^4 for the aerated slurry system most likely due to additional contributions from gas bubble-alumina particle and bubble-bubble interactions. This highlights the merit of using a gas-entrainment impeller over a conventional impeller for the same power number.

6.3.2. Estimation of gas dispersion rate and just suspended speed

Apart from the momentum transferred to the liquid phase by the impeller rotation, the gas recirculation momentum through the liquid phase is directly related to the gas flow through the gas exit orifices in the impeller blade, Q_g , which may be obtained from the use of Bernoulli's equation as:

$$Q_g = A_{orifice} \sqrt{\left(\frac{\rho_l (1 - \varepsilon_g)}{\rho_g} + \varepsilon_g \right) \left((\pi D_l N_s K_{loss})^2 + 2h_{f1} - 2gh \right) - 2h_{f2}} \quad (6.8)$$

where K_{loss} is the impeller speed loss coefficient for the impeller, $A_{orifice}$ is the cross-sectional area for the gas exit orifice, h_{f1} is the energy loss in the turbulent field (continuous phase) and h_{f2} is the energy loss during gas flow through the impeller shaft from inlet to exit. For a relatively smooth hollow shaft, h_{f2} may be considered negligible while $gh \gg h_{f1}$,

consequently, at the critical impeller speed, N_{cs} , where $Q_g = 0$, Equation (6.8) reduces to:

$$(\pi D_i N_{sc} K_{loss})^2 = 2gh \quad (6.9)$$

or

$$K_{loss} = \frac{\sqrt{2gh}}{\pi D_i N_{sc}} \quad (6.10)$$

Given that N_{cs} may be obtained from the Sawant-Joshi expression [16] (cf. Equation (3.11)), it is readily shown that

$$Q_g = A_{orifice}^T \sqrt{\left(\frac{\rho_l (1 - \varepsilon_g)}{\rho_g} + \varepsilon_g \right) \left(\left[\frac{N_s}{N_{sc}} \right]^2 - 1 \right) 2gh} \quad (6.11)$$

where $A_{orifice}^T$ is the total area for all orifices since there are 12 holes on the 4 impeller blades. Equation (6.11) was used to compute the gas flow Reynolds number, Re_G , as a function of impeller Reynolds number as displayed in Figure 6.8 . The resulting linear relationship between Re_G and Re_i is given by;

$$Re_G = 0.1105 Re_i - 1129.1 \quad (6.12)$$

is a distinct advantage of the gas-inducing mechanically agitated system over the independently gas-sparged stirred tank that requires additional power input in terms of gas compression costs. The critical impeller Reynolds number, Re_{lcr} , (for the onset of gas flow) from these data is 10218.1 corresponding to a critical stirring speed, N_{cs} of 3.64 rps (218 rpm) which is somewhat smaller than that obtained from Equation (3.11) (refer to chapter 3) i.e. 3.8 rps (233 rpm) perhaps due to the neglect of the energy losses (h_{f1} and h_{f2}) in the Bernoulli equation.

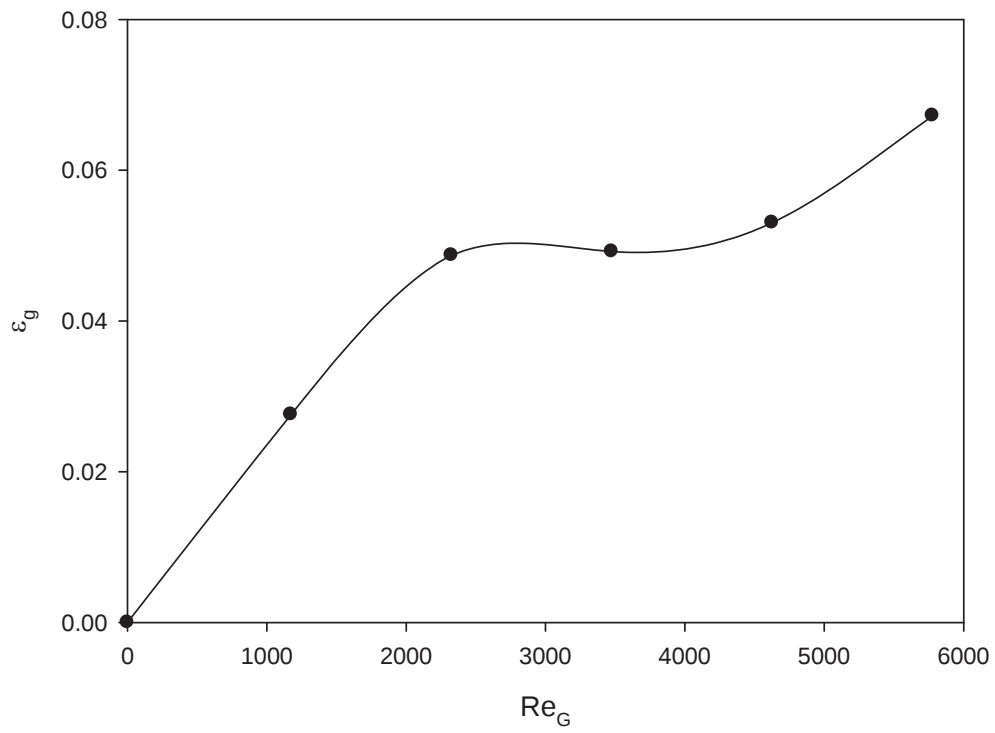


Figure 6.7 Gas phase hold-up (ϵ_g) as a function of gas Reynolds number (Re_G)

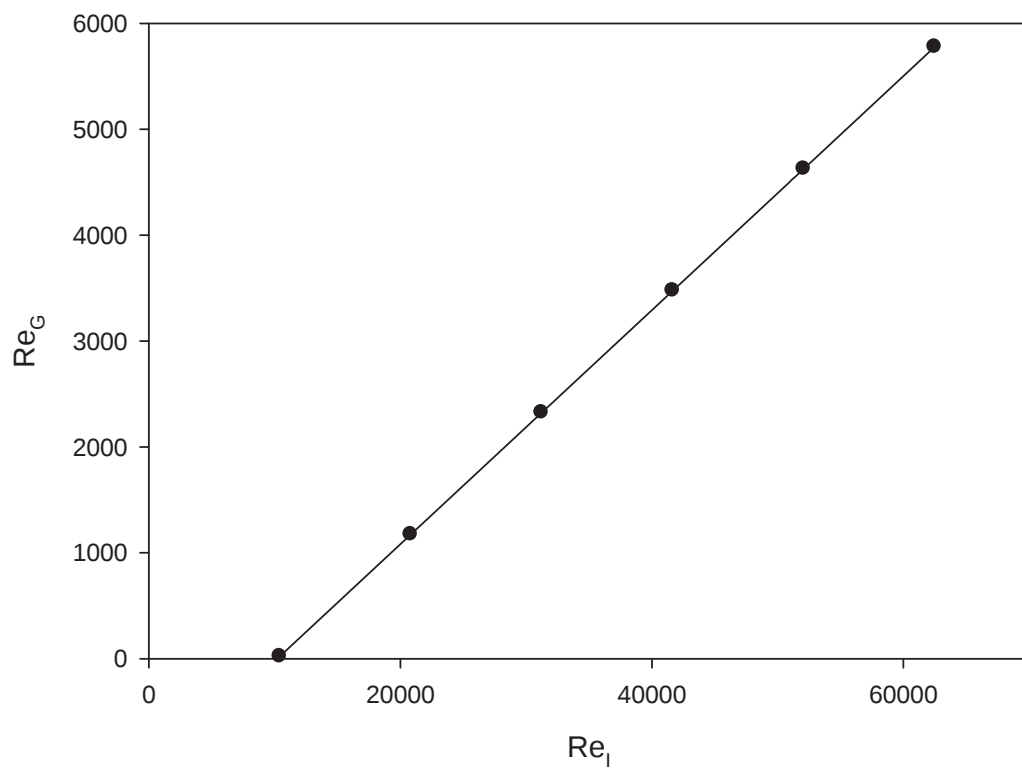


Figure 6.8 Gas Reynolds number (Re_G) as function of impeller Reynolds number (Re_I)

Figure 6.7 shows that the gas flow recirculation rate induced by the impeller, changed from laminar ($Re_G < 2500$) passing through a transition stage ($2500 < Re_G < 4500$) before finally entering the churn-turbulent regime ($Re_G > 4500$). This analysis indicates that whilst the liquid phase was in the turbulent regime ($Re_L > 10^4$), gas hydrodynamics may be laminar, transitionary or even churn-turbulent and hence, degree of gas-liquid mixing would vary. By the same token, the quality of solid particle dispersion is not solely determined by turbulence in the liquid phase.

While, it is apparent that the minimum speed required to just-suspend the solid particles in the stirred tank, N_{js} , has been exceeded for the run at 200 rpm in the gas-liquid-solid system. Indeed, using the correlation given by Baldi et al. [17], namely;

$$N_{js} = \frac{\beta_2 \mu_l^{0.17} (\rho_s - \rho_l)^{0.42} g^{0.42} d_s^{0.14} w^{0.125}}{\rho_l^{0.58} D_l^{0.89}} \quad (6.13)$$

where

$$\beta_2 = D_T/D_l$$

$$\rho_s = \text{density of solid particle (kg m}^{-3}\text{)}$$

$$\rho_L = \text{density of liquid respectively (kg m}^{-3}\text{)}$$

$$g = \text{the acceleration due to gravity (9.81 m s}^{-2}\text{)}$$

$$d_s = \text{the particle diameter (m)}$$

$$w' = \text{the percentage weight solid loading (g/100 g).}$$

Equation (6.13) gave N_{js} values varying from 48 to 57 rpm for the solid loading range (10–40 g L⁻¹) used in this study

6.3.3. Local analysis of dispersed phase hold-up

Tomogram analysis

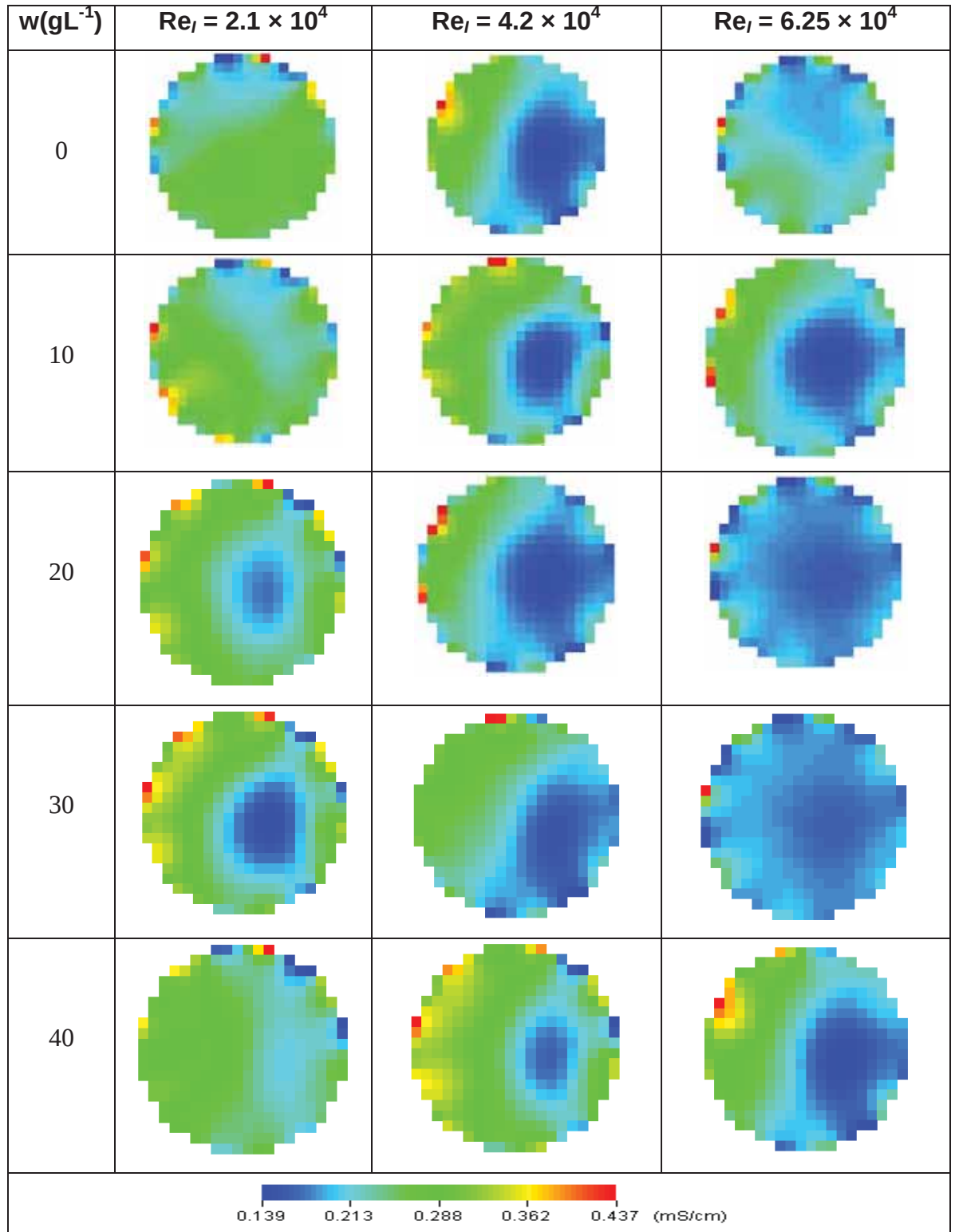
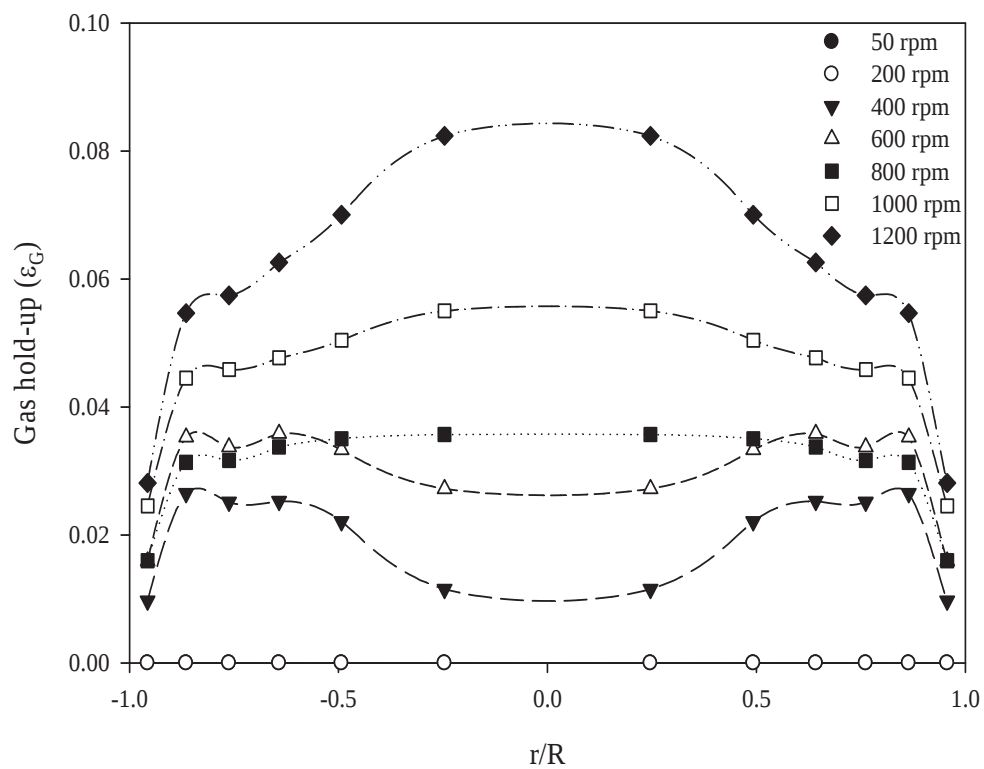


Figure 6.9 Variation of tomographic images at different loadings and stirring speeds

The tomograms shown in Figure 6.9 indicate a variation in the hue of the pixels across the vessel diameter and hence, the radial dispersed phase distribution may be obtained by substituting the time-averaged conductivity values for the pixels at different distances from the stirrer shaft.

6.3.4. Radial profile analysis



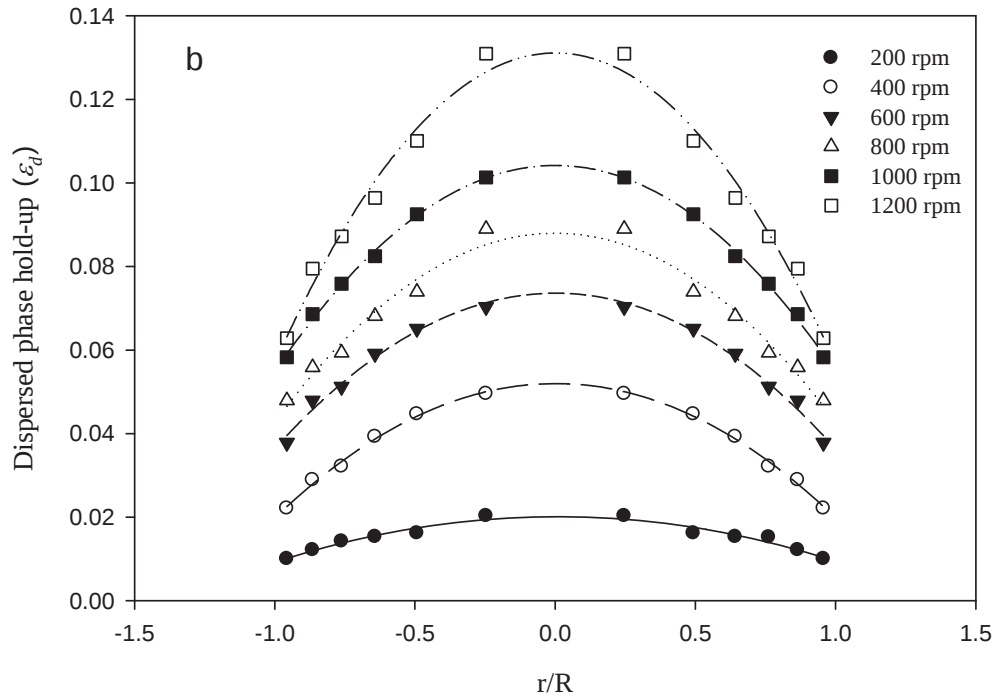


Figure 6.10 Radial distribution of phase holdup for (a) gas-liquid and (b) gas-liquid-solid systems at 10 gL^{-1} alumina loading.

Typical results are displayed in Figure 6.10 (a & b) for the gas-liquid and the gas-liquid-solid type of experiments. The profiles reveal the parabolic nature of the dispersed phase hold-up with respect to radial distance. As may be seen from Figure 6.10a, at rotational $Re_l < 4.2 \times 10^4$, the gas phase hold-up passed through a minimum at the centre ($r/R = 0$) but above this crossover speed, the profiles have a maximum at the centre. Incidentally this stirring speed corresponds to gas flow ($Re_G \approx 3.5 \times 10^3$) in the transition stage to churn-turbulent flow.

Indeed, with respect to Figure 6.7 and 6.10, it appears that the phase hold-up passes through a minimum at the centre if gas flow is in the laminar regime ($Re_G < 2500$; $Re_l < 3.1 \times 10^4$) while a maximum in radial phase hold-up profile is obtained for flow in the churn-turbulent zone ($Re_G > 4500$; $Re_l > 5.2 \times 10^4$). In both cases, however, the gas hold-up dropped sharply behind the PVC baffle and closer to the tank wall ($0.86 \leq r/R \leq 1.0$). At $Re_l < 3.1 \times 10^4$, gas flow was due to a predominant radial flow of the gas bubbles as they emerged from the gas ports (on the

impeller blades) and relatively low vertical (rise) gas velocity causing a high gas concentration in the annular space between the baffle and the impeller blade tip as evidenced in Fig. 12a at distance bounded by $(0.5 \leq r/R \leq 0.86)$ since impeller radius is 25 mm and tank radius is 50 mm. However, at high impeller rotations ($Re_i > 4.2 \times 10^4$), significant centrifugal force would push the liquid phase towards the wall with the gas phase displaced inwards and concentrated in the immediate vicinity of the shaft as a result of vortex effects and hence a maximum in the gas phase hold-up was observed at the vessel centre under this condition. For the gas-liquid-solid system, Figure 6.10b shows that the dispersed phase hold-up always passed through a maximum at the centre ($r/R = 0$) regardless of the stirring speed and solid loading.

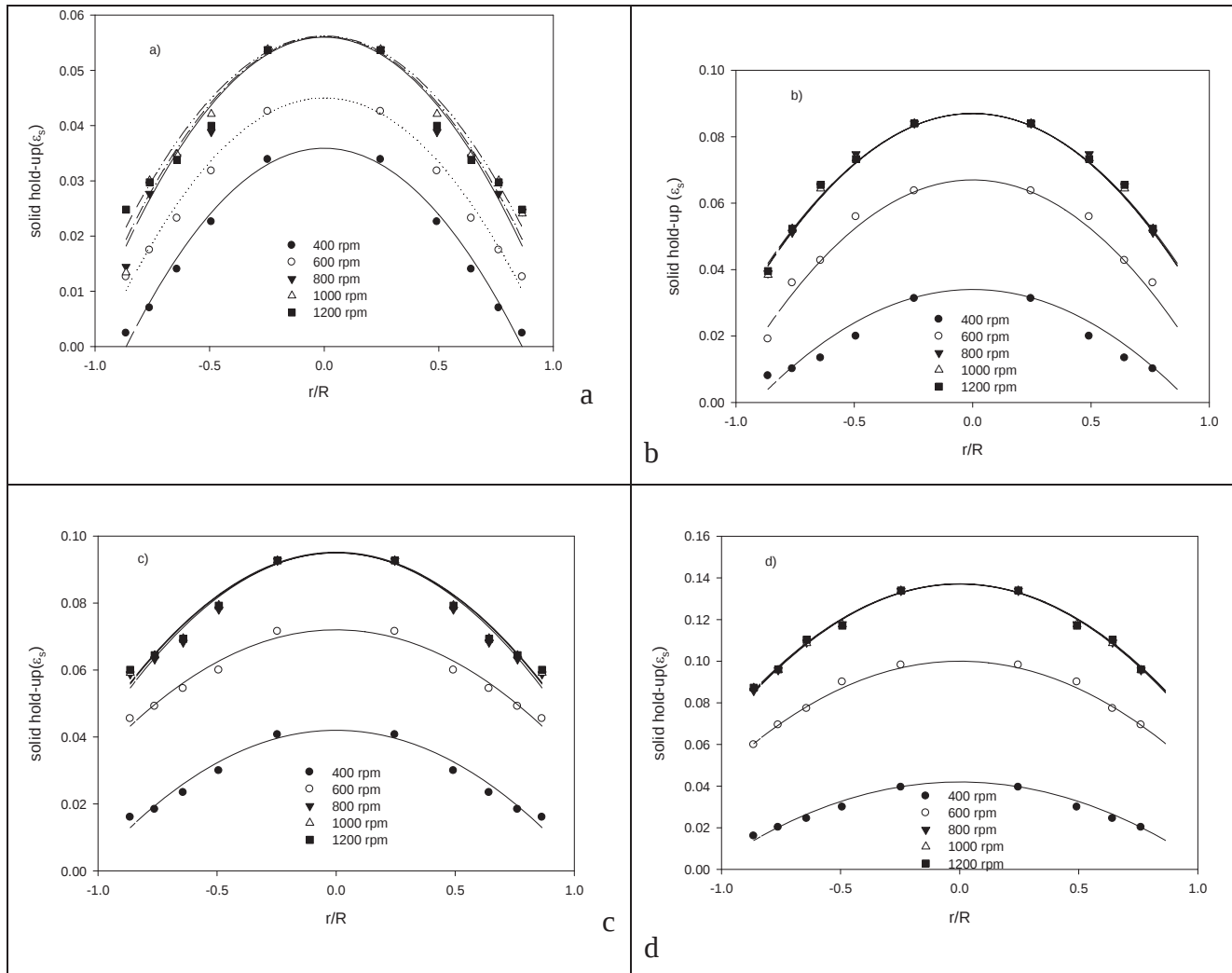
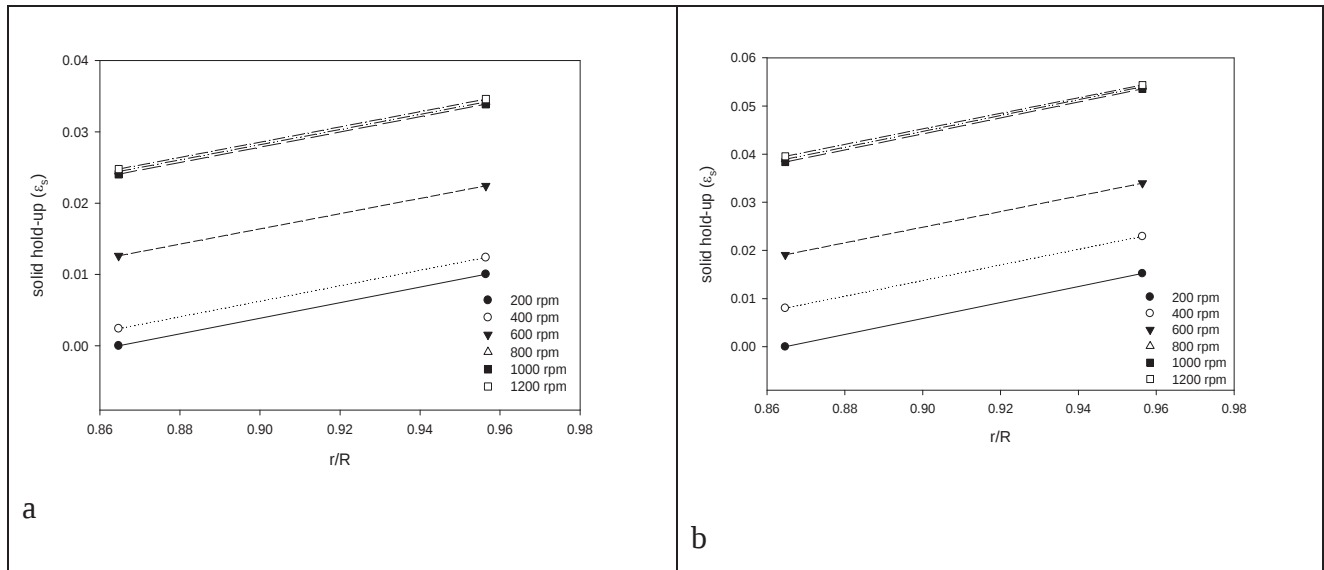


Figure 6.11 Solid phase hold-up at various radial positions ($-0.86 \leq r/R \leq +0.86$) for different catalyst loadings a) 10 gL^{-1} b) 20 gL^{-1} c) 30 gL^{-1} d) 40 gL^{-1}

Figure 6.11 (a to d) show the solid phase hold-up, ε_s , radial profiles for all solid loadings investigated in this study. The radial solid phase distribution profile at 200 rpm is similar to those at higher speeds, but not shown since the stirring rate was just below the critical impeller speed, N_{sc} , and hence, the dispersed phase hold-up values were somewhat diffused as a result of the cross-over into the gas-entrainment region. Even so, the similarity in shape (at the higher speeds) suggests that solid flow recirculation is governed by the same mechanism within the baffled space. However, behind the baffle, the solid phase hold-up increased linearly towards the wall (the reverse behaviour for gas bubbles) as may be seen in Figure 6.12 (a to d).



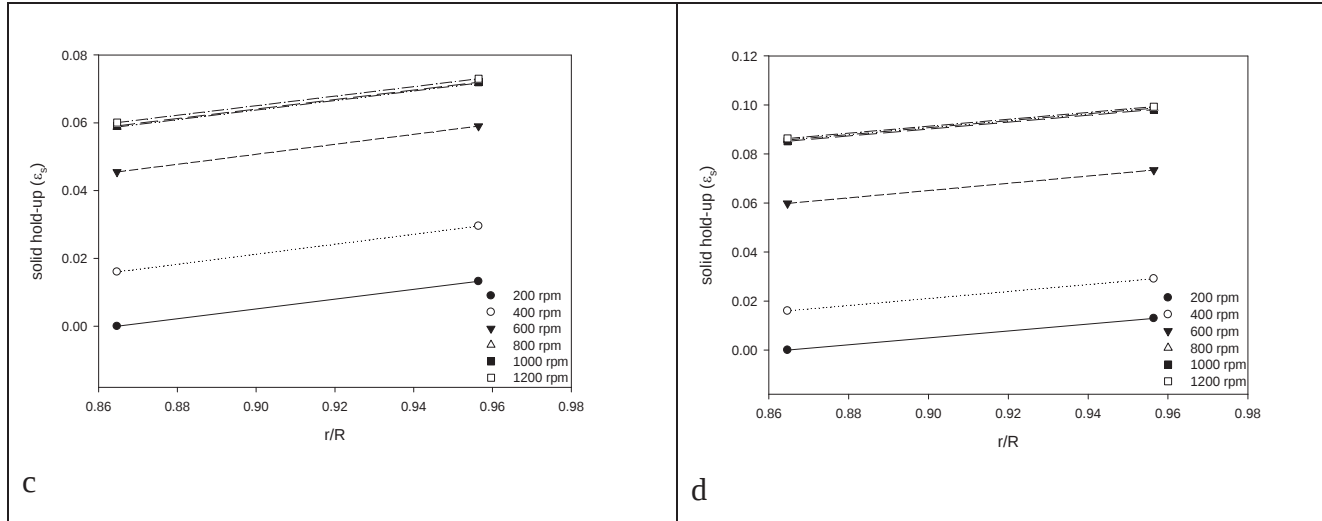


Figure 6.12 Solid phase hold-up at various radial positions ($\pm 0.86 \ll r/D \ll \pm 1.0$) for different catalyst loadings a) 10 g L^{-1} b) 20 g L^{-1} c) 30 g L^{-1} d) 40 g L^{-1}

The non-zero solid phase hold-up values at 200 rpm suggests that even before the onset of gas flow into the vessel, there was some solid content behind the baffle. These observations suggest that solid recirculation is primarily turbulent within the tank with impeller Froude number, Fr , varying between 18.52 and 666.7 over the range of stirring speeds used. The parabolic nature of these profiles implicates representation by a family of curves, namely;

$$\epsilon_s = \epsilon_{s0} - \psi \left(\frac{r}{R} \right)^2 \quad (6.14)$$

where ϵ_{s0} and ψ have the same functional form prescribed by Equation (6.14) yielding the associated parameters given in Table 6.2.

Table 6.2 Parameter estimates from Equations (6.14) to (6.18) for the local radial solid phase hold-up distribution.

Parameter	$\tau_{spp} \times 10^4$	m	M_P	γ_0	k
Global	2 ± 0.015	1.48 ± 0.01	166 ± 1.250	88.78 ± 0.669	1.32 ± 0.010
Centre	2 ± 0.025	1.72 ± 0.02	68.1 ± 0.857	123.78 ± 1.55	17.37 ± 0.218

Local	Radial	2±0.031	4.12±0.06	36.5±0.570	36.94±0.577	13.48±0.211
	compo					
	nent					

Specifically, ε_{s0} is the centre contribution to the local phase distribution while ψ constitutes the radial attenuating effect. The good agreement between Equation (6.14) and experimental data is exemplified by the parity plot shown in Figure 6.13.

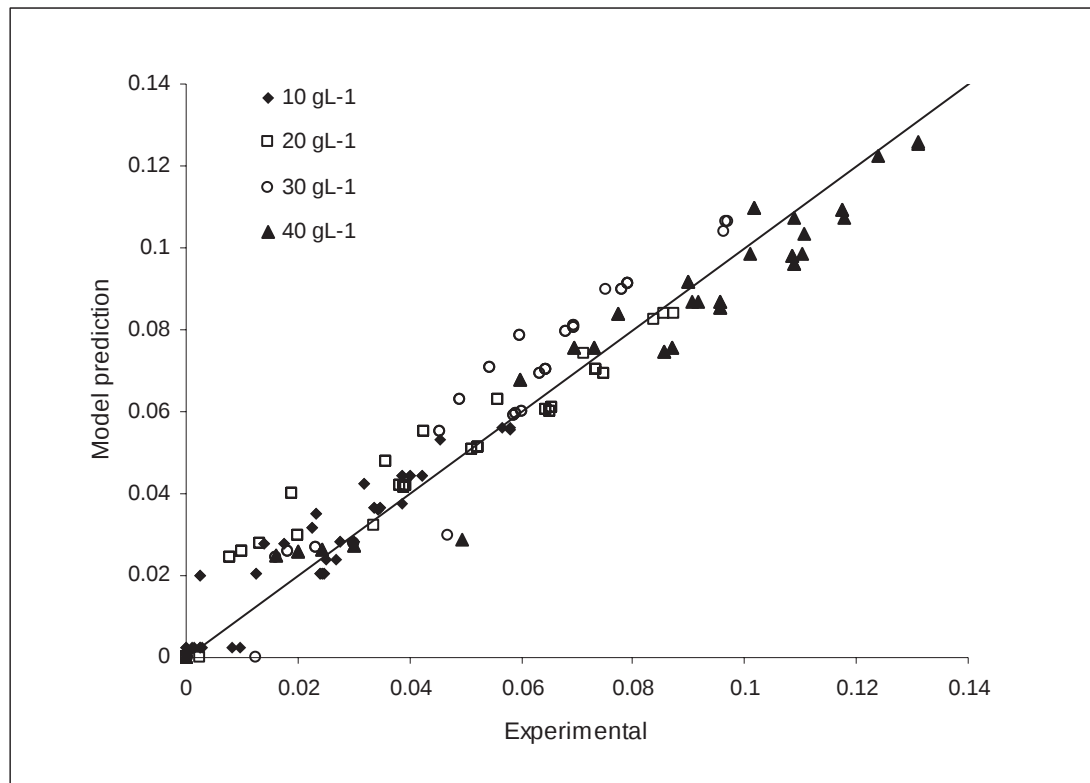


Figure 6.13 Parity plot for solid phase hold-up (ε_s)

In a slurry reactor, where the alumina particles may be the solid catalyst, Equation (6.14) suggests the possibility of radial reaction rate gradient due to solid phase hold-up radial distribution, even if external and internal transport resistances are negligible. Given that the catalyst activity is essentially the same on individual particles (as commonly assumed in

slurry reactor analysis), an estimate of the radial reaction rate gradient may be determined from Equation (6.14) for specified stirring speed and catalyst loading and hence, an *a priori* assessment may be made as to whether this radial variability is tolerable or not. Specifically, we obtain the relative change in radial solid phase hold-up profile with respect to the value at the reactor centre ($r=0$) as

$$\frac{1}{\varepsilon_{s0}} \frac{d\varepsilon_s}{dr} = -2(1.87w^{-0.34})\delta^\alpha \left(\frac{r}{R}\right) \quad (6.15)$$

where,

$$\delta = 1 - \exp(-2 \times 10^4 \text{Re}_i) \quad (6.16)$$

and

$$\alpha = \gamma_{0,\text{radial}} \exp\left(\frac{-k_{\text{radial}}}{w}\right) - \gamma_{0,\text{centre}} \exp\left(\frac{-k_{\text{centre}}}{w}\right) \quad (6.17)$$

Clearly, parametric sensitivity analysis may be conducted for different operating conditions using Equation (6.14). As far as we know, this type of relation is not available for stirred tank reactors [18] and will be especially valuable for reaction evaluation in slurry systems – the ultimate goal of our research. The relative change in solid phase hold-up distribution is a linear function of the radial distance from the centre (i.e. RHS of Equation (6.14)) as seen from Figure 6.14 where the slope (essentially the second derivative of ε_s with respect to r) is only dependent on the solid loading for a fixed impeller speed.

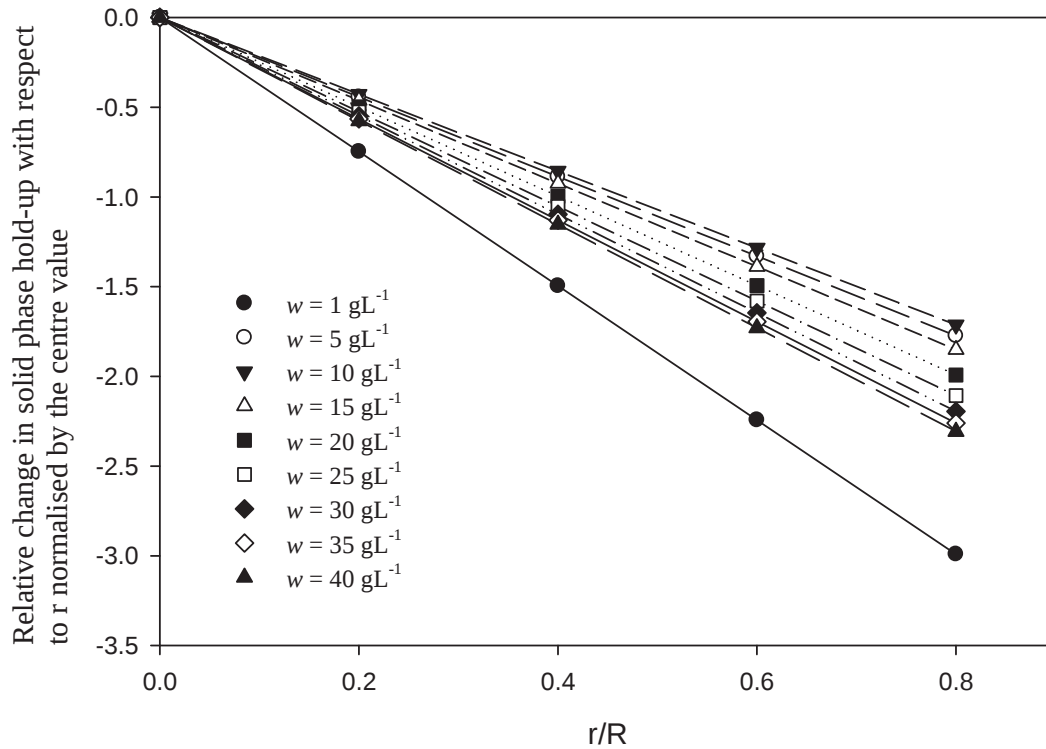


Figure 6.14. Relative change in solid phase hold-up with respect to r normalised by the centre value as a function of dimensionless r/R at $Re_l = 2 \times 10^4$.

Figure 6.15 plots the slope estimates in Figure 6.14 as a function of w for various Re_l . The strong solid phase hold-up radial gradient for $Re_l < 2 \times 10^4$ may be seen from this plot at all solid loadings examined even though the liquid recirculation velocity was in the turbulent regime – an indication that non-uniform solid mixing may still be obtained for turbulent liquid flow. On the other hand, at $Re_l > 2 \times 10^4$, the radial gradient in solid phase hold-up is practically independent of the solid loading ($w > 5 \text{ g L}^{-1}$) and hence provides an *a priori* indication that radial reaction gradient may be minimal. Obviously, as the w increases, a higher stirring speed will be required to ensure that the particles stay in suspension. Combining this information with other criteria such as requirement for solid particle suspension (cf. Equation (6.25)) will help in the determination of the range of solid (catalyst) loading to be used in

estimating the gas absorption and intra-particle mass transport resistances.

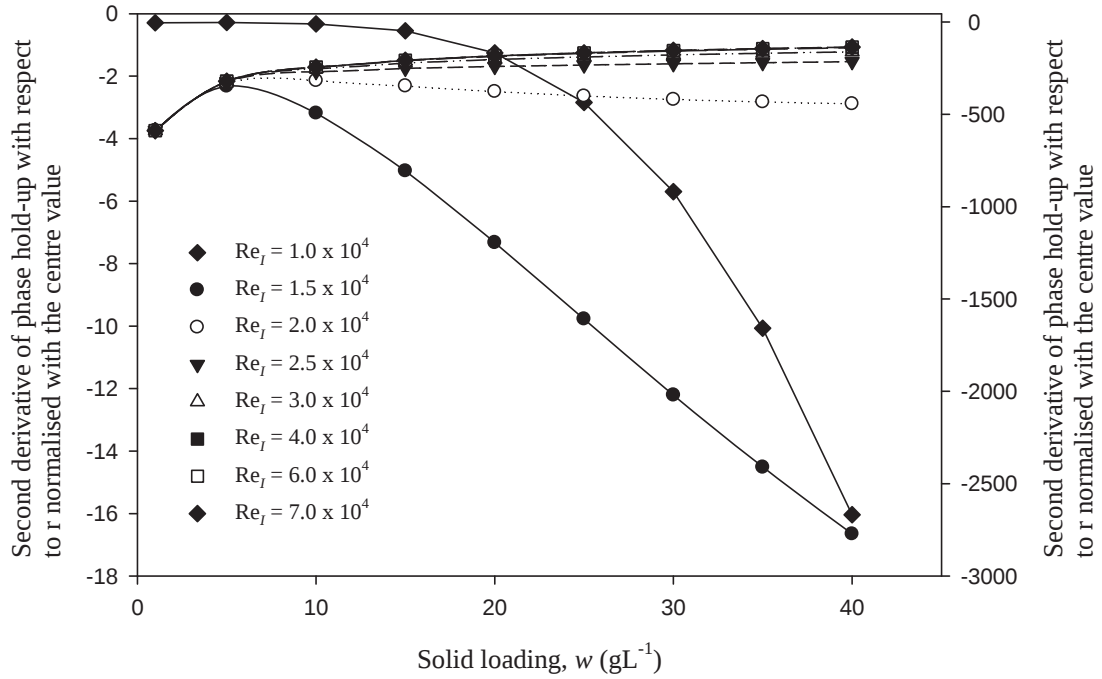


Figure 6.15 The second derivative of phase hold-up with respect to radius normalised with the centre value as a function of solid loading

A similar analysis for the solid phase hold-up distribution in the annular space between the PVC baffle and the reactor wall ($\pm 0.86 \leq r/R \leq \pm 1$) data (cf. Figure 6.12) suggests:

$$\varepsilon_s = 0.0011w^{2.26} \left[\text{Re}_I^{-\xi} + 68.36w^{-1.97} \left| \frac{r}{R} \right| \right] \quad (6.18)$$

where

$$\xi = 0.028w^{0.9} \quad (6.19)$$

Interestingly, while Equation (6.14) indicates that ε_s will be zero for contents within the baffled space ($-0.86 \leq r/R \leq 0.86$) once stirring has stopped ($\text{Re}_I = 0$), Equation (6.18) implicates a non-zero value for ε_s when $\text{Re}_I = 0$ suggesting that not all solid particles would settle back to the tank bottom once they have been initially dispersed. This hysteresis

effect was, in fact, observed in all our runs since alumina particles were formed on the wall and behind the baffle after stirring had ceased. From a practical standpoint, the annular space between the baffle and reactor wall must be as small as possible to minimise catalyst wastage.

6.4. Solid suspension behaviour

Instantaneous tomographic data were further analysed to provide information on the solid flow pattern during mixing. The statistical parameter, χ , defined as

$$\chi = \frac{1}{n_p} \sum_{i=1}^{n_p} \left(\frac{\varepsilon_i - \bar{\varepsilon}}{\bar{\varepsilon}} \right)^2 \quad (6.20)$$

where

ε_i = local solid voidage for the i^{th} pixel,

$\bar{\varepsilon}$ = average solid voidage for the entire cross-section

n_p = number of pixels (316)

indicates the degree of solid mixing (extent of homogeneity = $1-\chi$).

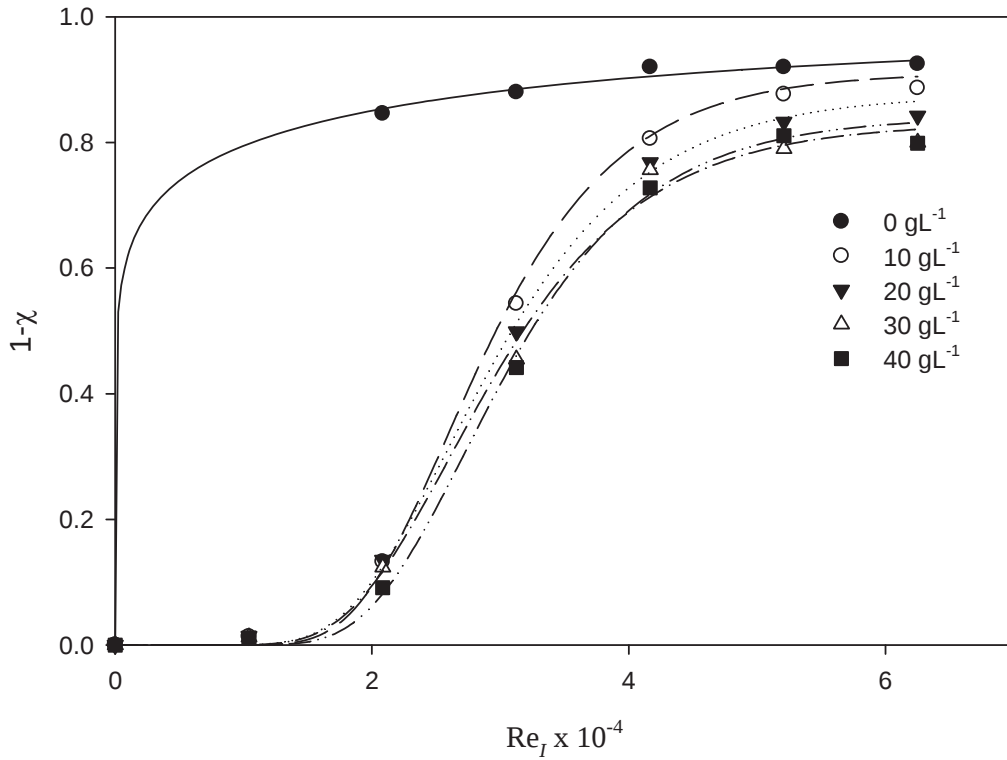


Figure 6.16 Degree of mixing as function of impeller Reynolds number (Re_i)

Figure 6.16 shows a plot of $(1-\chi)$ against the impeller Reynolds number, Re_i , for all stirring speeds investigated. Classification of solid suspension in stirred tanks [14] placed a multiphase mixture with $\chi \leq 0.2$ as a homogeneous (uniform) suspension while the contents are said to be in the off-bottom suspension stage for $(0.2 \leq \chi \leq 0.8)$ and incomplete suspension for $\chi \geq 0.8$.

It is apparent from Figure 6.16 that the degree of solid mixing, $(1-\chi)$, is dependent upon the initial solid loading and generally decreased with the latter variable. Uniform solid mixing was obtained at $Re_i > 4.2 \times 10^4$ as indicated by the relatively constant value of $(1-\chi)$. The solid suspension behaviour appears to be closely linked with fluid phase vertical recirculation since $Re_i > 4.2 \times 10^4$ also corresponds to the region for churn-turbulent gas flow ($Re_G > 4500$). It is noteworthy that the gas-liquid

system shows $\chi \leq 0.2$ for all speeds, confirming that the two-phase mixture is a pseudo-homogeneous solution.

Although direct measurements of solid particle velocity could not be determined from a single plane ERT sensor, the dimensionless solid mixing time, t'_{mix} , may be obtained from:

$$t'_{mix} = n_p \sum_{i=1}^{n_p} \frac{\varepsilon_i^2}{\sum_{i=1}^{n_p} \varepsilon_i} \quad (6.21)$$

and plotted as a function of Re_i as seen in Figure 6.17. The dimensionless solid mixing time, t'_{mix} , is the ratio of the solid recirculation rate to the particle velocity in the vessel. However, independent measurement of the particle velocity was not acquired in this study.

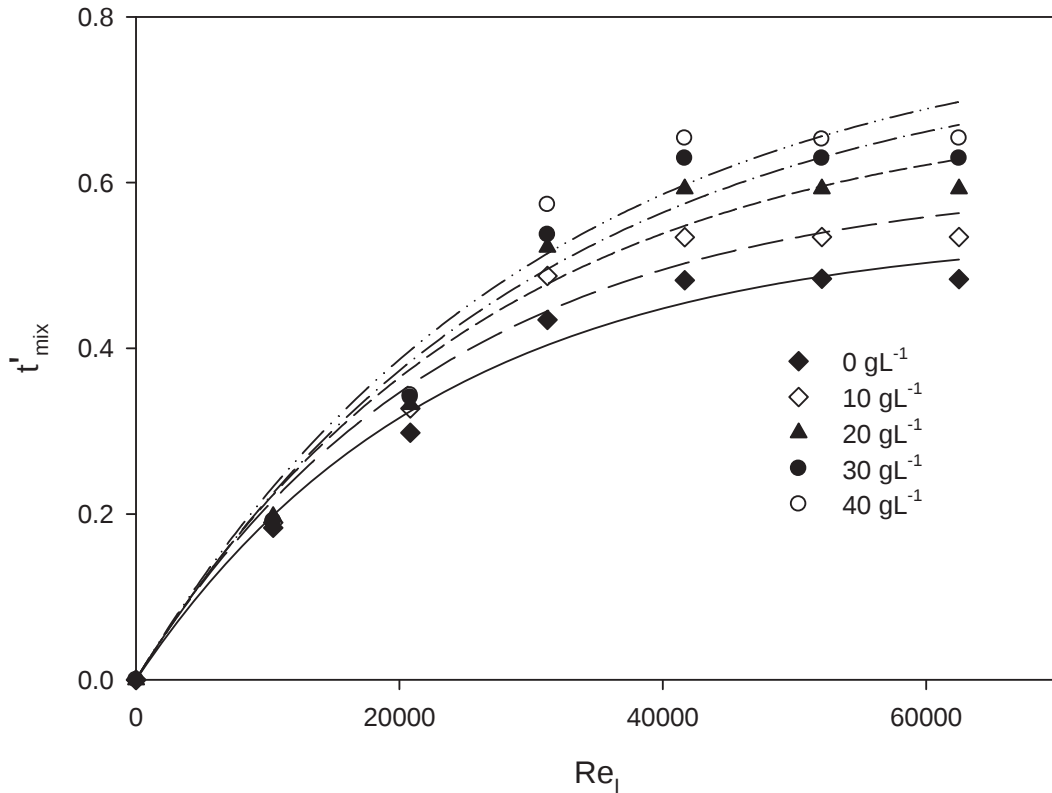


Figure 6.17 t'_{mix} as function of impeller Reynolds number (Re_i)

This figure shows that t'_{mix} initially increased rapidly with Re_l but approached a limiting value at $Re_l > 5 \times 10^4$. As a result, the behaviour may be represented by

$$t'_{mix} = a(1 - \exp(-bRe_l)) \quad (6.22)$$

where both a and b are functions of the solid loading and are given by;

$$a = 0.5156 + 3.8 \times 10^{-3}w \quad (6.23)$$

and

$$b = 4 \times 10^{-3} \exp(-0.0074w) \quad (6.24)$$

Figure 6.18 shows the parity between experimental data and model prediction from Equation (6.22).

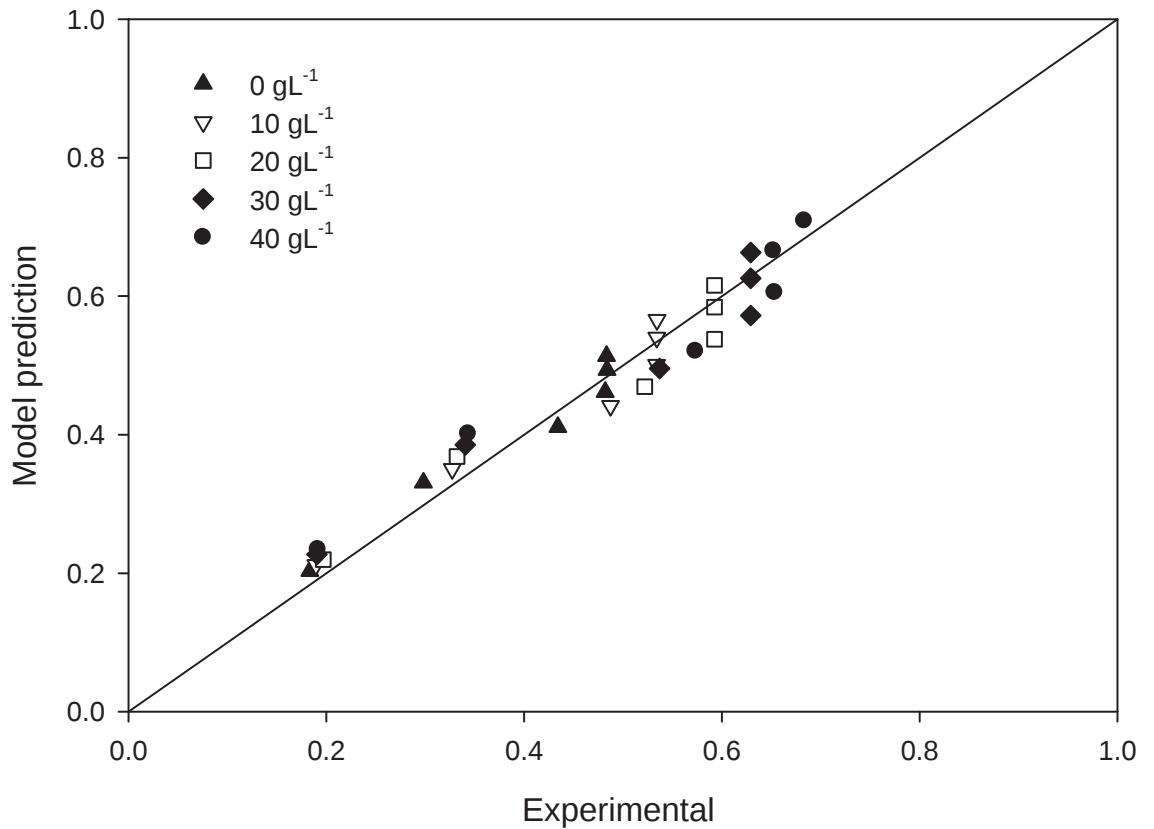


Figure 6.18 Parity plot for t_{mix}

6.5. Effect of particle size

Two set of experiments were carried out in order to investigate the effect of particle size, namely: a) gas-liquid system, and; b) gas-liquid-solid system with different sizes (see details of experimental set-up in Chapter 3). The data obtained in the gas-liquid system were used to retrieve the information on solid phase volume fraction which is discussed in a subsequent sub-section.

6.5.1. Physical properties

Electrical capacitance tomography (ECT) was employed as an organic liquid (paraffin oil) was the continuous phase in this particular study. Experimental runs were conducted for gas-liquid and gas-liquid-solid operations using impeller speeds ranging from 50 to 1200 rpm ($Re_i = 8 \times 10^2$ to 2.0×10^4) for 4 different alumina particle sizes (45, 90, 200 and 425 μm) with constant alumina loading of 10 g L^{-1} . The dispersed phase hold-up, ε_D , was determined from the Maxwell equation [19] (cf. Equation 3.12). The physical properties of air, alumina and paraffin oil are given in Table 6.3.

Table 6.3 Physical properties of paraffin oil and alumina particles

Parameter	Paraffin oil	Alumina	Air
Viscosity at 20°C $\text{kg m}^{-1} \text{s}^{-1}$	1.93×10^{-3}	-	1.70×10^{-5}
Density, kg m^{-3}	804	1400	1.2
Relative permittivity	2.2	9	1

6.5.2. Minimum agitation rate and just suspended speed calculations

The minimum speed for the onset of gas recirculation in a gas-inducing stirrer is given by the Sawant-Joshi correlation [16] (cf. Equation (4.5) in chapter 4). For the present stirred tank arrangement, $h = 66$ mm, $D_I = 50$ mm and with the paraffin oil liquid phase, $\mu/\mu_{water} = 1.93$, Equation (6.32) gives $N_{sc} = 5.07$ rps (304 rpm). Figure 6.19 shows the dispersed phase hold-up profiles as a function of impeller Reynolds number for the air-liquid paraffin only and when alumina particles of different sizes were introduced into the liquid phase. The initial delay in the dispersed phase hold-up value up to about $Re_I = 3.3 \times 10^3$ (300 rpm) for the paraffin oil profile is due to the lack of gas flow through the liquid before the attainment of the minimum speed for gas induction as seen in Figure 6.19. However, for the runs with alumina loading (10 g L^{-1}), the holdup value is non-zero (ca. 0.025) initially since alumina particles are regarded as entities of the dispersed phase from an ECT perspective. Even so, a similar delay in this case is due to insufficient vertical momentum required to first lift all the solid particles from the tank bottom into the liquid. The minimum speed required to just suspend all solid particles in a stirred tank, N_{js} , has been given by Baldi *et al.* [17] (cf. Equation 6.13).

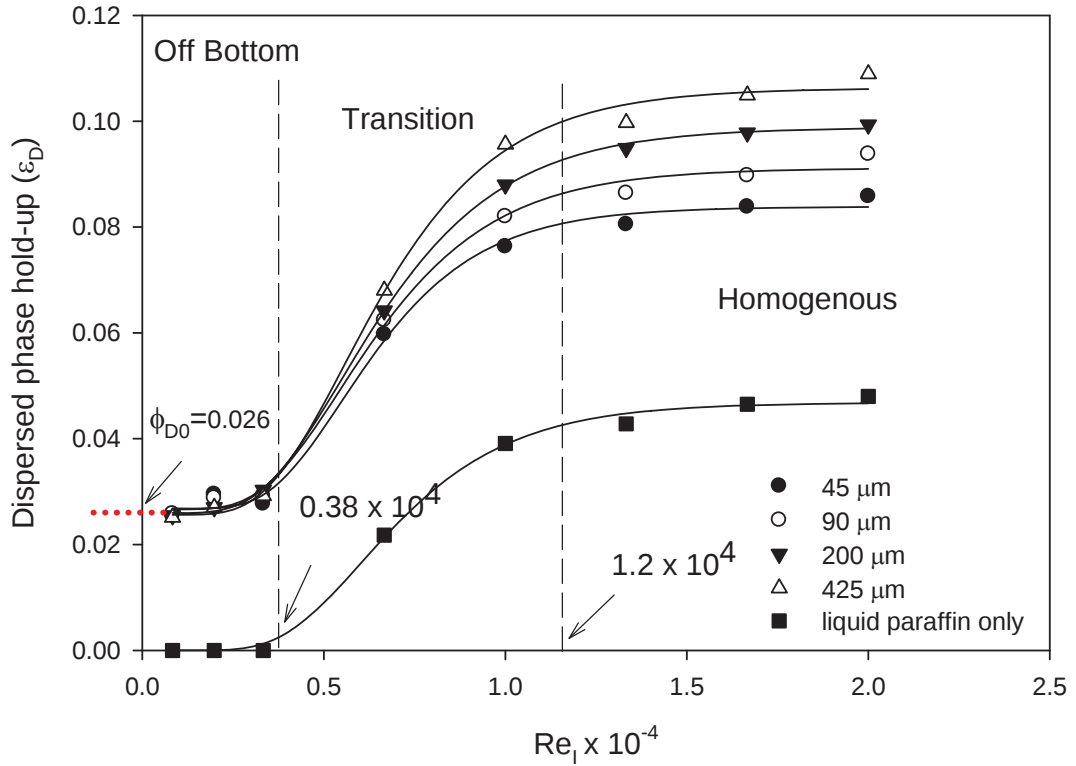


Figure 6.19 Dispersed phase hold-up as function of Impeller Reynolds number

For the particle size range used in this study, the N_{js} estimates spanned 97-132 rpm ($Re_I = 1.6-2.2 \times 10^3$). Nonetheless, in both of gas-liquid and gas-liquid-solid system, the sigmoidal shape of dispersed phase hold-up can be adequately described by the Chapman-Richards model given by;

$$\varepsilon_D = \varepsilon_{D0} + \varepsilon_{D1} \left[1 - \exp(-\tau_{dpp} Re_I) \right]^\gamma \quad (6.25)$$

where ε_D is the overall dispersed phase hold-up, γ is the particle clustering activity in the liquid phase due to inter-particle forces and τ_{dpp} is a dimensionless dispersed phase mixing time constant and $\varepsilon_{D,0}$ and $\varepsilon_{D,1}$ are the initial and deviation between the initial and maximum dispersed phase hold-up respectively. Nonlinear regression analysis of the data in Figure 6.19 using Sigmaplot® version 10.0, yielded estimates detailed in Table 6.4. It is clearly seen from the Figure 6.19 that three distinct

regimes exist in the system namely; off-bottom, transition and homogenous regimes. In off-bottom regime, no gas bubbles were forming as evidence in the Figure 6.19 for gas-liquid system. This result is in agreement with the estimation from Sawant and Joshi correlation [16] ($N_{cs} = 304$ rpm). This point is attributed as the first transition point which marks the onset of the transition regime ($Re_l = 0.38 \times 10^4$). As the mixing intensity increases, bubbles coalescence and large bubbles break-up commence until the point that the break-up and coalescence become rapid and equilibrium. This corresponds start of fully developed homogenous regime ($Re_l = 1.2 \times 10^4$). Therefore, any increase in stirring speed after this point, would not affect the overall gas phase hold-up which evidenced in Figure 6.19.

Table 6.4: Parameter estimates of Equation (6.26)

d_p (micron)	ϵ_{D0}	ϵ_{D1}	γ	$\tau_{dpp} \times 10^4$
45	$0.026 \pm 2.6 \times 10^{-5}$	$0.057 \pm 5.7 \times 10^{-5}$	$13.24 \pm 13.2 \times 10^{-3}$	$4.3 \pm 4.3 \times 10^{-3}$
90	$0.026 \pm 2.6 \times 10^{-5}$	$0.065 \pm 6.5 \times 10^{-5}$	$9.74 \pm 9.7 \times 10^{-3}$	$4.3 \pm 4.3 \times 10^{-3}$
200	$0.026 \pm 1.3 \times 10^{-5}$	$0.073 \pm 3.6 \times 10^{-5}$	$9.06 \pm 4.5 \times 10^{-3}$	$4.3 \pm 2.2 \times 10^{-3}$
425	$0.026 \pm 1.3 \times 10^{-5}$	$0.081 \pm 4.1 \times 10^{-5}$	$4.30 \pm 2.2 \times 10^{-3}$	$4.3 \pm 2.2 \times 10^{-3}$

A constant value of 4.3×10^{-4} for τ_{dpp} suggests an identical solid particle or gas bubbles mixing mechanism within the vessel and in particular, ϵ_{D0} is also independent of the particle size. However, both ϵ_{D1} and γ varied with particle size. Since the dispersed phase was made up of both gas bubbles and solid particles the decoupling of contributions from each of these entities will be useful in further analysis. Unfortunately, ECT cannot discriminate between gas bubbles and alumina particles. As a result, experiments were conducted with a standard non gas-inducing stirrer (with identical dimensions to the gas-inducing impeller) at different solid loadings so that the dispersed phase is only alumina particles. As may be seen from Figure 6.20, the dispersed phase in both cases varied linearly with solid loading as expected due to increased concentration n of alumina particles. However, the constant difference between the results for the standard non gas inducing impeller and the gas-inducing type is primarily due to the additional gas introduced into the liquid phase with the latter stirrer [20].

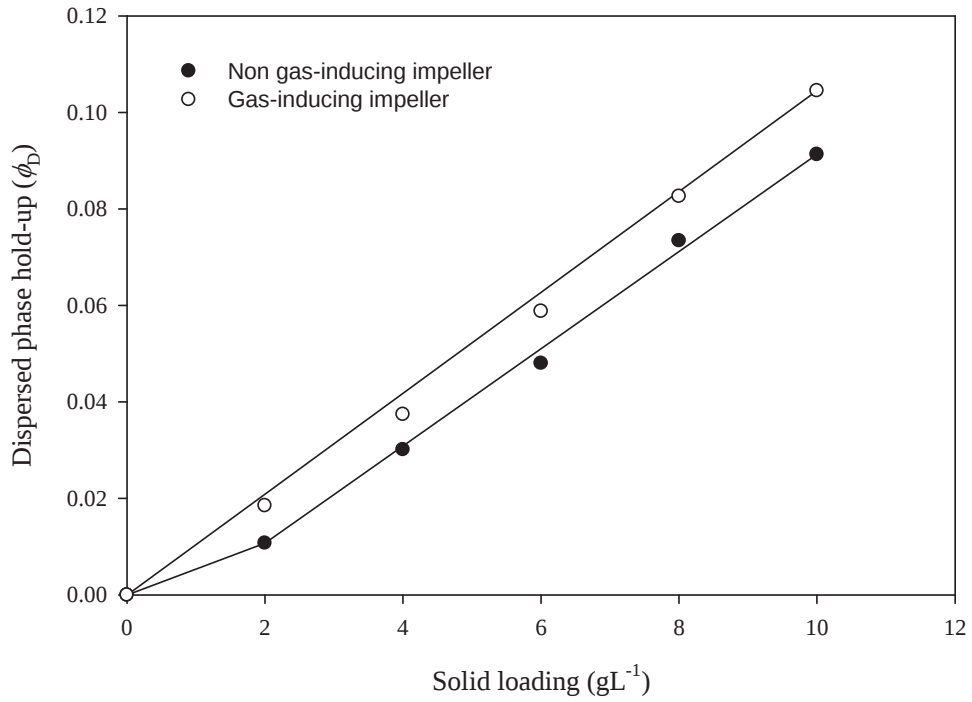


Figure 6.20 Dispersed hold-up as function of solid loading

Consequently, the dispersed phase, ε_D , in a gas-liquid-solid stirred tank may be written as;

$$\varepsilon_D = \varepsilon_S + \varepsilon_G \quad (6.26)$$

where ε_S and ε_G are the solid and gas phase hold-up respectively. Since the dispersed phase for the paraffin oil only was air, Equation (6.26) was used to compute the solid phase hold-up data, ε_S from the paraffin oil-alumina curves (cf. Figure 6.20).

Figure 6.21 plots the solid phase hold-up as a function of the impeller Reynolds number, Re_I . The sigmoidal shape is retained and hence, the Chapman-Richards expression for the solid phase hold-up model may be given as:

$$\varepsilon_S = \varepsilon_{S0} + \varepsilon_{S1} \left[1 - \exp(-\tau_{spp} Re_I) \right]^\xi \quad (6.27)$$

where τ_{spp} is a dimensionless characteristic particle time constant for the system and the exponent, ζ , is the particle clustering activity in the liquid phase. A fit of data to Equation (6.28) revealed that τ_{spp} is independent of particle size at a value of 5.0×10^{-4} and ε_{s_0} is 0.022.

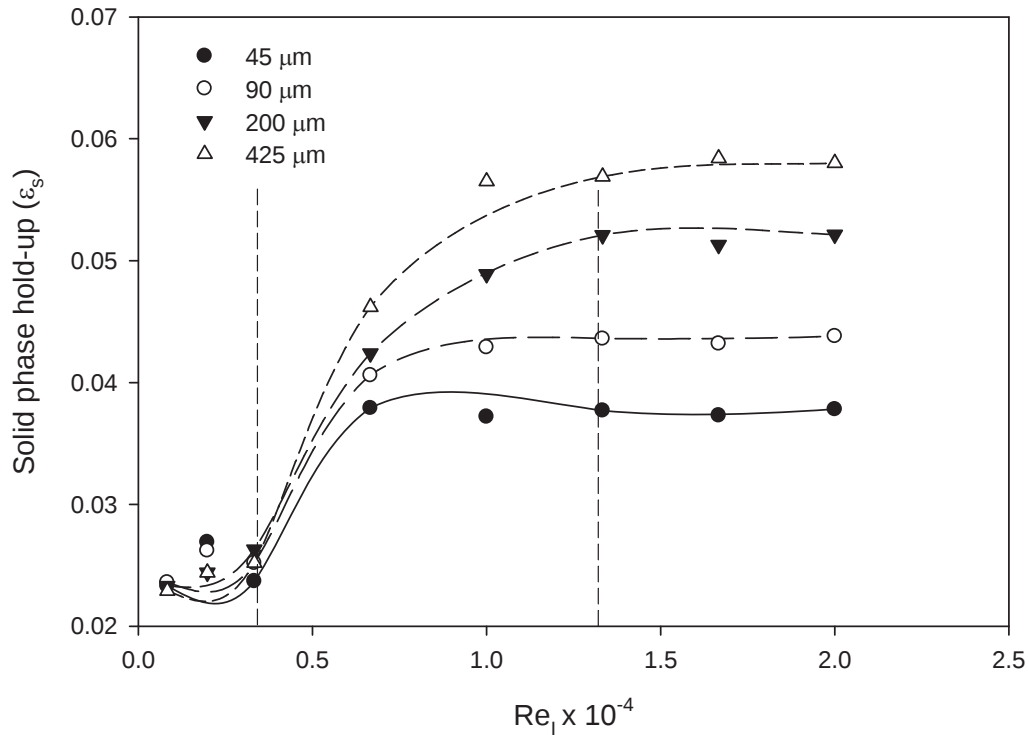


Figure 6.21 Solid phase hold-up as function of Re_l .

The mixing time constant, τ_{spp} , suggests that alumina recirculation rate (reciprocal of τ_{spp}) was higher than the combined gas-solid recirculation rate ($1/\tau_{dpp}$) from Equation (6.26). However, both ε_{s_1} and ξ are dependent on particle size and are exclusively properties of the solid phase. The relationship of both parameters to particle size, d_p , is shown in Figure 6.22 and 6.23 respectively.

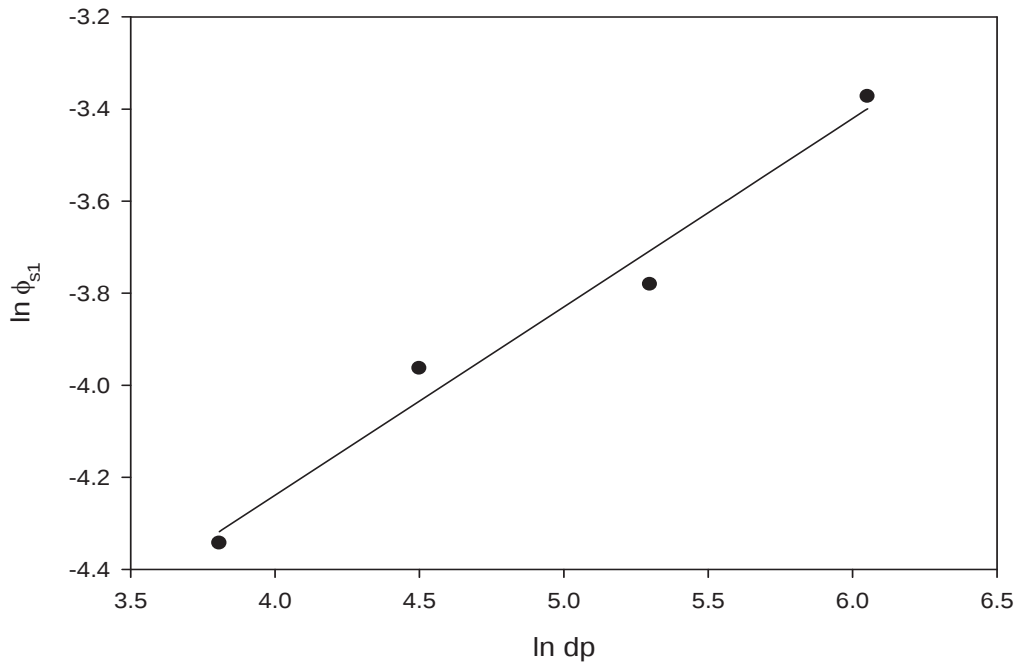


Figure 6.22 Fit of experimental data for eq. 6.

Based on the data regression, $\varepsilon_{s,1}$ may be correlated as a function of particle size as;

$$\varepsilon_{s_1} = \frac{d_p^{1/m}}{M_p} \quad (6.28)$$

where m is the minimum number of particles to initiate solid cluster formation in the liquid phase and M_p is the effective number of particles in a stable colloid per unit volume of solution. Estimates of m and M_p were obtained as 24 and 356 respectively. Figure 6.23 also implicates an Arrhenius-type relation between ξ and d_p as;

$$\xi = \xi_0 \exp\left(-\frac{k}{d_p}\right) \quad (6.29)$$

where ξ_0 is the clustering propensity of alumina particles in the liquid phase and k is an intrinsic constant for alumina colloid formation in

continuous phase and akin to the Arrhenius parameter (E/R) for chemically-reactive particles.

The parameters ξ_0 and k were estimated to be 1.6×10^2 and 3.48 respectively.

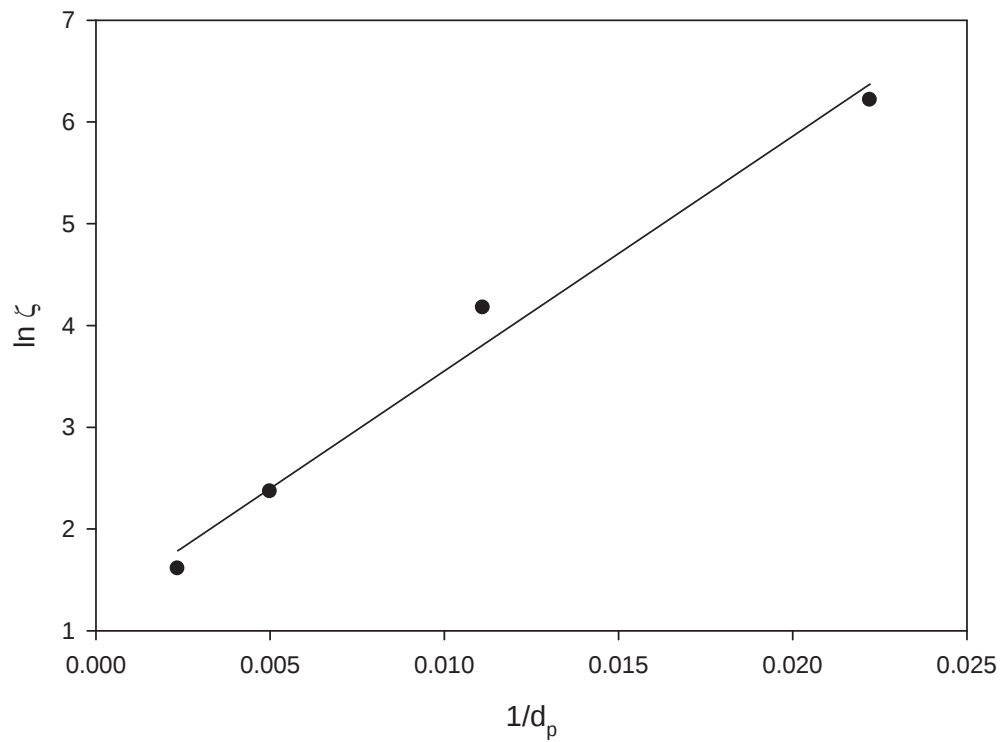


Figure 6.23 A fit experimental data for Equation (6.30)

Figure 6.24 shows the measured mean dispersed phase hold-up as a function of radial distance at various stirring speeds for the gas-liquid system. The data were computed from the analysis of tomograms at various distances from the impeller shaft using *ITS system 2000 tool-suite* software.

6.5.3. Radial profile analysis

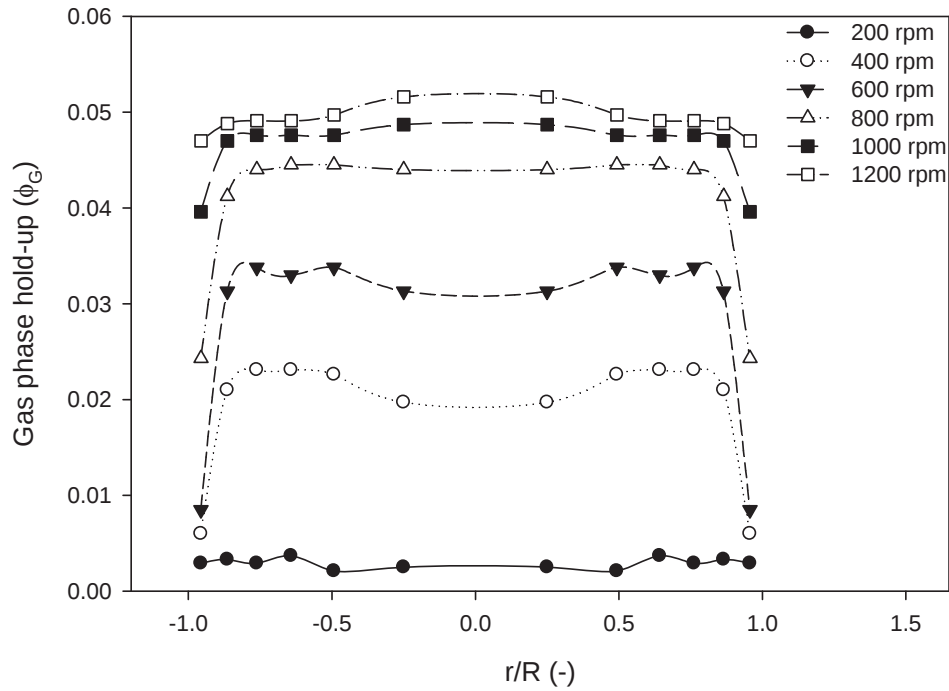


Figure 6.24 Radial profile for gas-liquid system in gas-inducing stirred tank reactor

The radial gas phase hold-up profiles may be classified into two types. The first class represents profiles for impeller rotational speed less than 600 rpm which are characterised by a minimum at the stirrer shaft ($r/R = 0$), while in the second class (for stirring speed greater than 800 rpm), the profiles exhibited a maximum gas hold-up at $r/R = 0$. The change in radial gas hold-up behaviour may be associated with the presence of vortex effects at high stirring rate. In a mechanically-stirred tank, the existence of vorticity is indicated by the Taylor number, Ta , given as:

$$Ta = N_s r_m^{\frac{1}{2}} b^{\frac{3}{2}} \frac{\rho_c r_r}{\mu_c r_s} \quad (6.30)$$

where N_s is the angular velocity in rps, r_r and r_s are radii of rotor (impeller) and stator (stirred vessel) respectively, r_m is the mean radius, $(r_s + r_r)/2$, cm, b is the annular width, $r_s - r_r$, cm, ρ_c is the density of continuous phase and μ_c is viscosity of the continuous phase. For a stirred tank, the critical Ta value of 1700 indicates the onset of vortex effects and equation (6.30) yields a stirring rate of 11.07 rps (664 rpm) for the vessel geometry employed in this work. This is in agreement with the switch from a minimum to a maximum radial profile between 600 and 800 rpm observed in Figure 6.24.

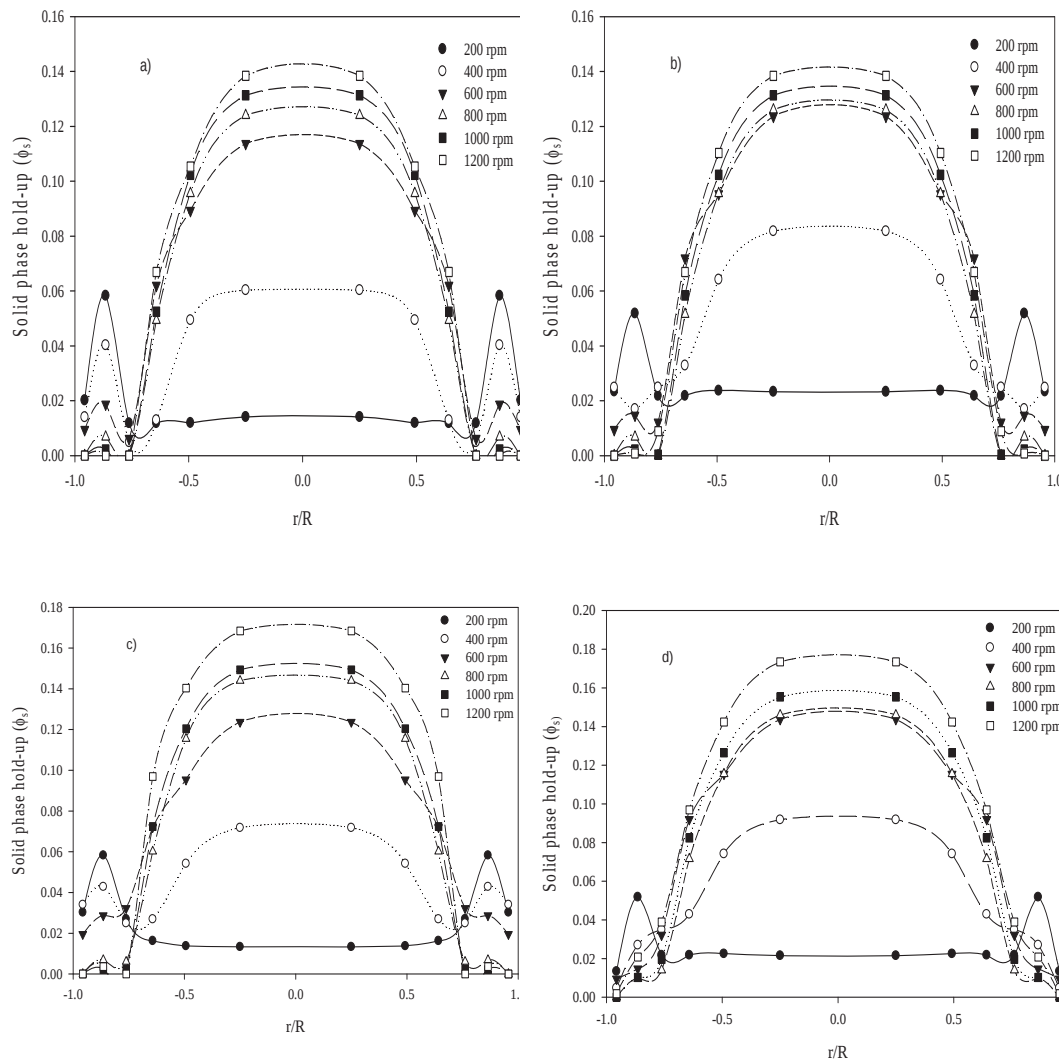


Figure 6.25 The radial profile for various particle sizes a) 45 μm b) 90 μm c) 200 μm and d) 425 μm

Based on the Figure 6.25(a-d), the parabolic profiles for all the stirring speeds (except at 200 rpm) are maximum curves (at the shaft) indicating the solid mixing was predominantly vertical recirculation. However, at 200 rpm, the dispersed hold-ups are virtually flat suggesting that the solid particles were essentially unperturbed by the swirling in the paraffin oil phase. The sudden drop of dispersed phase hold-up behind the baffle may be due to the accumulation of combined gas bubbles and alumina particles. Nonetheless, at higher agitation rate, the vast majority of the dispersed phase hold-up behind the baffle may have come from the alumina particles. The relative solid phase hold-up for small particles is higher than of large particles at position closed to the vessel wall due to smaller particles contained less dense material and easily to being pushed away towards the wall especially at low stirring speed (higher stirring speed provides enough momentum for the particles to bounce back towards the centre).

The quality of solid mixing in the multiphase reactor may be determined from the tomographic data obtained at different speeds using the statistical relation (cf. Equation 6.20);

The parameter χ indicates the degree of solid mixing (extent of homogeneity = $1-\chi$). Figure 6.26 shows a plot of $(1-\chi)$ against the impeller Reynolds number, Re_i , for all stirring speeds investigated. Kasat *et al* [14] classified a mixed multiphase system with $\chi \leq 0.2$ as a homogeneous (uniform) suspension while the contents are said to be in the off-bottom suspension stage for $(0.2 \leq \chi \leq 0.8)$ and incomplete suspension for $\chi \geq 0.8$. It is evident from Figure 6.26 that alumina-paraffin oil mixing across the range of impeller speeds used in this study exhibited behaviour in each of these three categories.

It is clear that the paraffin oil-alumina mixture may be regarded as a homogeneous solution at $Re_i > 1.5 \times 10^4$ (>850 rpm) while the air-paraffin oil mixture attained the same quality of mixing at a much lower Re_i value of about 6×10^3 . In particular, the gas-liquid system behaviour does not

exhibit the S-shape profile typified by the solid-liquid system. The dimensionless solid recirculation time constant was computed from the transient tomographic data using Equation (6.20) and plotted as a function of Re_l as seen in Figure 6.27. Interestingly, the profiles for both degree of solid mixing and t'_{mix} are in similar pattern than of the effect of catalyst loading in water. These similarity implies that both solid loading and particle size as function of Re_l .

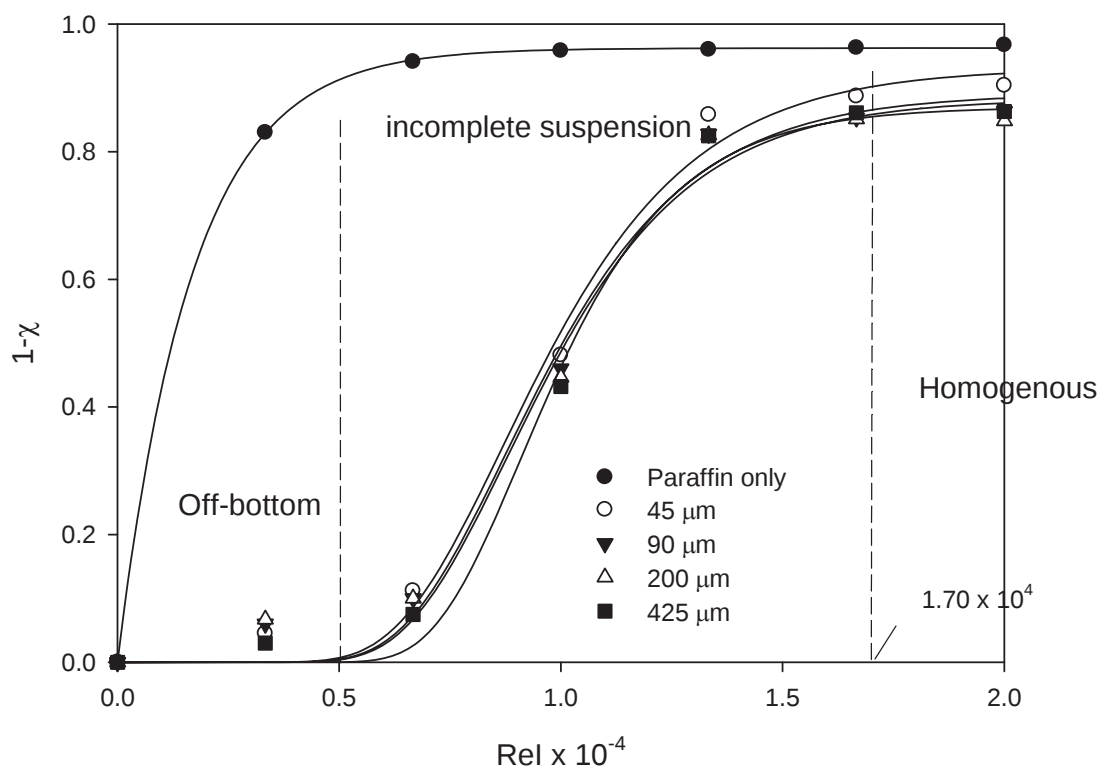


Figure 6.26 The influence of impeller speed on the quality of mixing in the gas-inducing stirred tank

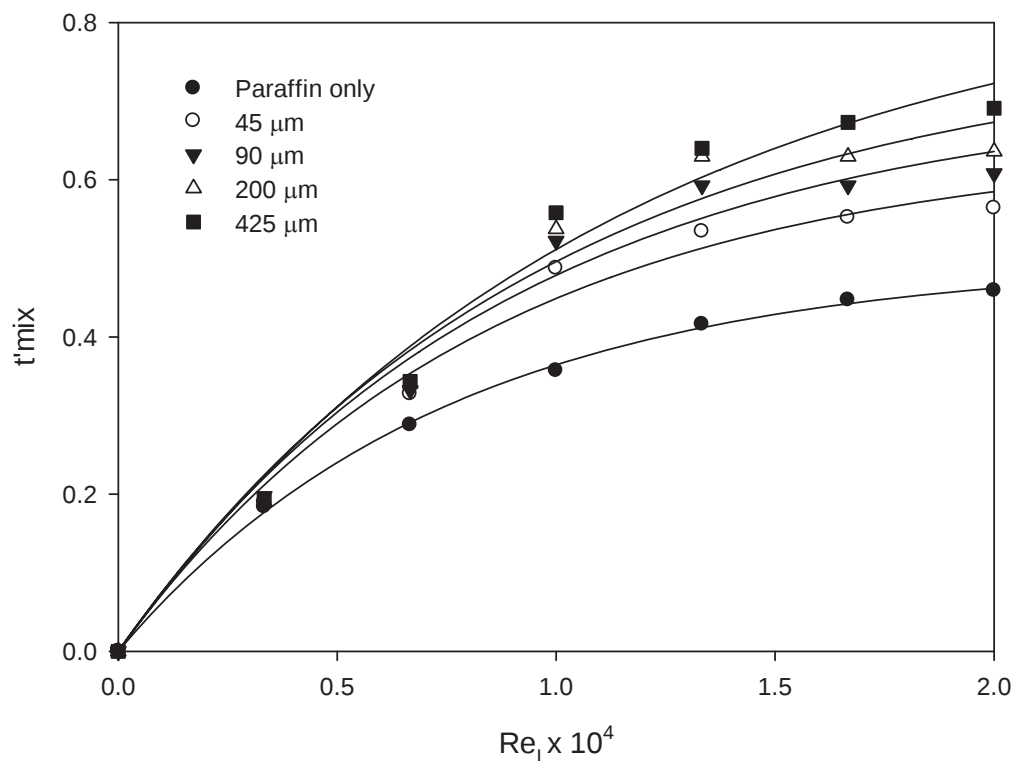


Figure 6.27 Solid recirculation time constant dependency on stirring speed for different particle sizes.

Based on the Baldi correlations (cf. Equation (6.13)), heavier particles for a similar size would take longer time for particles to start lifting off from the bottom of tank (off bottom regime). However, the phase hold-up at finite stirring speed would remain the same regardless of the particles density.

6.6. Gas-liquid-solid Mass Transfer Evaluation

6.6.1. Effect of stirring speed and solid loading

Figure 6.28 shows that volumetric mass transfer coefficient, $k_L a$, increases with impeller Reynolds number, Re_i until it plateaus around $Re_i = 5.2 \times 10^4$ ($N_s = 1000$ rpm) irrespective of solid loading. It is clearly seen that the $k_L a$ for the gas-liquid system gave better performance than the gas-liquid-solid system. However, the effect of solid loading is masked by the influence of gas-inducing impeller performance. As

previously shown, the gas-inducing impeller achieved better mass transfer compared with a conventional impeller.

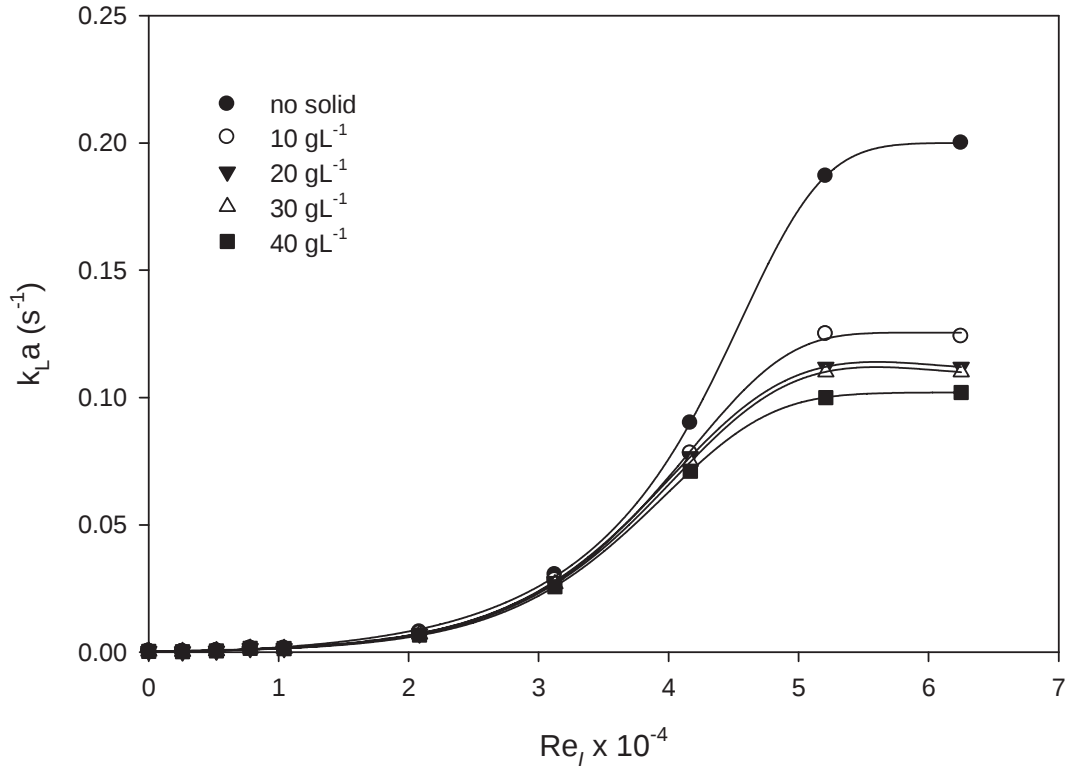


Figure 6.28 Volumetric mass transfer coefficient as a function of Re_i

To reveal the effect of solid loading, dimensionless $k_L a/k_{La0}$ is plotted against Re_i as seen in Figure 6.29 as the k_{La0} is the volumetric mass transfer coefficient with no solid present. These curves show that the solid loading does not influence the $k_L a$ value which is in agreement with many other studies previously reported [18, 21, 22]. Moreover, this indicates that the presence of alumina particles become an attenuation factor of mass transfer coefficient, $k_L a$ in the slurry aqueous system.

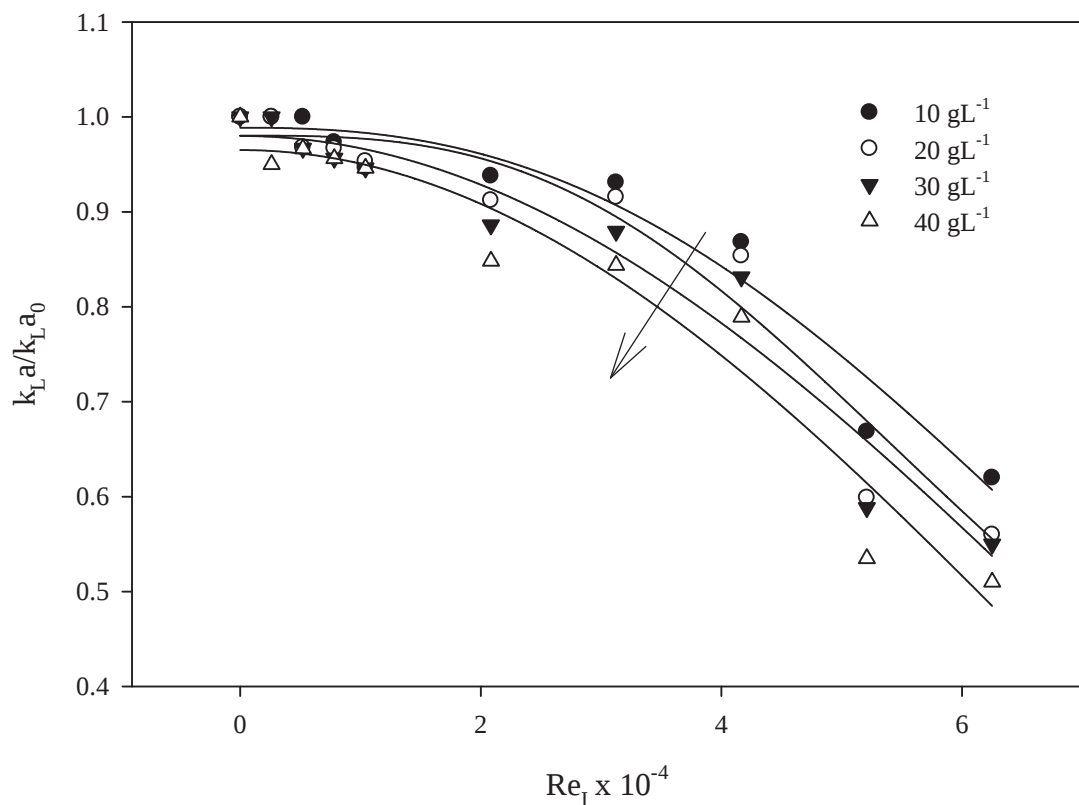


Figure 6.29 The effect of solid loading with increasing stirring speed on $k_L a$ in gas-inducing stirred tank reactor

6.6.2. Effect of solid phase hold-up

With the aid of tomography data taken simultaneously with the $k_L a$ measurement, we were able to correlate the $k_L a$ value with solid phase volume fraction (hold-up) as displayed in Figure 6.30. The results show an abrupt decrease of $k_L a$ at a critical value of solid hold-up. For example in the case of 10 g L^{-1} , the $k_L a$ value dropped sharply after $\varepsilon_s = 0.00305$. This phenomenon suggests that only slight changes of solid fraction can affect $k_L a$ substantially due to adsorption at the gas-liquid interface. It is interesting to observe in this study that the critical value of solid fraction shifted to the right as solid loading increased. Therefore, we can conclude from this study that the $k_L a$ is a function of both stirring speed and solid phase hold-up. Similar patterns were observed from other studies suggesting that by adding a small amount of catalyst particles in the aqueous system can have an unfavourable effect to $k_L a$.

values [23-26]. Although the exact mechanisms of this behaviour was not fully understood, the nature of physico-properties of the liquids i.e interfacial area may have contributed to this phenomenon. This is further evidenced by the works from Lindner *et al.* [27] on the different liquids (2.2 M H_3PO_4 and 3.0 M KNO_3) showed a significant increased of $k_L a$ as function of solid phase hold-up.

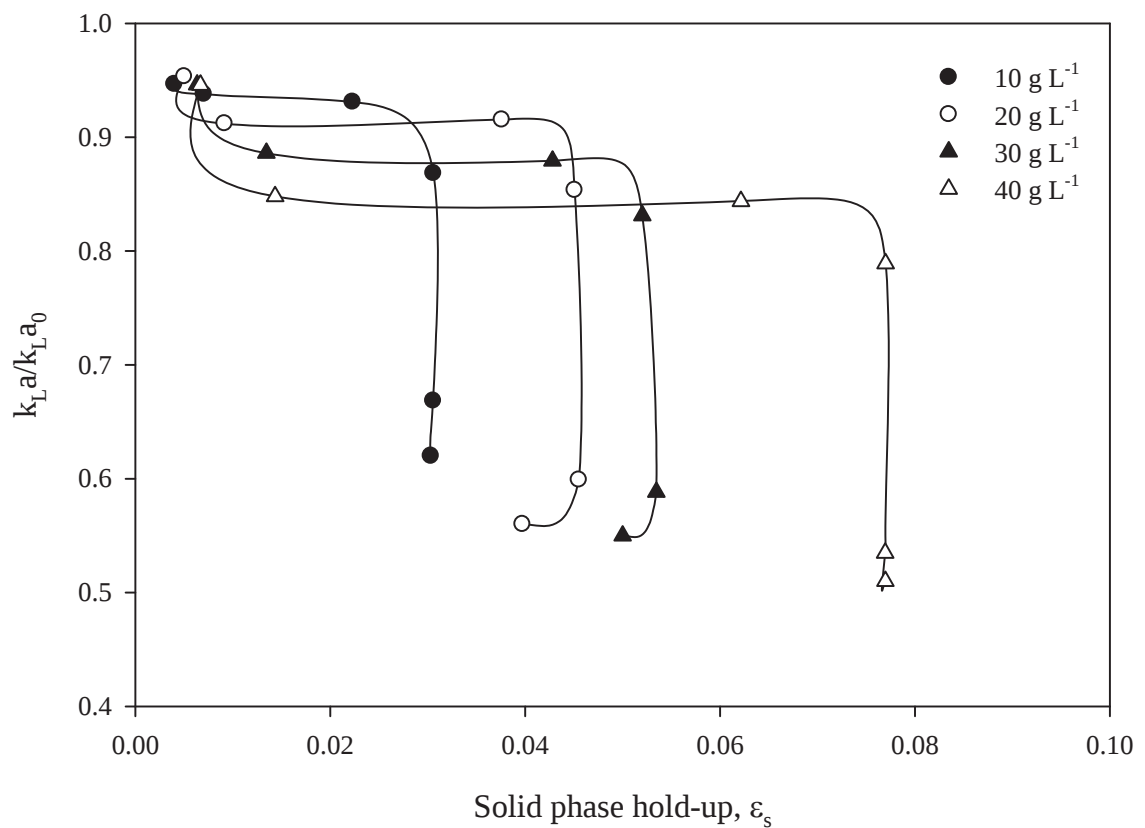


Figure 6.30 Effect of solid volume fraction, ϵ_G on $k_L a$ in GIST at various solid loadings

6.7. Power Analysis for Solid Mixing

Apart from enhanced phase mixing with a gas-inducing impeller, the power consumption per unit volume is an important performance index in multiphase mixing operations. In particular, a reliable correlation between this index and the operational variables (solid loading, fluid type, etc)

would permit an informed decision among competing objectives such as mixing efficiency, costs (capital and running) for different agitators. The gas-liquid-solid mixing in the tank was carried out using a Heidolph motor (model RZR 2102) equipped with a torque, T , display for the chosen rotational speed, N_s . The power input, P , in a reactor with a gas-inducing impeller is given by [28];

$$P = \rho_l W N_s \left(\frac{D_l}{2} \right)^4 \left[C_{DO}^* - C_{DY}^* \left(1 - \frac{1}{\Phi Fr} \right)^3 \right] + 2\pi N_s T \quad (6.31)$$

where W is the impeller width, C_{DO}^* and C_{DY}^* are the impeller drag coefficients in the gas-liquid dispersion conveying and central zone estimated as 1.0, Φ , the vortexing constant is 1.7 [29] and Fr is the Froude number based on impeller submergence depth.

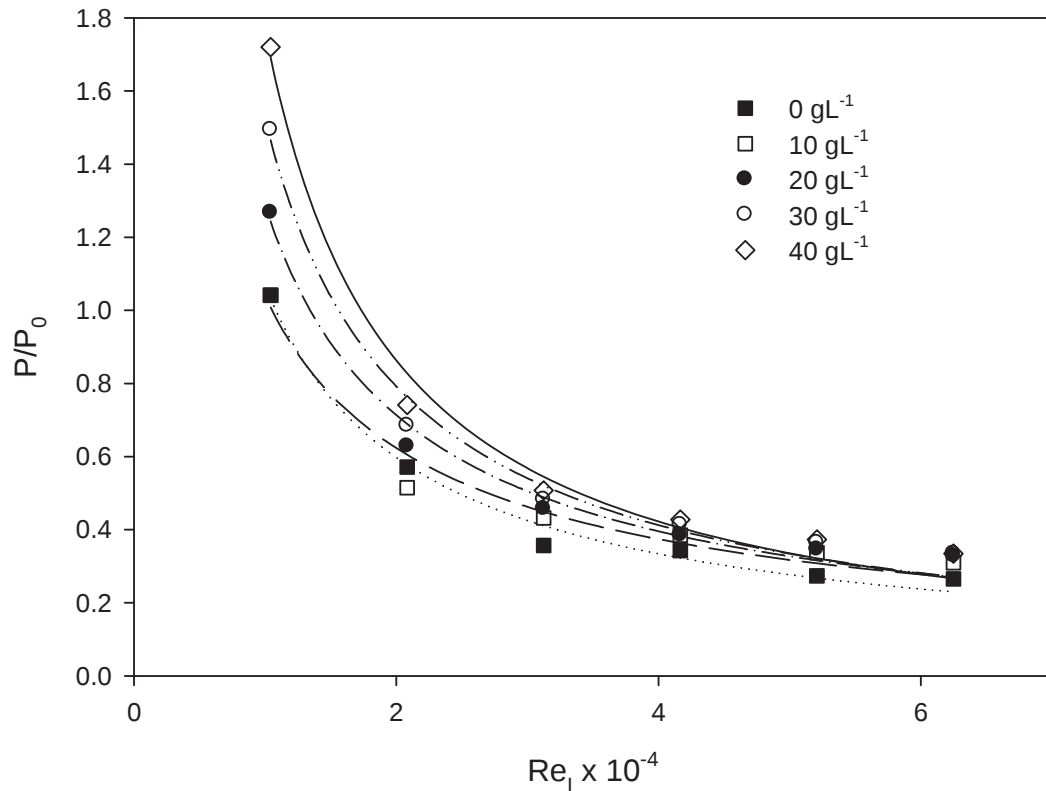


Figure 6.31 Correction factor, P/P_0 , for power consumption in the presence of gas bubbles as function of impeller Reynolds number (Re_I)

The power consumed by gas-entrainment impeller relative to conventional impeller (P/P_0), is depicted in Figure 6.31. For a conventional impeller with no gas involvement, P_0 is calculated from the expression:

$$P_0 = N_{P0} \rho_l N_s^3 D_I^5 \quad (6.32)$$

where $N_{P0} = 4$ for a standard 4-blade impeller (Ramachandran and Chaudhari, 1983 [5]). This correction factor, P/P_0 , is not only a function of impeller Reynolds number, but also of the solid loading employed in this study and is given by the power-law relation:

$$\frac{P}{P_0} = \kappa Re_I^{-\theta} \quad (6.33)$$

where

$$\kappa = 7.28w^2 - 159.44w + 1353.61 \quad (6.34)$$

and

$$\theta = 5.55[1 + \exp(-(w - 10.28)/19.97)]^{-2} - 0.0698w \quad (6.35)$$

Indeed, Equations (6.36) to (6.38) suggest that, for a solid-free liquid system, the impeller Reynolds number, $Re_I > 9088$ if the gas-inducing impeller is to have any practical advantage over the conventional stirrer. Interestingly, this estimate agrees with the requirement for $Re_I > 10417$ suggested by Sawant and Joshi [16] for the onset of gas induction. Figure 6.32 shows excellent agreement between the experimental values for P/P_0 and the model prediction.

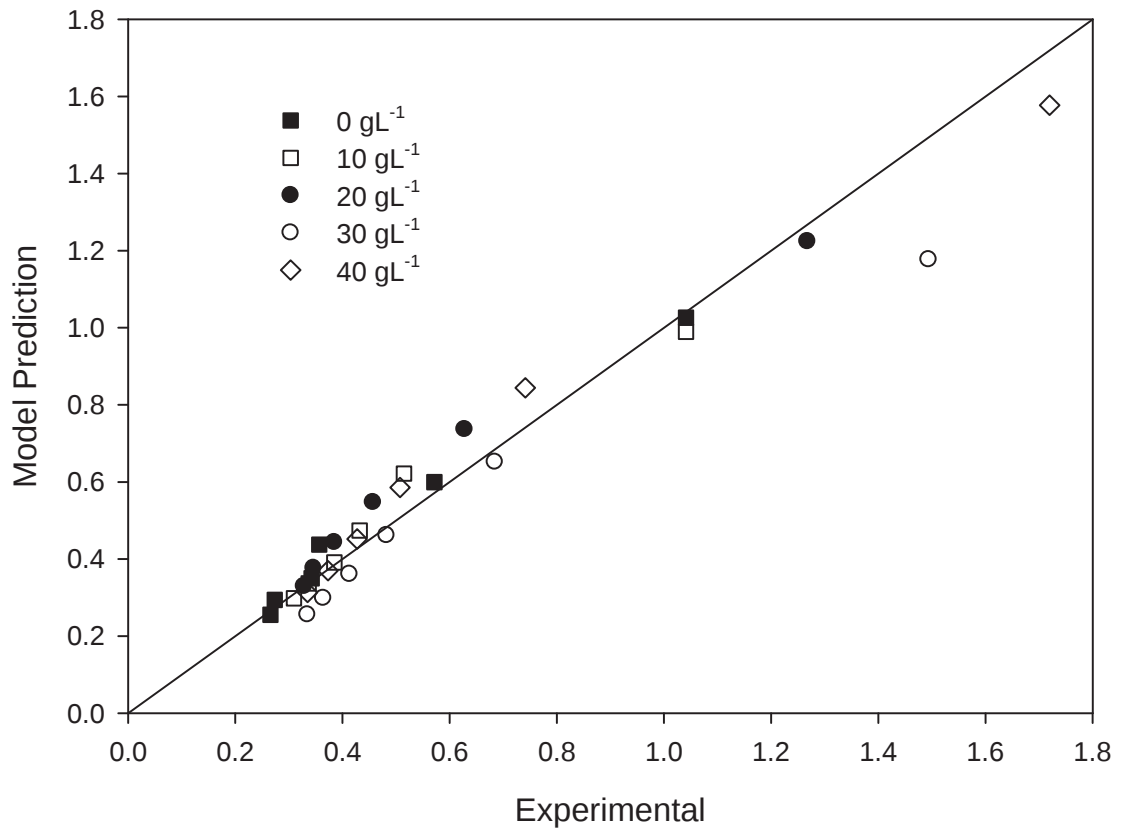


Figure 6.32 . Parity plot for correction factor, P/P_0 , for power consumption in the presence of gas bubbles

6.7.1. Power number estimation

The power number, N_P , which gives an indication of the power requirement for mixing is given by;

$$N_P = \frac{P}{\rho_l N_s^3 D_I^5} \quad (6.36)$$

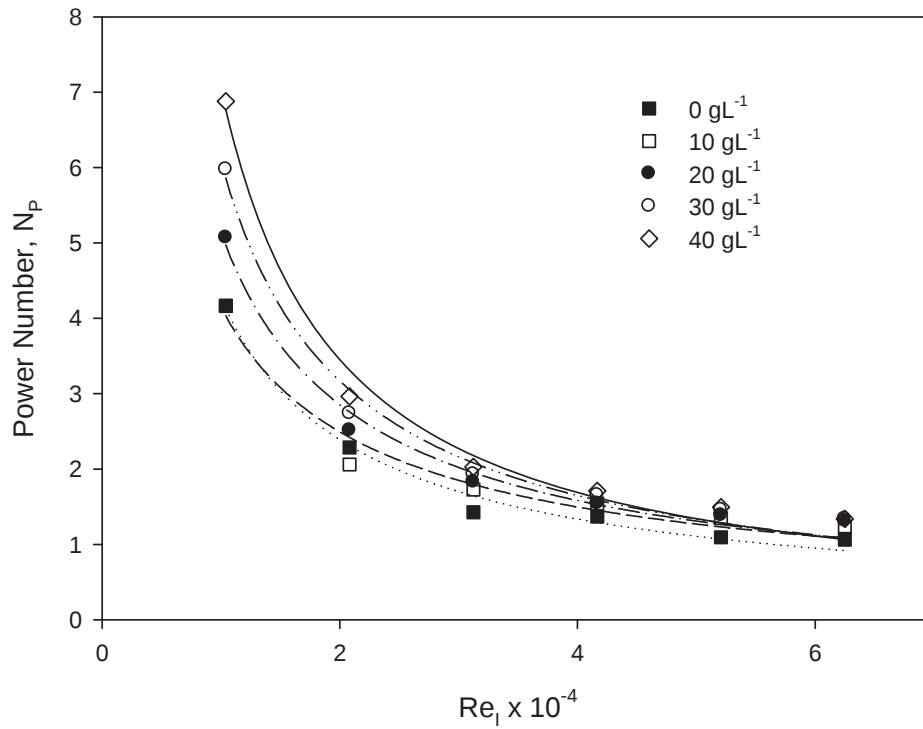


Figure 6.33 Power number as a function of impeller Reynolds number (Re_I)

Consequently, the family of curves describing the relationship between N_P and Re_I was produced as shown in Figure 6.33. These empirical data may be represented by the power-law expression:

$$N_P = N_{P,GIST} Re_I^{-\theta} \quad (6.37)$$

where

$$N_{P,GIST} = 29.12w^2 - 637.87w + 5413.5 \quad (6.38)$$

Figure 6.34 illustrates a decent description of the experimental data by Equation 6.37.

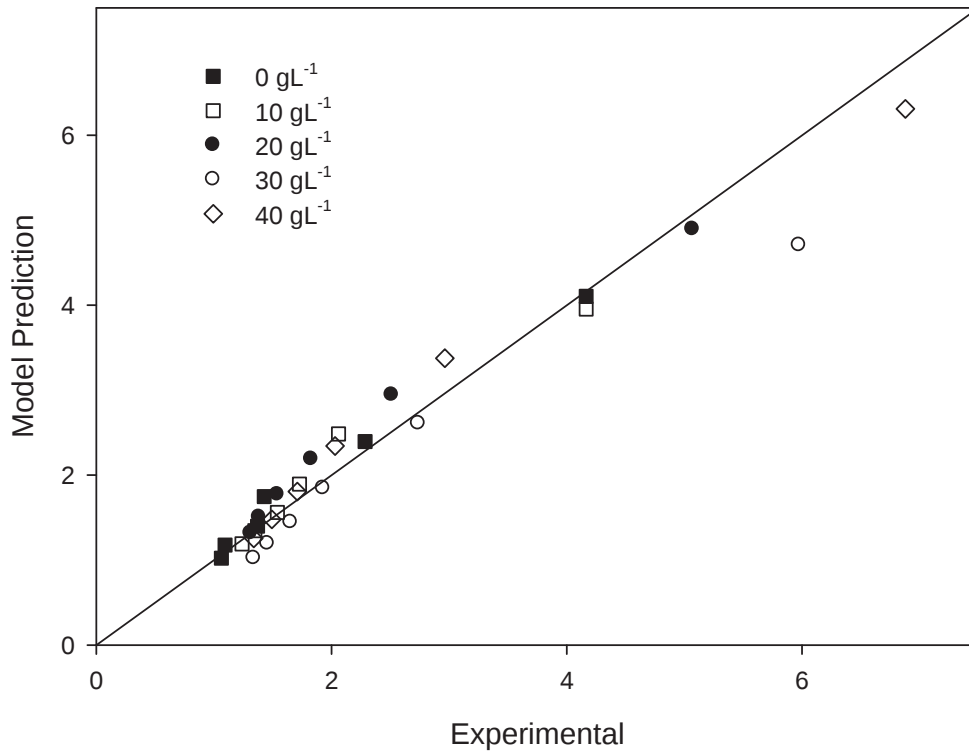


Figure 6.34 Parity plot for power number

6.8. Conclusions

Electrical resistance tomography (ERT) and Electrical capacitance tomography (ECT) have been used to probe the nature of gas-liquid-solid mixing in a gas-induced slurry stirred tank (GIST) reactor. Although the liquid phase was turbulent ($Re_l > 10^4$), both gas and solid flows went through different hydrodynamic regimes and experienced radial hold-up gradients over the range of impeller speeds employed. The behaviour of solid hold-up for both solid loading and particle size can be explained using the Chapman-Richards model which reveals that the maximum solid hold-up (ε_{S1}) and particle clustering activity (ξ) are dependent on particle size and solid loading. It exhibited a sigmoid-shape with respect to the impeller Reynolds number, suggesting three possible solid suspension regimes. The dispersed phase (solid and gas) hold-up profiles for the three-phase system were, however, all characterised by a maximum at the centre ($r/R=0$). Not surprisingly, ε_d values at $r/R = 0$ increased with shaft speed suggesting the solid particles were more concentrated near the tank centre at all impeller speeds, but also

experienced axial recirculation. The degree of mixing, $1-\chi$, was strongly correlated to the impeller Reynolds number (Re_I). It confirmed the previous proposition that the hydrodynamic behaviour over the range of operating conditions traversed three regimes for solid phase hold-up. Statistical treatment of the tomographical data also showed that regardless of particle size, uniform solid-liquid mixing was achieved at rotational speeds higher than 850 rpm ($Re_I > 1.5 \times 10^4$). The effect of particle size on dispersed phase hold-up was successfully investigated using ECT in a gas-inducing stirred tank reactor. It is clear from the data analysis that larger alumina particles gave higher dispersed phase hold-up. Global analysis indicates three flow regimes exist in the slurry reactor namely; incomplete suspension, transition and homogenous regimes at different agitation rate. However, dimensionless particle time constant (τ_{spp}) and initial solid phase hold-up ($\varepsilon_{s,0}$) are found to be independent of particle size and stirring speed. In the 3-phase system, $k_L a$ increased with stirring speed albeit the solid loading showed no improvement on $k_L a$ values. It is revealed that at low concentration of solid particles, $k_L a$ value decreased less compared to high concentration. This suggests that the alumina particles act as an attenuating factor on $k_L a$ in the 3-phase system.

6.9. References

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7 ■ Fischer-Tropsch Synthesis

7.1. General Consideration

In this chapter, non-intrusive electrical capacitance tomography (ECT) has been used to analyse the dynamic feedback between the fluid phase characteristics (such as dispersed phase hold-up, mixing time constants, and etc.) and reaction metrics in a gas-liquid-solid reactor using the FTS as a case study. The coupling between these two processes (transport and reaction) is due of the changing physicochemical properties of the liquid phase medium as product accumulates with reaction progression. Some materials presented in this chapter are excerpts from our publication, Abdullah *et al.* [1], *accepted for publication* in ACS Symposium Series.

7.2. Catalyst preparation

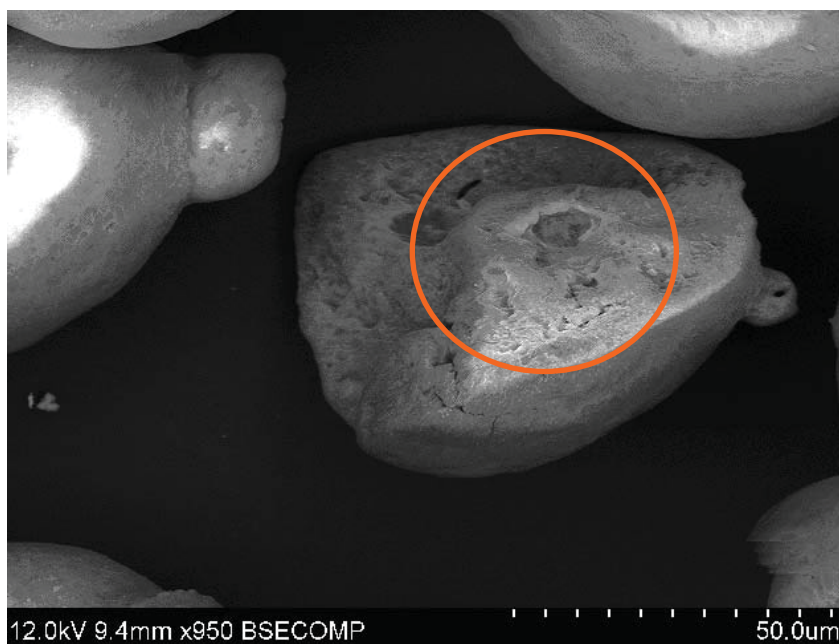
Based on preliminary catalyst characterisation study in Chapter 4, monometallic cobalt catalyst on γ -alumina support (10wt%Co/Al₂O₃) was synthesised by impregnating a quantitative amount of cobalt nitrate solution onto spray-dried gamma-alumina particles (60-90 μm obtained from Saint-Gobain Nopro Corporation, USA) at 298 K for 3 h under constant stirring and at constant pH of 3.6 (5M HNO₃ solution as pH control) using a Metler-Toledo T90 Titration Excellence system. The resulting slurry was dried in the oven at 303 K for 20 h. Dried catalyst was then calcined in the oven at 673 K for 5 h at a rate of 5 K min⁻¹. The calcined solid was crushed and sieved to 45-90 μm using Retsch AS 200 Analytical Sieve Shaker before charging into a stainless steel fixed bed

reactor (OD = 12.5 mm) where activation was carried out at 623 K for 8 h in 5% CO/H₂ mixture at a heating rate of 5 K min⁻¹. High purity research grade H₂ (99.99%), CO(99.99%) and N₂(99.99%) supplied by Linde (Sydney) were used in all runs. Gas flowrates were controlled and metered via calibrated mass flow controllers (Brooks 5850E).

7.3. *Physicochemical attributes*

7.3.1. Catalyst Morphology

SEM analysis on the calcined cobalt catalyst shows the metal dispersion on the porous surface of the alumina support and its relatively spherical shape as seen in Figure 7.1. This indicates the success of wet impregnation and drying steps that are critical in catalyst preparation in which uniform metal dispersion is often desired. Relatively rough surface indicating the presence of Co atoms, which were resulted from the interaction between metal and alumina. The image also reveals that the surface of calcined catalyst endowed high-level Co dispersion within the pores of alumina.



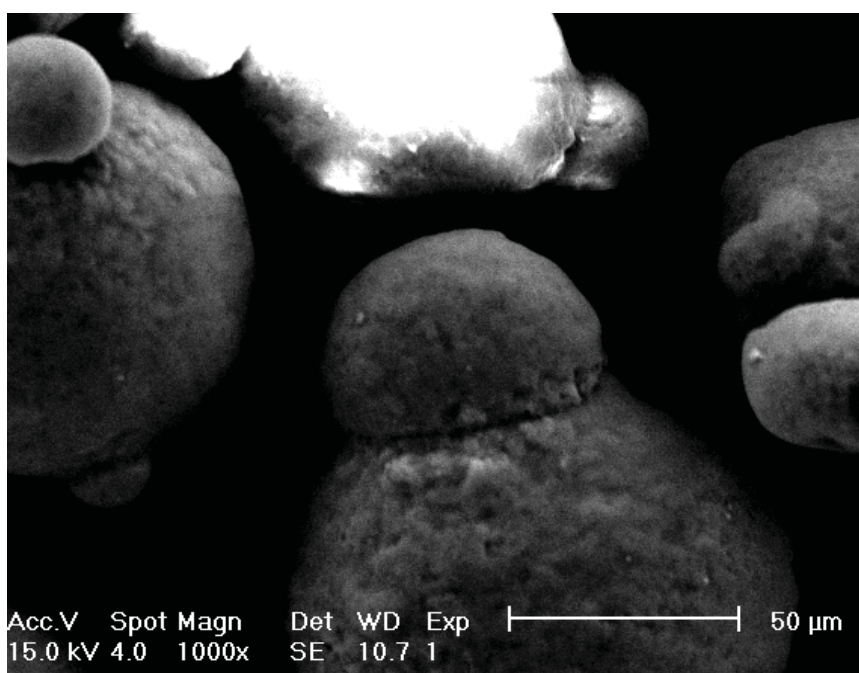
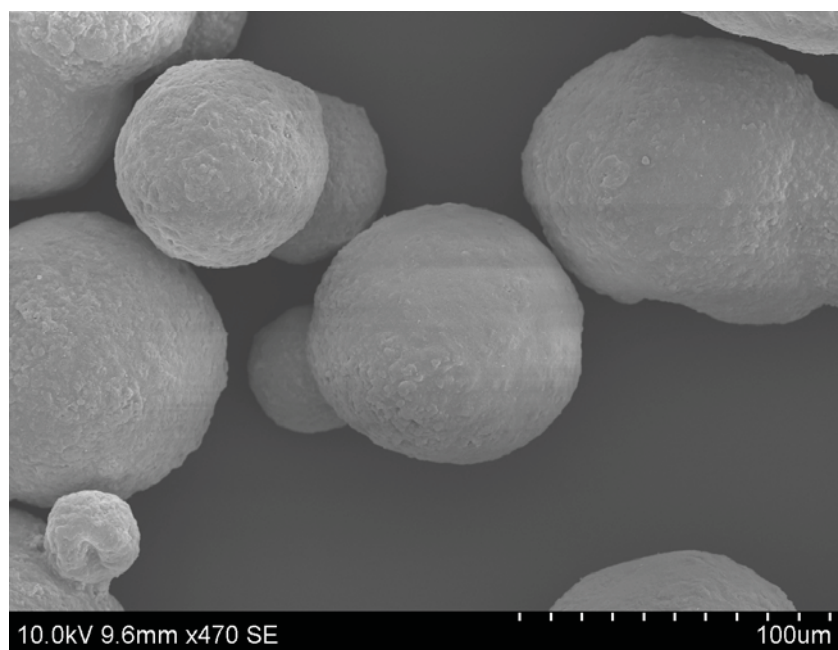


Figure 7.1 Low images of catalyst surface

Table 7.1 summarises the physicochemical properties of the catalyst. The BET surface area and pore volume of $170.8 \text{ m}^2 \text{ g}^{-1}$ and 0.474 ml g^{-1}

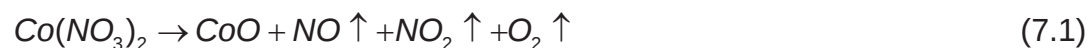
respectively are lower than the corresponding values for the calcined alumina support probably due to pore blockage by the Co oxide crystallites [2].

7.4. Catalyst Characterisation

7.4.1. Calcination and Activation Analysis

Calcination profile in Figure 7.2(a) shows two peaks corresponding to the weight loss associated with the decomposition of cobalt nitrate and oxidation to form Co_3O_4 . The large peak located between 470 K corresponding to Co_3O_4 and a shoulder peak at 503 K for aluminate phase [3].

The formation of cobalt oxides during cobalt nitrate decomposition in the calcination phase proceeded according to the reactions given by Equations (7.1) to (7.3) below.



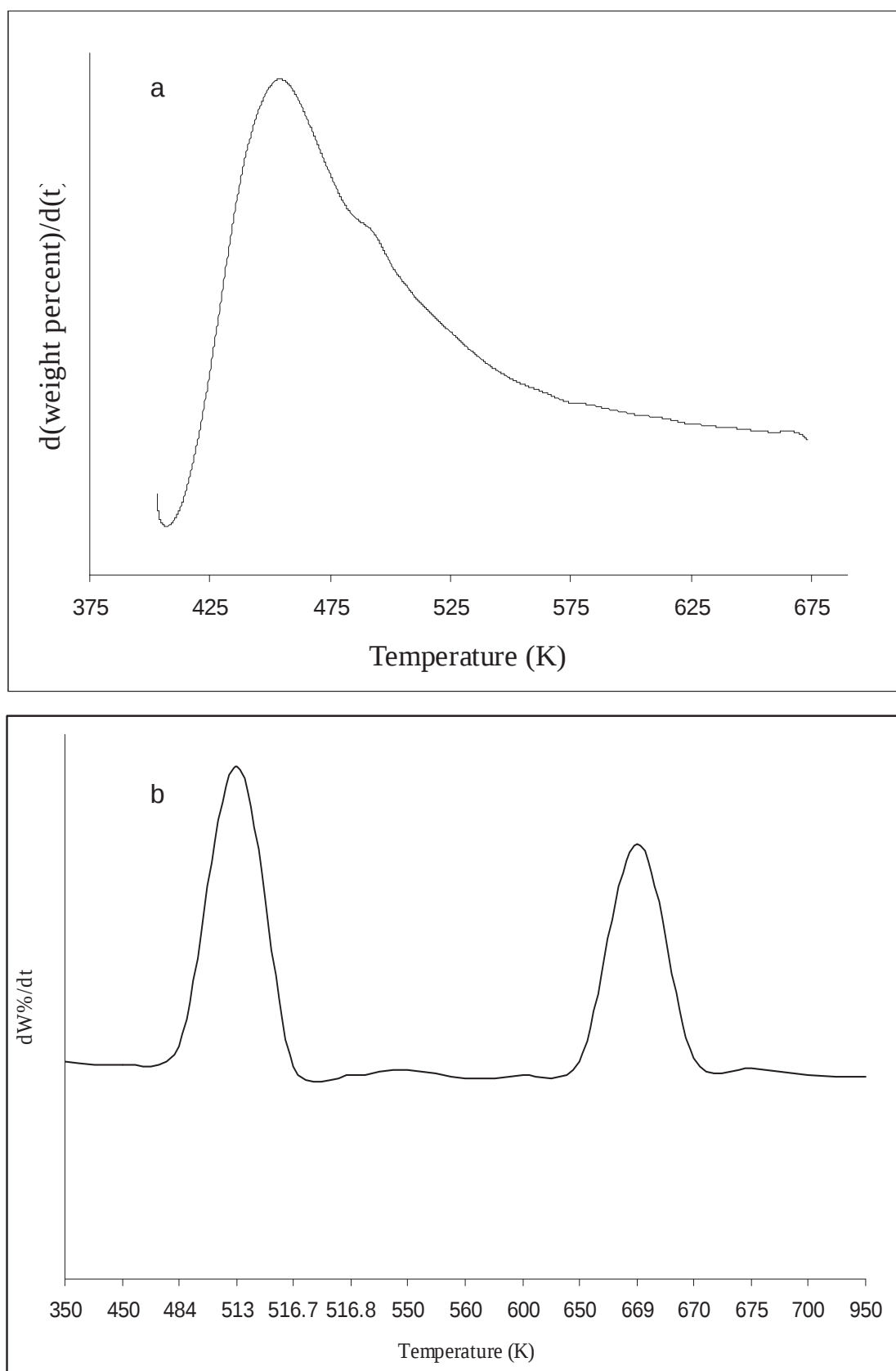


Figure 7.2 Derivative weight profile of a) temperature-programmed calcination b) temperature-programmed reduction (TPR)

While, TPR profile as seen in Figure 7.2(b) displays two major peaks at 513 K and 613 K corresponding to the two-step reduction process [4]. The first peak (513 K) attributed to reduction Co_3O_4 to CoO , while the second peak ascribed of formation elemental cobalt from CoO . Reduction of aluminate phase occurs at higher temperature ($T > 950$ K) which did not appear in the TPR profile [5]. The active sites for FTS were produced during the activation (reduction) stage, namely;



7.4.2. Solid State Kinetics models

Solid state kinetics models were fitted to the thermogravimetric (TGA) data of calcination and reduction profiles in which the transient solid conversion, α_{TGA} , for each solid-state reaction was calculated;

$$\alpha_{TGA} = \frac{W_i - W}{W_i - W_f} \quad (7.7)$$

where

w = the instantaneous weight

w_i = the initial weight

w_f = the final weight

Figure 7.3 displays the sample of transient solid state conversion profile corresponding to the cobalt oxide formation or reduction. The sigmoid profile is indicative of a multi sequential step process.

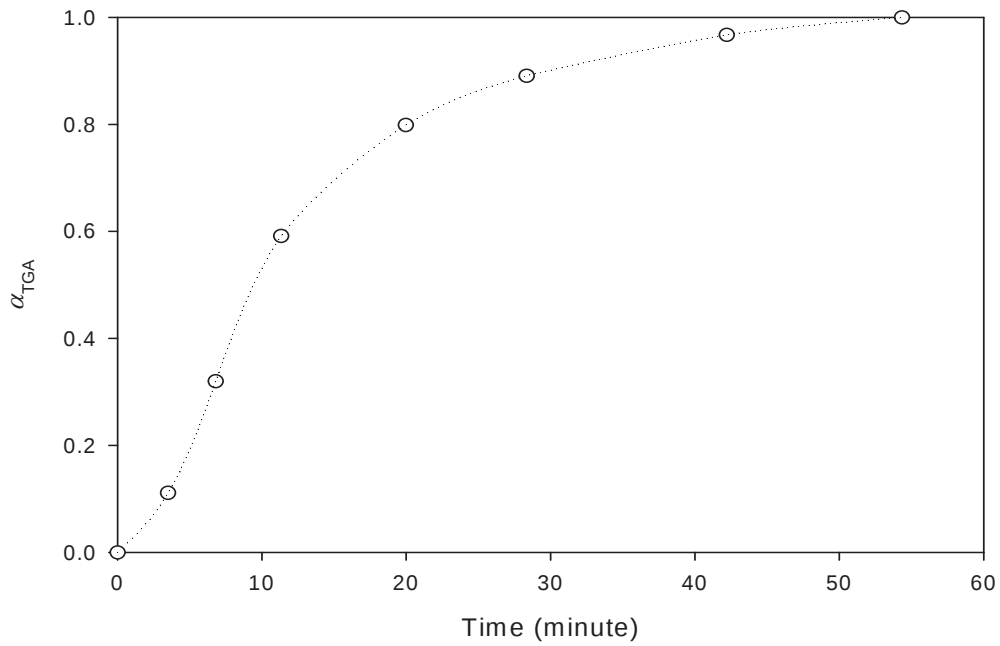


Figure 7.3 Transient solid conversion profile

The rate for gas-solid reaction may be given as;

$$\frac{d\alpha_{TGA}}{dt} = k(T)f(\alpha_{TGA}) \quad (7.8)$$

where $f(\alpha_{TGA})$ is the reaction rate function while $k(T)$.

The standard Arrhenius behaviour from the Coats-Redfern equation [6] may be applied:

$$\ln[g(\alpha_{TGA})/T^2] = \ln[(AR/E\psi)(1-2RT/E)] - E/RT \quad (7.9)$$

where

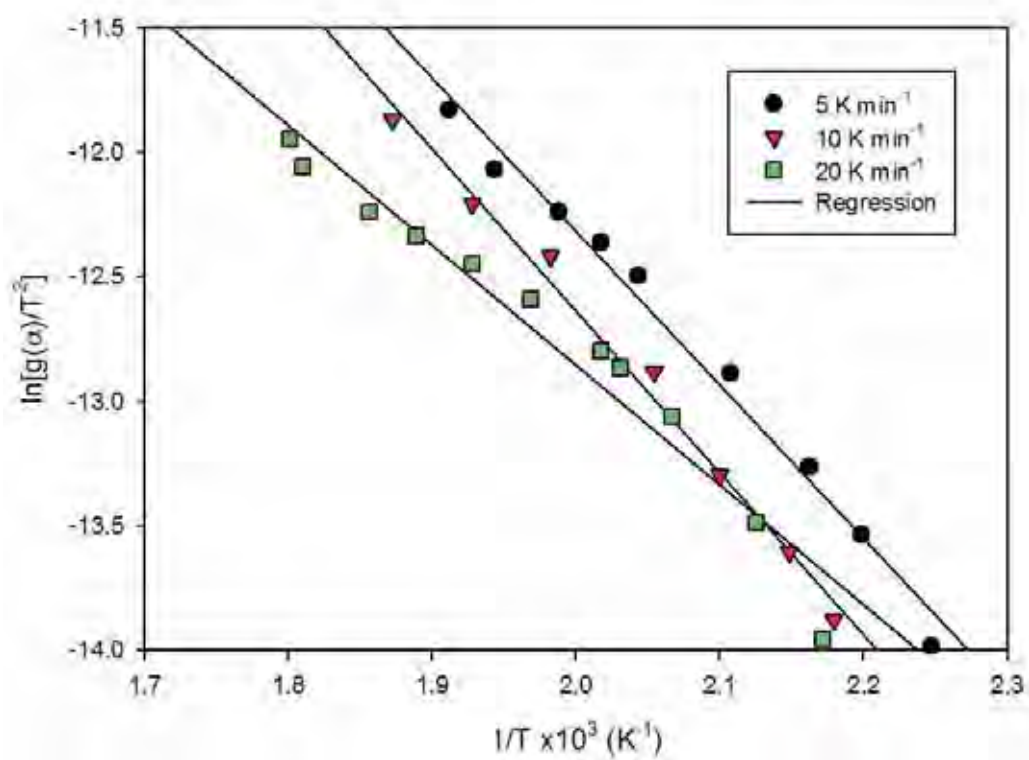
ψ = the heating rate ($K \min^{-1}$)

$g(\alpha_{TGA})$ = integrated form of reaction function

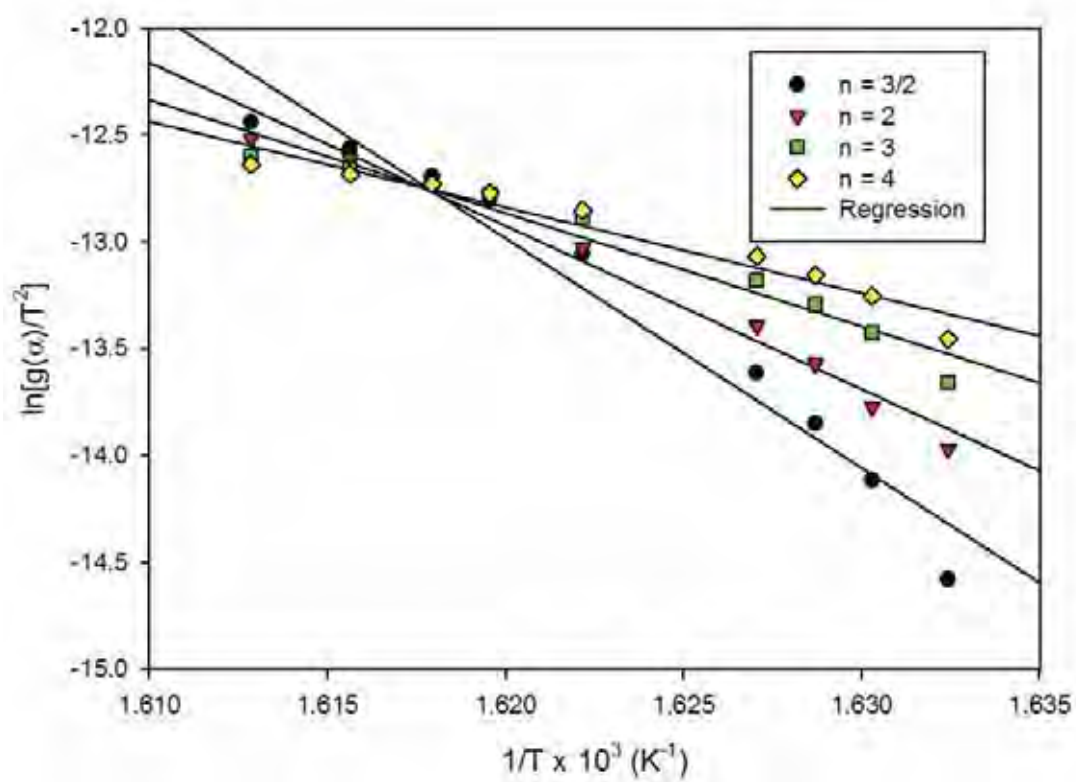
The transient calcination profile was best-fitted to the surface contracting (or expanding) model given as;

$$g(\alpha_{TGA}) = 2[1 - (1 - \alpha_{TGA})^{1/2}] \quad (7.10)$$

This gas-solid reaction model represents the system where surface area changes accompany the reaction. In particular, the BET surface area measurements increased approximately 15% for oven-dried and calcined catalysts ($150 \text{ m}^2 \text{ g}_{\text{cat}}^{-1}$ and $171 \text{ m}^2 \text{ g}_{\text{cat}}^{-1}$ respectively). It evidences that additional pore creation during calcination process is in agreement with the observed kinetic model (c.f. Figure 7.4a). The calcination activation energy values ($52\text{-}56 \text{ kJ mol}^{-1}$) that calculated from Equations (7.9-7.10) at different heating rates ($5\text{-}20 \text{ K min}^{-1}$) indicate the nitrate decomposition mechanism did not change with heating rate. The low activation energy may be described the mechanism employed during physical process of surface contraction during nitrate decomposition and physically steps are associated with low activation energy values.



(a)



(b)

Figure 7.4 Example of (a) calcination and (b) reduction model-fitting

The H₂ reduction profile as seen in Figure 7.4b was best-fitted to an n^{th} order Avrami-Erofeev model [7]:

$$g(\alpha_{TGA}) = [-\ln(1 - \alpha_{TGA})]^{1/n}, \quad n = 3/2; 2; 3; 4 \quad (7.11)$$

The R-square of 0.99 was fitted to the model with $n=2$, and corresponds to the activation energy of 430 kJ mol⁻¹.

7.5. Physicochemical properties

Table 7.1 displays the physicochemical properties for both calcined alumina support and Co/Al₂O₃ used in this study. A BET surface area of 170.8 m² g⁻¹ consistent with other study for transition metal-alumina supported catalyst [3, 8]. The pore volume and BET surface area for cobalt catalyst are relatively smaller than the alumina support due to possible blockage by the impregnation of cobalt oxide particles. Low metal dispersion of 0.72% implicates the high metal loading used and demonstrated by the large metal particles of 139 nm obtained from H₂ chemisorption runs.

Table 7.1 Physicochemical properties of alumina support and cobalt catalyst

Parameters	γ -alumina support (Calcined in air at 673 K)	Co/Al ₂ O ₃
BET area (m ² .g ⁻¹)	205.1	170.8
Pore volume (cm ³ g ⁻¹)	0.62	0.47
Average pore size, (nm)	12.0	11.1

Metal dispersion (%)	NA	0.72
Metal surface area (m ² g ⁻¹)	NA	0.48
Active particle size (nm)	NA	139.0
$\Delta H_{d,NH_3}$ (kJ mol ⁻¹)	61.75	47.52 (Peak I)
	NA	73.80 (Peak II)
Acid site concentration (μmol m ⁻²)	1.20 (Weak)	0.79 (Weak)
	NA	2.47 (Strong)
$\Delta H_{d,CO_2}$ (kJ mol ⁻¹)	32.57 (Peak I)	54.23 (Peak 1)
	42.61 (Peak II)	45.69 (Peak II)
Basic site concentration (μmol m ⁻²)	0.41 (Weak)	0.03 (Weak)
	0.59 (Strong)	0.04 (Strong)
Acid : Basic sites ratio	2.93 (Weak)	26.3 (Weak)
	NA (Strong)	61.75 (Strong)

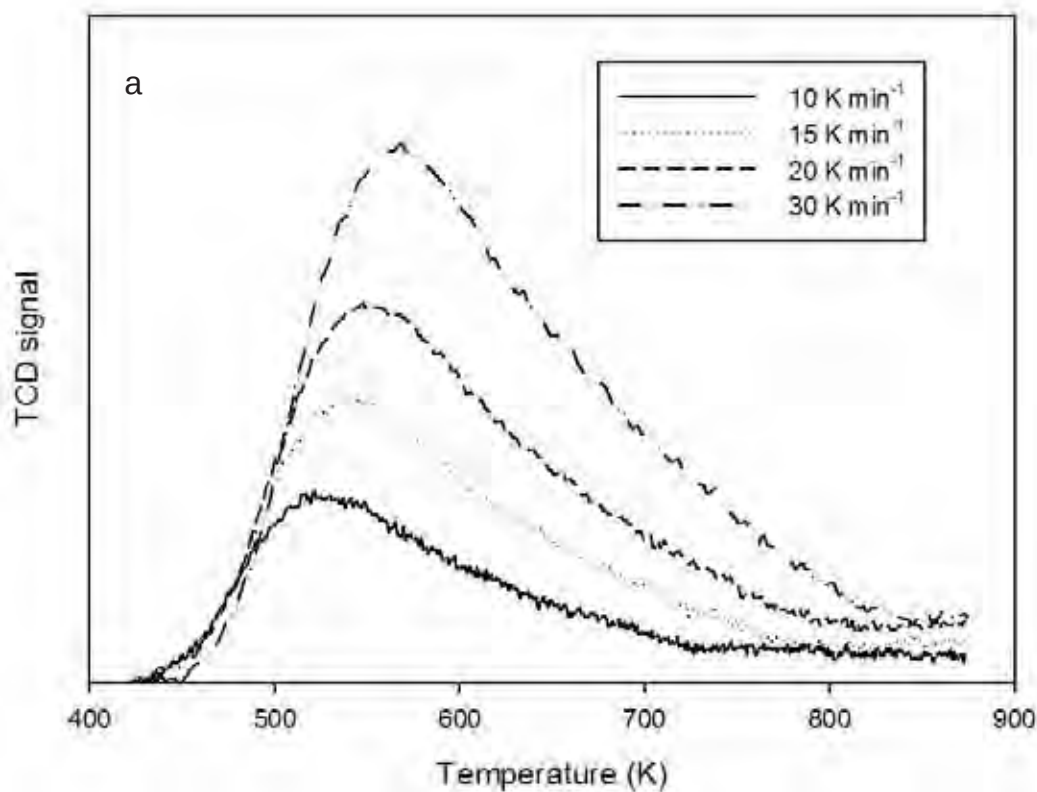
7.5.1. Acid and Base properties

NH₃ temperature-desorption curves as seen in Figure 7.5a implicated the existence of two acid sites on the catalyst surface. A fit of the data to,

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{\Delta H_d}{RT_p} + \frac{\Delta H_d A_{acid}}{RC} \quad (7.12)$$

gave straight lines in all cases having R-squared values of between 0.93 to 0.99 with slope and intercept used to evaluate the surface acidity parameters. Acid site strength and concentration on the solid sample are represented by the NH₃ heat of desorption, ($-\Delta H_d$), and the acid site concentration, A_{acid} , respectively. This suggests that the reduced cobalt atoms were most likely strong Lewis acid centres since the introduction

of Co significantly increased this type of acid site concentration (from $1.2 \mu\text{mol m}^{-2}$ in calcined support and $3.17 \mu\text{mol m}^{-2}$ in the Co catalyst). Figure 7.5 (a and b) illustrate the NH_3 -TPD spectra for the calcined alumina support and the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst respectively. Desorption spectra at peak 1 on both calcined alumina and Co catalyst attributes to common acid sites which the Peak 2 (680–740 K) indicates the presence of new acid sites possibly due to the metal-metal oxide and/or metal oxide-alumina interaction. The low temperature peak corresponds to a weak acid site while the high temperature peak indicates a strong acid site [9]. The estimation of relevant acid sites concentration and heat of desorption were tabulated in Table 7.1. Calcined alumina support demonstrates weak acid site concentration of $1.2 \mu\text{mol m}^{-2}$ with strength of $61.75 \text{ kJ mol}^{-1}$ while cobalt catalyst exhibits weak acid site of $0.79 \mu\text{mol m}^{-2}$ and strong acid site of $2.47 \mu\text{mol m}^{-2}$ respectively. The cobalt catalyst possesses the strength of 47.52 and $73.80 \text{ kJ mol}^{-1}$ for weak and strong acid sites respectively.



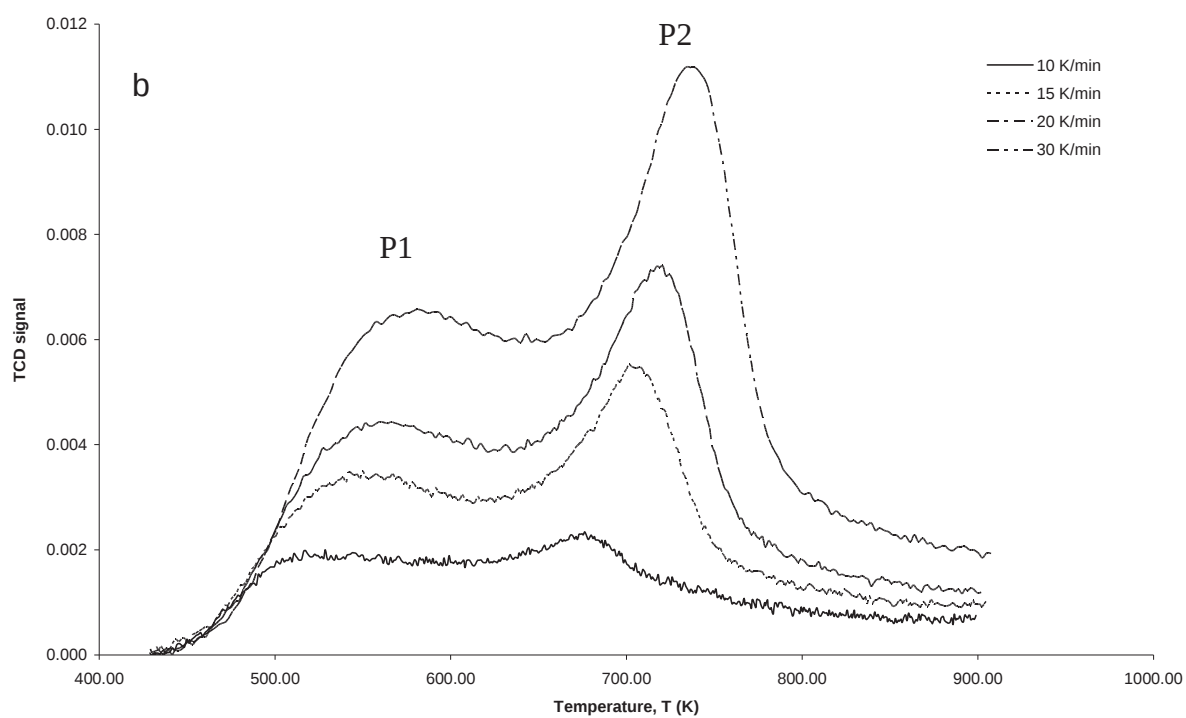


Figure 7.5 NH₃ temperature-programmed desorption profiles a) calcined alumina support b) Co/Al₂O₃ catalyst

a

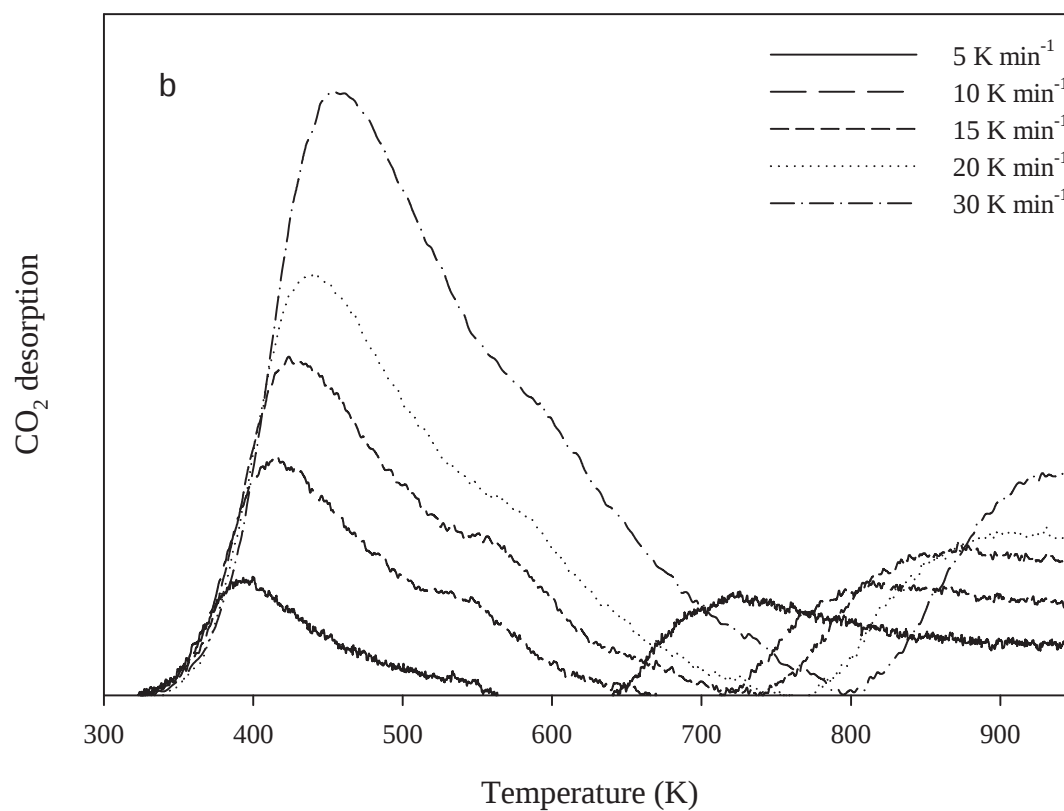
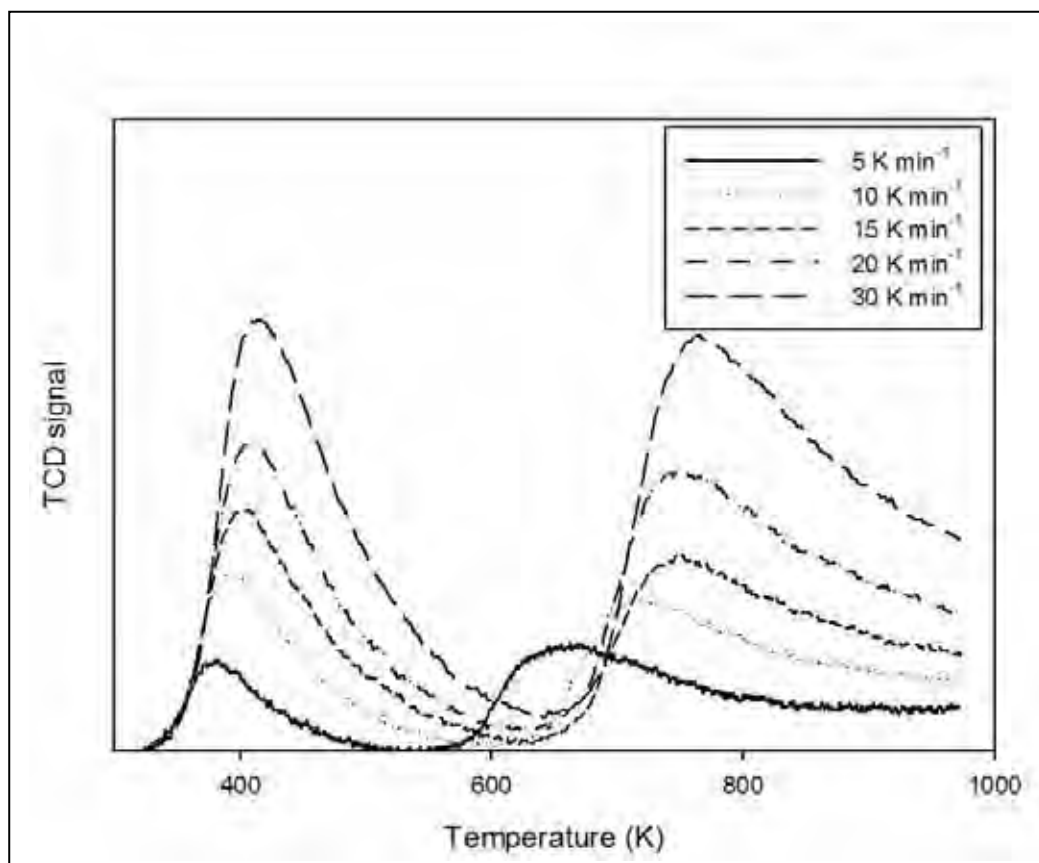
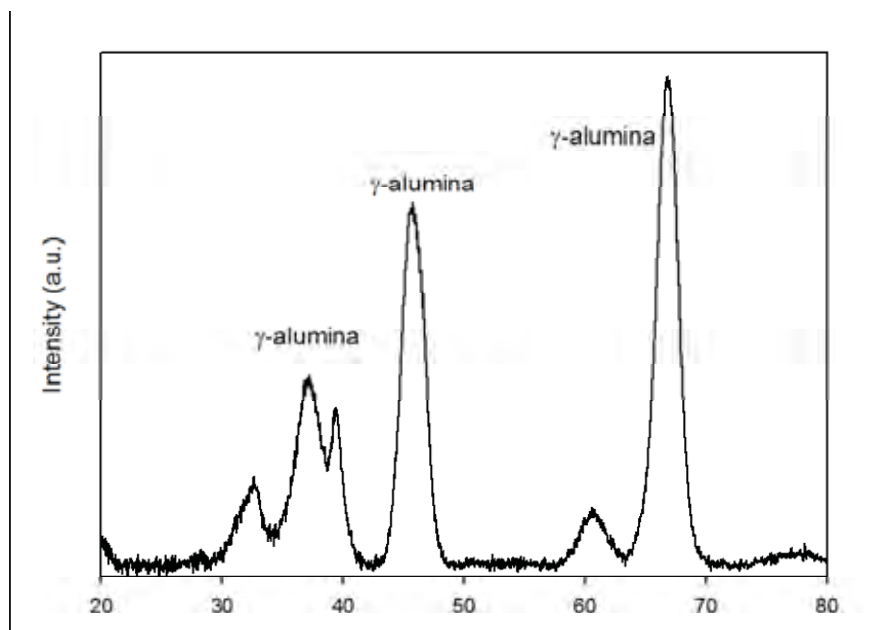


Figure 7.6 CO₂ temperature-programmed desorption profiles for a) calcined alumina support b) cobalt catalyst

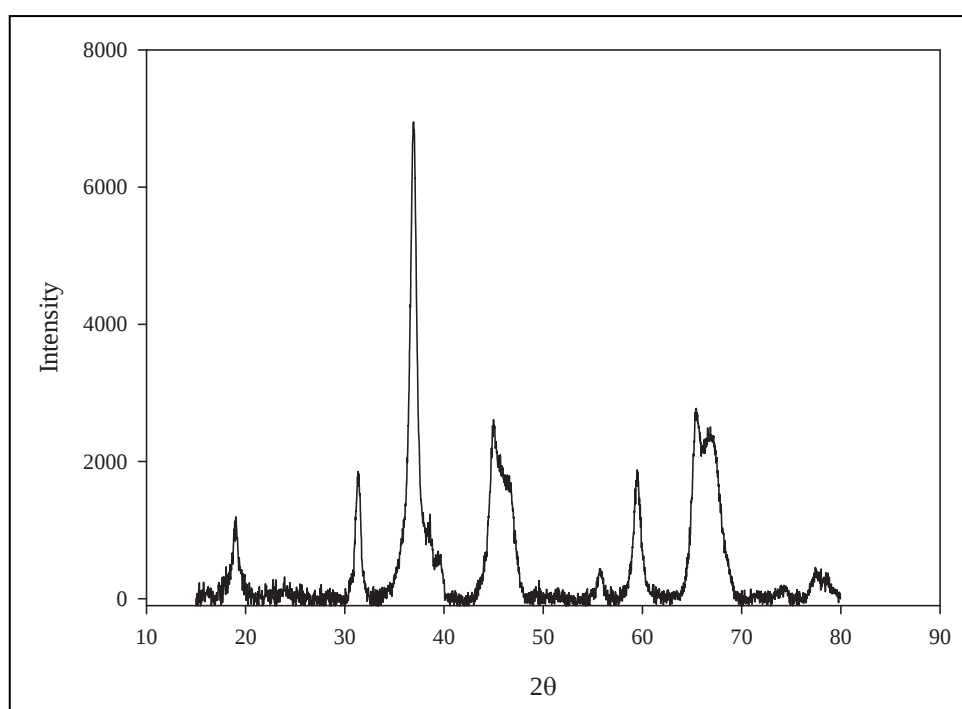
Figure 7.6 (a and b) display the CO₂-TPD profiles for calcined alumina and Co catalyst. Interestingly, both of the solids exhibit two major peaks indicating the presence of interstitial hydroxyl group for low temperature peak (390-430 K) and interaction of CO₂ with surface hydroxyl species on the alumina surface corresponds to the high temperature peak (650-950 K [10]. Basic site concentration for Co catalyst 0.03 and 0.04 $\mu\text{mol m}^{-2}$ for weak and strong acid sites respectively. Interestingly, the weak basic sites seemed to decrease with addition of Co because they were supplanted by the strong acid sites during impregnation and subsequent calcination. Table 7.1 estimates the basic sites concentration for both calcined alumina support and co catalyst.

7.5.2. XRD analysis

Qualitative examination of the crystalline phases present in the calcined cobalt supported alumina catalyst was performed by X-ray diffractogram (XRD) analysis and the result is illustrated in Figure.7.7. The presence of CO₃O₄ at several small peaks ($2\theta = 31.2^\circ$ and 18.5°) while the aluminate phase (CoAl₂O₄) present in the catalyst at major peak 32° . The diffracted peaks at 44° and 64° attribute to the presence of CoO in Co catalyst. The small peak at $2\theta=58.0^\circ$ may be attributed to the existence of CoAl₂O₄ phase. This XRD analysis is in agreement with different bulk oxide phases identified from calcination processes (cf. Equations (7.1)-(7.3)). Alumina crystalline structure is present on the cobalt catalyst as evidence from peaks at $2\theta=37.0^\circ$, 39.2° , 45.7° , 60.0° , and 67.0° .



a



b

Figure.7.7 XRD of a) calcined alumina support b) a freshly calcined cobalt

catalyst at 673 K.

7.6. Preliminary study

Preliminary experiments were carried out using a conventional stirrer (with no gas inlet port on the shaft or exit ports on the impeller blades) with identical geometry and dimensions to the gas-inducing agitator. As evidence from Figure 6.20 (cf. Chapter 6), it reveals that the dispersed phase hold-up initially increased with solid loading for both impellers. Both runs were conducted under non-reactive conditions with N₂ as the inert gas and alumina particles as the solid entities. Comparing the results for the conventional stirrer and gas-inducing stirrer shows that at the speed used (1200 rpm), there was a constant difference between the two stirrer types which represents the gas phase hold-up (since gas was not introduced into the reactor during the run with the conventional stirrer). Consequently, it may be assumed that the dispersed phase hold-up is simply the sum of the solid and gas phase hold-ups over the range of solid loading employed. Thus,

$$\varepsilon_D = \varepsilon_S + \varepsilon_G \quad (7.13)$$

Additionally, the effect of temperature on fluid phase permittivity (and hence, hold-up) was investigated. As may be seen from Figure 7.8, the dispersed phase hold-up for the conventional stirrer was essentially invariant with temperature between 293-530 K (which covers the range for subsequent FTS runs).

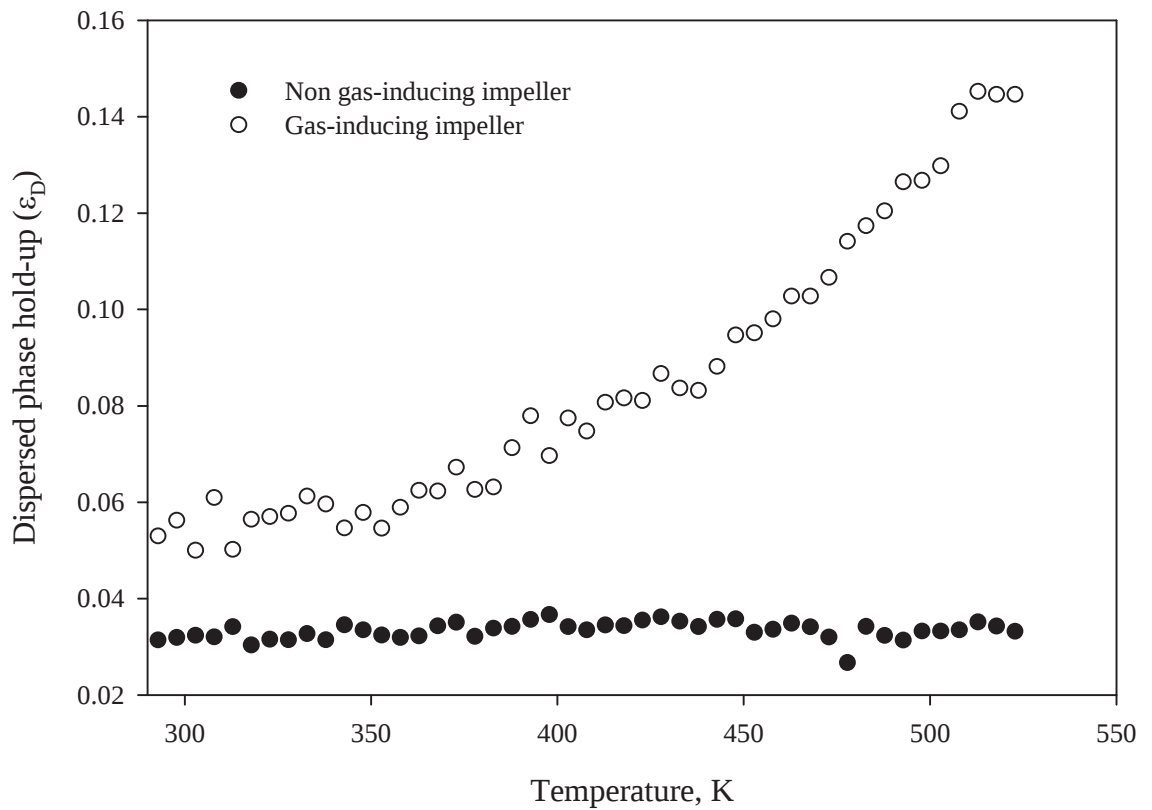


Figure 7.8 Effect of dispersed hold-up as function of temperature for different impeller geometry

7.7. FT steady-state analysis

7.7.1. Product distribution

The Anderson-Schulz-Flory (ASF) equation [11] is the most widely accepted product distribution model and the hydrocarbon rate data were adequately described with the exception of the methane, as,

$$r_n = k_{ASF} (1 - \alpha_{FT})^2 \alpha_{FT}^{n-1} \quad (7.14)$$

where

r_n = the total production rate for all hydrocarbons with n carbon atom

α_{FT} = the chain growth probability

k_{ASF} = a pseudo-rate constant equal to the CO consumption rate

ASF model can be re-written in logarithm form and yields,

$$\log r_n = n \log \alpha_{FT} + \log \left(\frac{[k - \alpha_{FT}]^2}{\alpha_{FT}} \right) \quad (7.15)$$

A plot of $\log r_n$ against carbon number, n would yield a linear relationship in which the $\log \alpha_{FT}$ represents a slope and termination rate is determined from the y-intercept. Figure 7.9 depicts the plot r_n as function of carbon number at various reaction temperatures. The outlying data for C_1 and C_2 may have come from the hydrogenation of bulk cobalt catalysts in addition to the surface reactions. Further, exclusive methanation sites would account for the excess methane while ethylene readsorption to the surface for reincorporation into growing chains may have been responsible for under-estimation of these species. Similar results also have been reported by Cooper *et al.* [3]. It is apparent from that α_{FT} has a weak dependency on temperature while k_{ASF} follows Arrhenius behaviour with the associated activation energy, E_{ASF} , value of 87 kJ mol^{-1} . The corresponding pre-exponential factor, k_{ASF}^0 , has a value of $1.7 \times 10^3 \text{ s}^{-1}$.

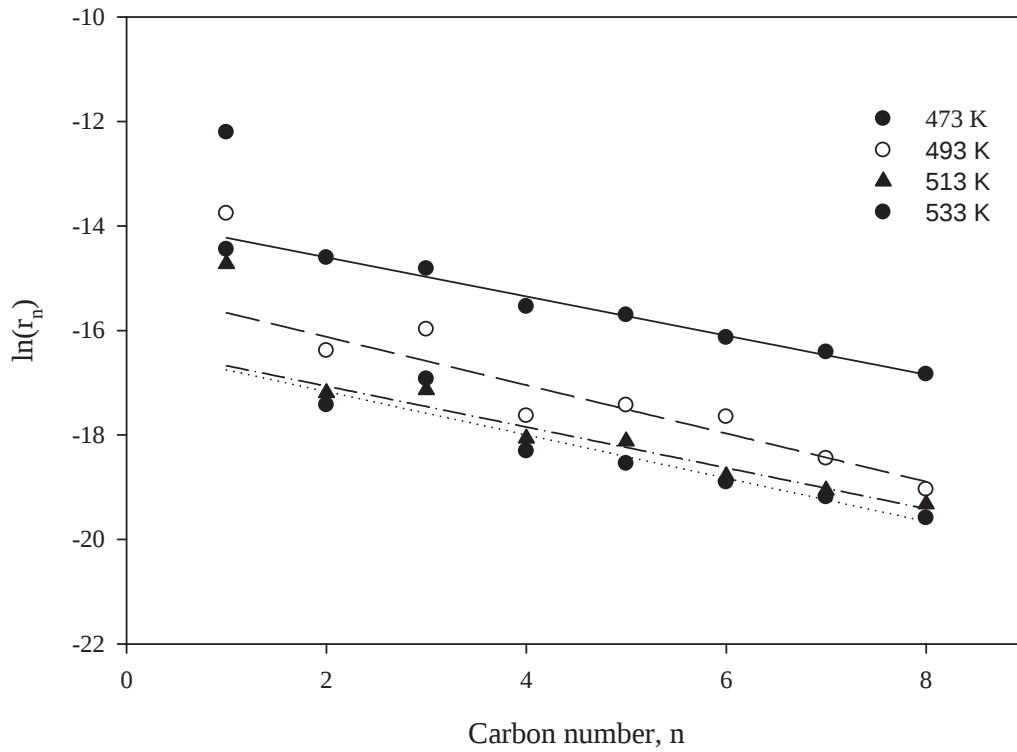


Figure 7.9 ASF trends for stoichiometric feed composition ($y_{H_2}=0.67$) at $P = 21$ atm

Adesina [12] indicated that the intrinsic propagation and termination rates can be calculated from steady-state data using the intercept of the ASF plot. The chain growth probability can be defined as,

$$\alpha_{FT} = \frac{r_p}{r_p + r_t} \quad (7.16)$$

where r_p and r_t are the propagation and termination rates respectively. Adesina [12] has elucidated further this derivation to,

$$r_p = \alpha_{FT} k_{ASF} \quad (7.17)$$

and

$$r_t = (1 - \alpha_{FT}) k_{ASF} \quad (7.18)$$

For this feed composition, the values of r_p and r_t are shown in Table 7.2 at various reaction temperatures. Ratio of r_p to r_t greater than unity indicates favourable conditions for polymerization to higher hydrocarbons. The temperature of 533 K gave the highest r_p/r_t (=2.22) suggesting that the most favourable conditions occur at this temperature. Fu and Bartholomew [13] define the average carbon number, $\langle n \rangle$ as a function of chain growth probability as,

$$\langle n \rangle = \frac{1}{1 - \alpha_{FT}} = N_{CO} \frac{1}{r_t} \quad (7.19)$$

where N_{CO} is the specific activity. The average chain length values at different reaction temperatures can be seen in Table 7.2. Adesina [14] has illustrated that the propagation and termination rates can be obtained if the specific site concentration on the surface of catalyst is available, as,

$$k_p = \frac{r_p}{n_{as}} \quad (7.20)$$

The effect of temperature on ASF parameters indicates the α_{FT} value has weak dependency on temperature. In contrast, the ASF rate constant appreciates with temperature. Table 7.2 displays the ASF parameters at various temperatures.

Table 7.2 ASF related parameters at different reaction temperatures

Temperature (K)	Chain growth probability, α_{FT}	ASF rate constant, k_{ASF} ($\times 10^7$) (mol g _{cat} ⁻¹ s ⁻¹)	Propagation rate, r_p ($\times 10^7$) (mol g ⁻¹ s ⁻¹)	Termination rate, r_t ($\times 10^7$) (mol g ⁻¹ s ⁻¹)	Average carbon number, $\langle n \rangle$
473	0.66	4.6	3.0	1.56	2.94
493	0.63	11.5	7.2	4.26	2.70
513	0.68	14.9	10.1	4.77	3.13
533	0.69	68.0	46.9	21.1	3.23

7.7.2. Olefin-to-paraffin ratio (ROP) over Co catalyst

In general, Figure 7.10 shows $(ROP)_n$ decreases with temperature ($y_{H_2}=0.67$). This behaviour may be attributable to the higher activation energy or temperature dependency of the termination rate constant as compared to its propagation rate constant. Higher pressure and longer residence time provide an avenue for the slurry FT GIST reactor to have better gas-catalyst mass transfer, consequently increasing olefin to paraffin product distribution. However, at lower carbon number ($n=2$), lower ROP_n was observed suggesting the re-adsorption of ethylene to participate in secondary reactions and incorporation into growing hydrocarbon chains. The decay in ROP with carbon number beyond $n=3$ implicates the increased absorptivity and lower diffusion coefficients for α -olefins with growing chain length [15]. The behaviour of ROP as a function of n can be adequately captured by

$$ROP_n = \frac{ROP_{\max}}{1 + \left(\frac{n - n_{\max}}{b} \right)^2} \quad (7.21)$$

where $ROP_{\max}$ is maximum olefin-to-paraffin ratio at carbon number, $n_{\max}$ while b is a model parameter determined by non-linear regression analysis. The model estimates in good agreement with the experimental data as seen in Figure 7.11.

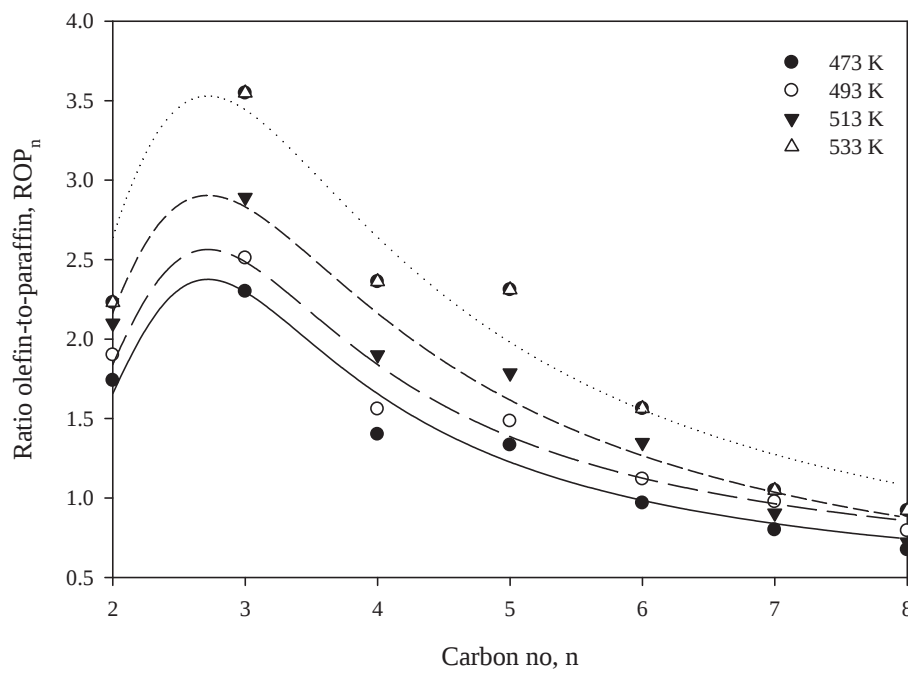


Figure 7.10 ROP_n behaviour as function of carbon no. at various temperatures for hydrogen mole fraction of 0.67 ($y_{H_2}=0.67$)

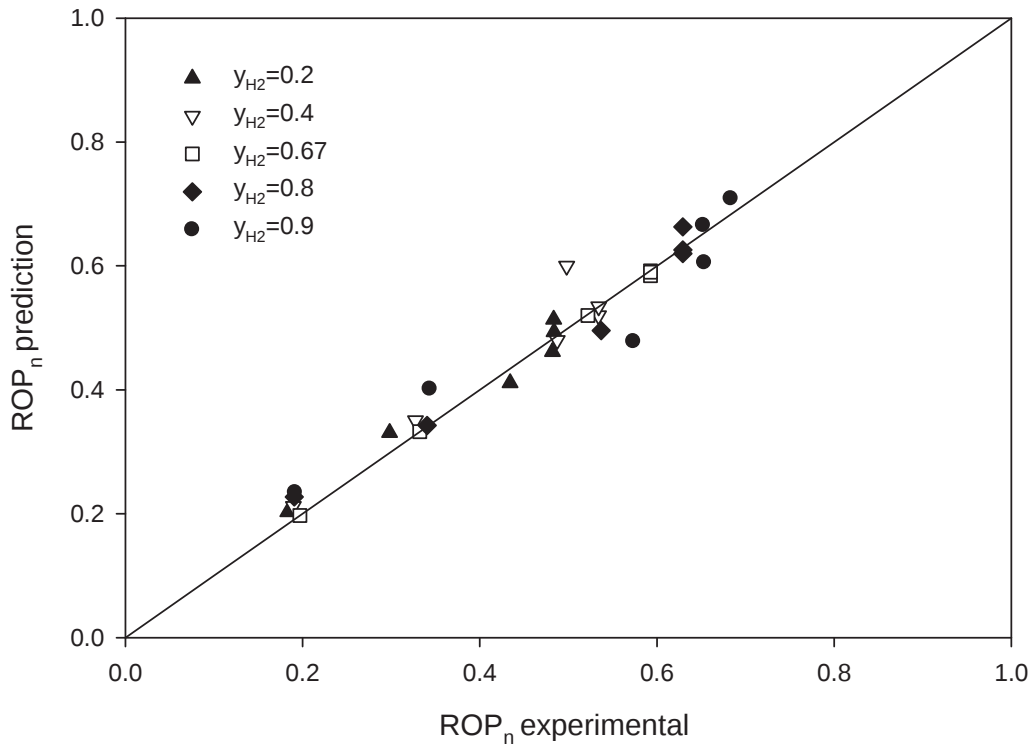


Figure 7.11 Parity plot for ROP model over Co catalyst at different feed compositions

7.7.3. Individual activation energy estimation

The activation energy values for the individual products were calculated using the following expression:

$$r_i = A_i \exp\left(-\frac{E_i^a}{RT}\right) \quad (7.22)$$

where r_i is the individual component reaction rate in $\text{mol g}_{\text{cat}}^{-1}\text{s}^{-1}$ and A_i is the corresponding pre-exponential factor of individual component.

In general, individual activation energies as seen Table 7.3, E_i^a , are between $70\text{--}110 \text{ kJ mol}^{-1}$ consistent with the previous study of Chen and Adesina [16]. These estimates also indicate that higher hydrocarbon formation probably controls the overall CO consumption rate since the

E_i^a of C_{4+} species appear to be generally higher than that obtained from the k_{ASF} value (87 kJ mol^{-1}).

Table 7.3. Estimated activation energy for individual hydrocarbon

Component	E_i^a (kJ mol^{-1})	R^2
CH_4	79.4	0.996
C_2H_6	91.6	0.996
C_2H_4	80.6	0.992
C_3H_8	74.2	0.994
C_3H_6	73.5	0.984
C_4H_{10}	105.1	0.859
C_4H_8	99.8	0.980
C_5H_{12}	107.5	0.921
C_5H_{10}	96.2	0.992
C_6H_{14}	101.4	0.932
C_6H_{12}	103.7	0.973
C_7H_{16}	102.5	0.861
C_7H_{14}	108.6	0.932
C_8H_{18}	108.2	0.830
C_8H_{16}	96.2	0.924

Note: $y_{\text{H}_2}=0.67$, $P=21 \text{ atm}$, $\text{GHSV}=3 \text{ l(STP)gcat}^{-1}\text{h}^{-1}$

7.7.4. Effect of Feed Composition

In the FTS reaction where the CO_2 formation is deemed negligible, thus, the theoretical hydrocarbon rate can be expressed as follow;



While, the stoichiometric H_2 mole fraction for each product can be calculated using the following equation;

$$y_{H_2}^{ST} = \frac{x + \frac{y}{2}}{2x + \frac{y}{2}} \quad (7.24)$$

Theoretical stoichiometric H_2 mole fraction, $y_{H_2}^{ST}$, for each hydrocarbon component is displayed in Table 7.4.

Table 7.4 Theoretical stoichiometric H_2 mole fraction

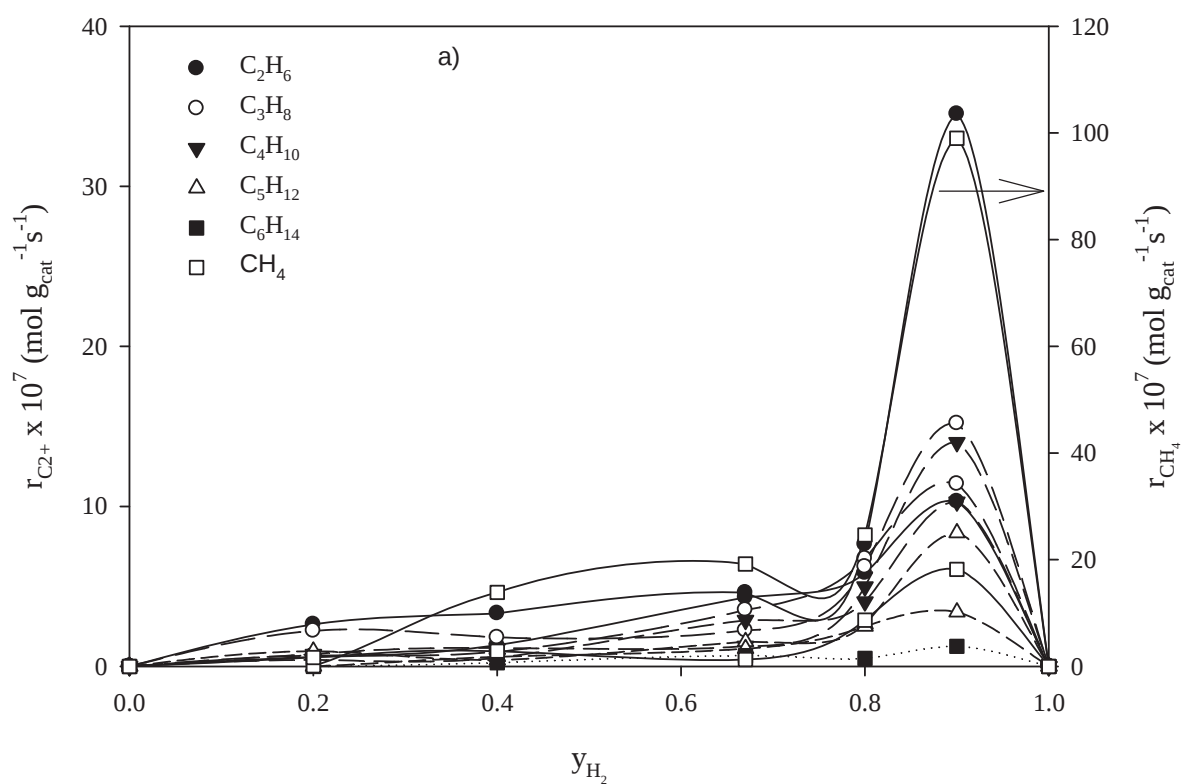
Hydrocarbon species	Stoichiometric H_2 mole fraction
Methane, CH_4	0.75
Ethene, C_2H_4	0.67
Ethane, C_2H_6	0.71
Propene, C_3H_6	0.67
Propane, C_3H_8	0.70
Butene, C_4H_8	0.67
Butane, C_4H_{10}	0.69
Pentene, C_5H_{10}	0.67
Pentane, C_5H_{12}	0.69
Hexene, C_6H_{12}	0.67
Hexane, C_6H_{14}	0.68

Heptene, C_7H_{14} 0.67

Heptane, C_7H_{16} 0.68

Octene, C_8H_{16} 0.68

Octane, C_8H_{18} 0.67



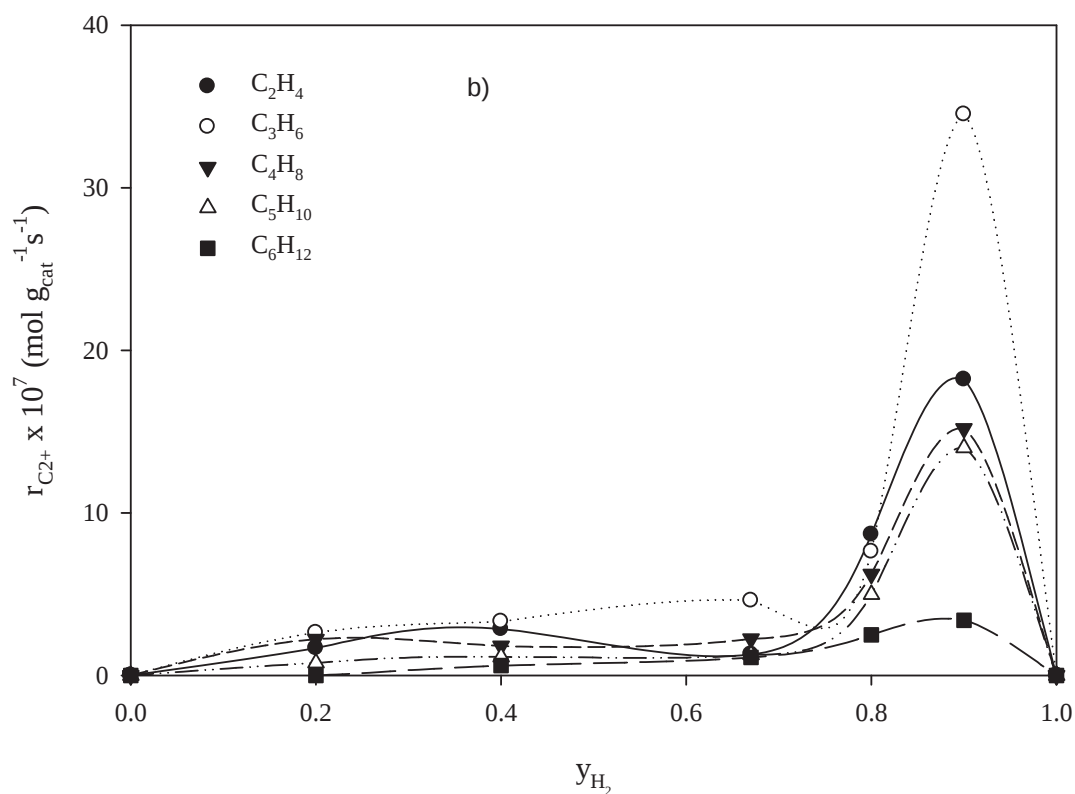


Figure 7.12 Reaction rate as a function of feed composition a) Paraffins b) Olefins

Effect of feed composition for each individual carbon number, both for paraffins and olefins are displayed in Figure 7.12. As expected, the optimum feed composition is skewed toward higher H_2 ratio ($y_{H_2}=0.9$) for all cases. For paraffins, the methane produces the highest rate regardless of the feed composition.

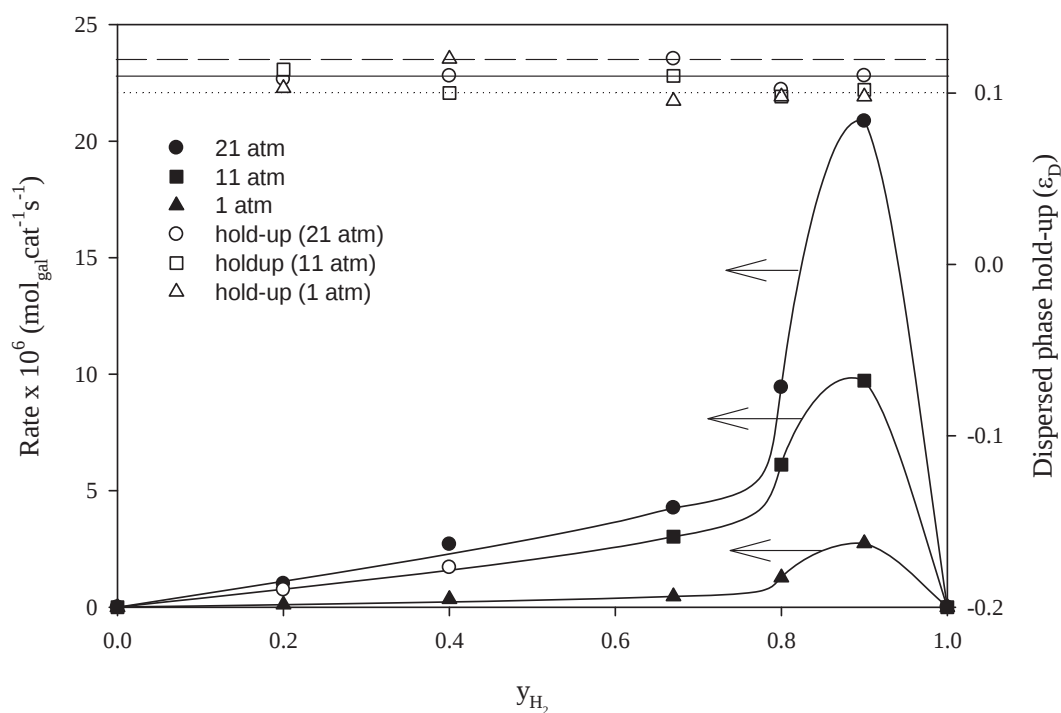


Figure 7.13 Effect on reaction rate and dispersed hold-up of syngas feed composition at $T = 523\text{ K}$

Figure 7.13 further shows that the reaction rate–composition profiles are similarly shaped at all three total operating pressures investigated. The optimum composition is a feed gas with $y_{H_2}=0.9$ in all cases. These qualitative features suggest that the FT reaction mechanism was probably unchanged at the different operating pressures used. Indeed, as evident from Figure 7.14, the hydrocarbon synthesis rate has a linear dependency on the total operating pressure with a proportionality constant of $9.73 \pm 0.13 \times 10^{-7} \text{ mol g}_{\text{cat}}^{-1} \text{ s}^{-1} \text{ atm}^{-1}$.

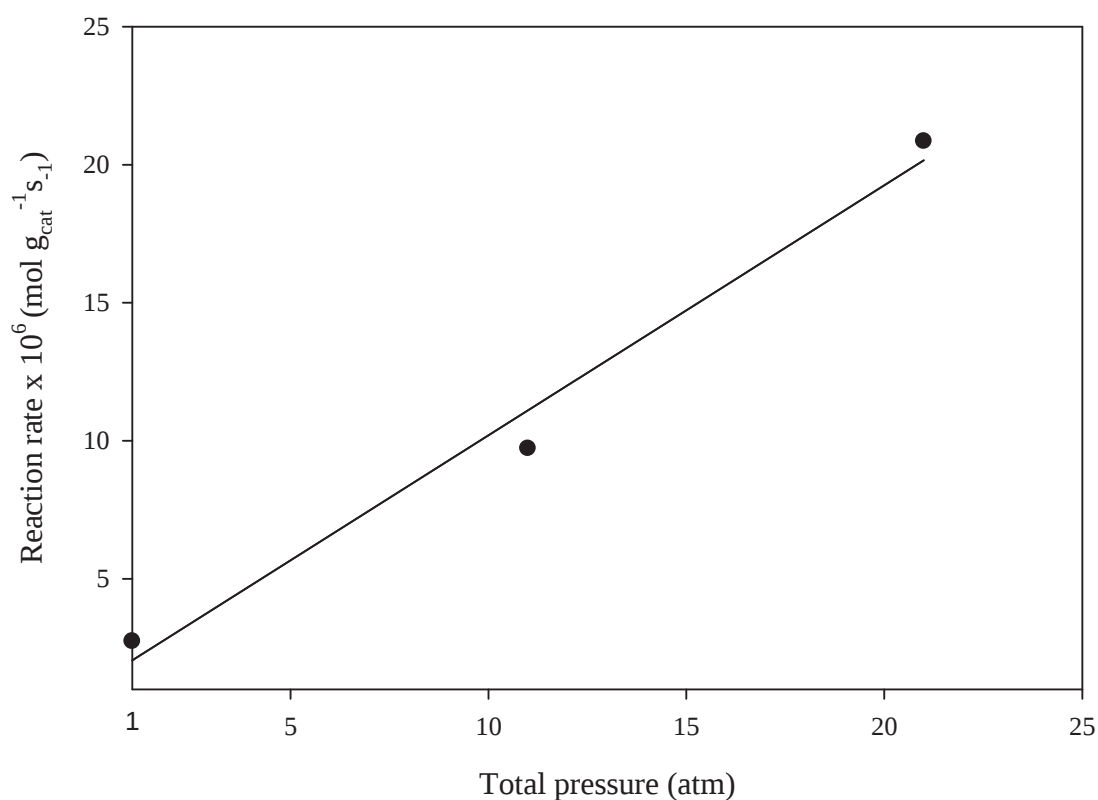


Figure 7.14 Reaction rate as function of total pressure

The chain growth probability, α_{FT} , was obtained from a fit of the individual hydrocarbon formation rate to the Anderson-Schulz-Flory (ASF) model given by:

$$r_{C_n} = k(1 - \alpha_{FT})^2 \alpha_{FT}^{n-1} \quad (7.25)$$

Figure 7.15 displays the variation of α_{FT} with feed composition at the three operating total pressures used.

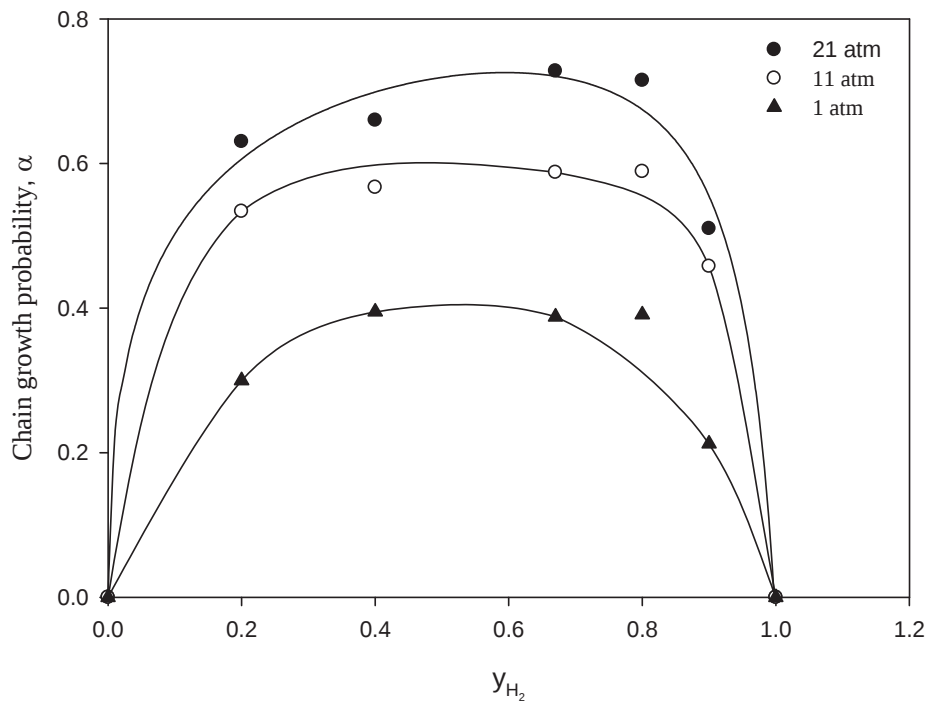


Figure 7.15 Effect of chain growth probability, α_{FT} on syngas feed composition

As was observed in the case of rate envelopes, the shape similarity of these curves is indicative of a common reaction mechanism regardless of the pressure employed. In particular, the “plateau” in chain growth probability values for syngas composition with $0.4 \leq y_{H_2} \leq 0.8$ implicates the existence of a common surface monomeric species in the propagation step – most likely a CH_2 species - for higher hydrocarbon formation. However, the average carbon chain length, $\bar{n} = \frac{1}{1 - \alpha_{FT}}$, clearly increased with total pressure as may be expected for a surface polymerization reaction. In fact, the linear expression;

$$\bar{n} = \bar{n}_0 + \psi P_T \quad (7.26)$$

governs the relationship between $\bar{n}$ and P_T . where, $\bar{n}_0$ is the average carbon number for FTS at sub-atmospheric pressure and estimated as

1.48 and ψ is the pressure coefficient for chain growth obtained as 0.087 atm^{-1} for the present catalyst.

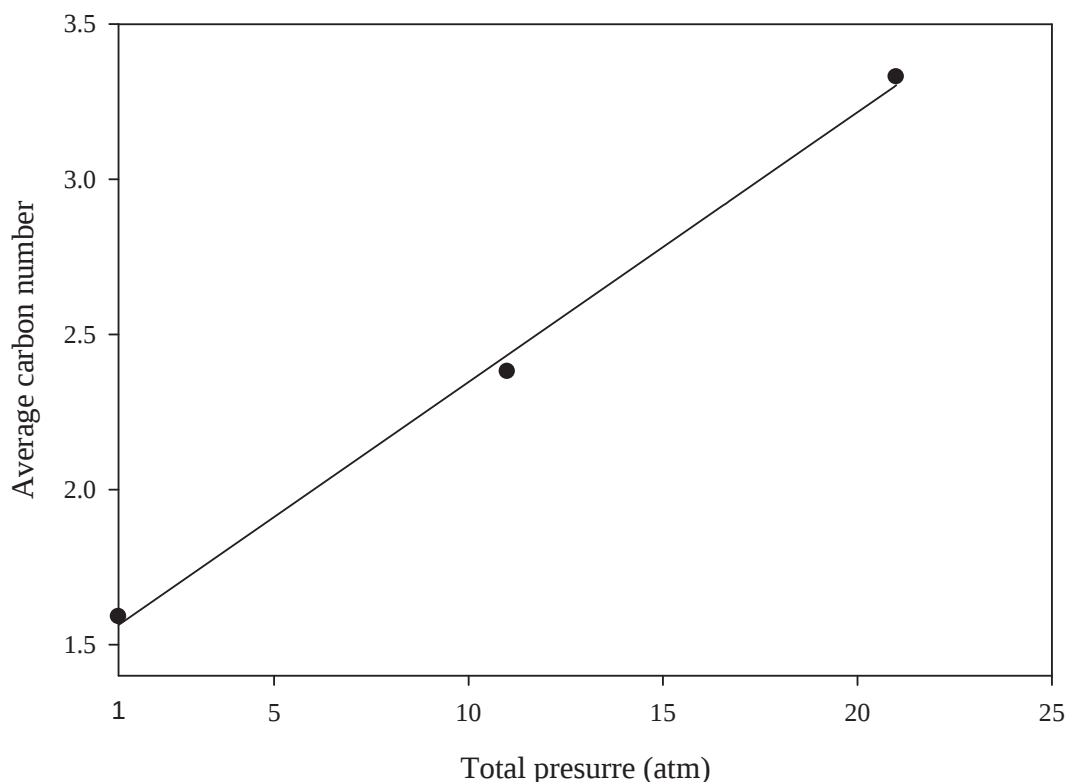


Figure 7.16 Average carbon number as function of total pressure

This finding is in agreement with the reports of other investigators [17-19] on the beneficial effects of high pressure operation for FTS although other FT catalysts will be characterized by different values of $\bar{n}_0$ and ψ . Equation (7.26) may be used to estimate the required total pressure for a desired value of $\bar{n}$ or α_{FT} .

The behaviour of the olefin-to-paraffin ratio, ROP, as a function of hydrogen mole fraction in the feed, y_{H_2} , plotted in Figure 7.17 reveals that propene and butene are the most favoured olefins on the catalyst since the maximum ROP may be located between carbon number 3 to 4 across the range of syngas compositions studied. The ROP values for

C_{7+} species would appear to be well below 2 suggesting that the rate with which the olefins or paraffins for the higher hydrocarbons were produced was probably the same due to the nearly identical H:C ratio in these species at $n \geq 7$. Additionally, the gas phase composition of the species may be less reliable because of their higher solubilities in the liquid phase and the relatively smaller amounts produced under FTS conditions.

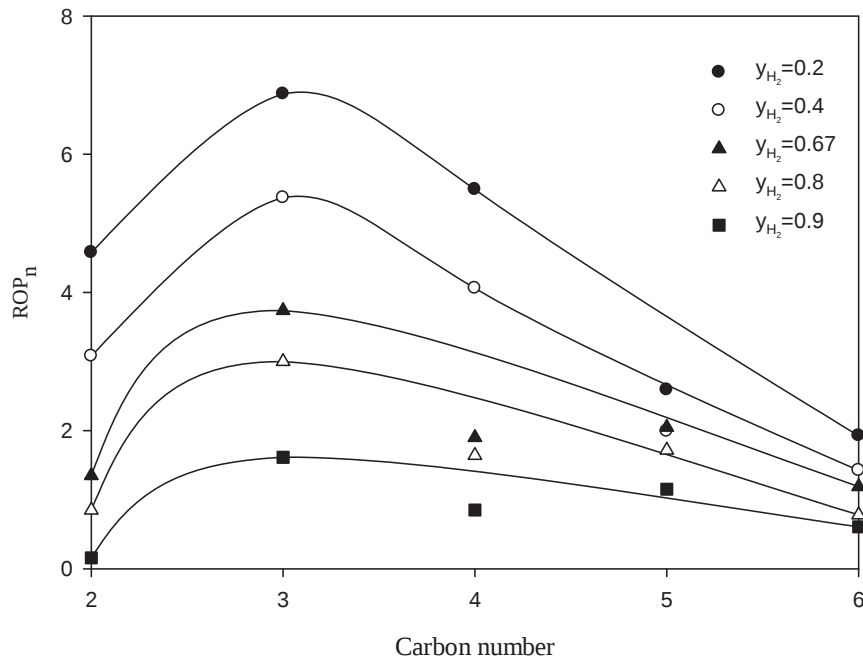


Figure 7.17 The behaviour of olefin-to-paraffin ratio, ROP as function of syngas feed composition at different carbon number

The relationship between ROP and the carbon number, n , irrespective of the syngas composition may be adequately described by:

$$ROP = \frac{\Lambda}{1 + \omega(n - \eta)^2} \quad (7.27)$$

where Λ represents the maximum ROP value with η as the carbon number at which it may be produced while ω is an olefin attenuation index. A similar observation has also been made by Vo *et al.* [20].

Table 7.5 The estimate of parameter of Equation (7.27)

Feed composition, y_{H_2}	Model parameters		
	Λ	η	ω
0.2	6.97 $\pm$ 0.04	3.14 $\pm$ 0.02	0.40 $\pm$ 0.01
0.4	5.42 $\pm$ 0.03	3.21 $\pm$ 0.02	0.50 $\pm$ 0.01
0.67	3.26 $\pm$ 0.08	3.28 $\pm$ 0.08	0.44 $\pm$ 0.01
0.8	3.18 $\pm$ 0.16	3.30 $\pm$ 0.17	0.58 $\pm$ 0.03
0.9	1.25 $\pm$ 0.10	3.89 $\pm$ 0.30	0.27 $\pm$ 0.02

Table 7.5 contains the estimates of these parameters obtained from nonlinear regression of the data. It is manifest from this table that while olefin selectivity (Λ) decreased with increasing feed H_2 content, the maximum carbon chain length (η) exhibited an opposing trend. It would therefore seem that it is infeasible to simultaneously optimize both olefin selectivity and carbon chain length by manipulating only feed composition. This is a recurring paradox in the Fischer-Tropsch synthesis reaction and underscores the need for a multipronged approach to the process technology.

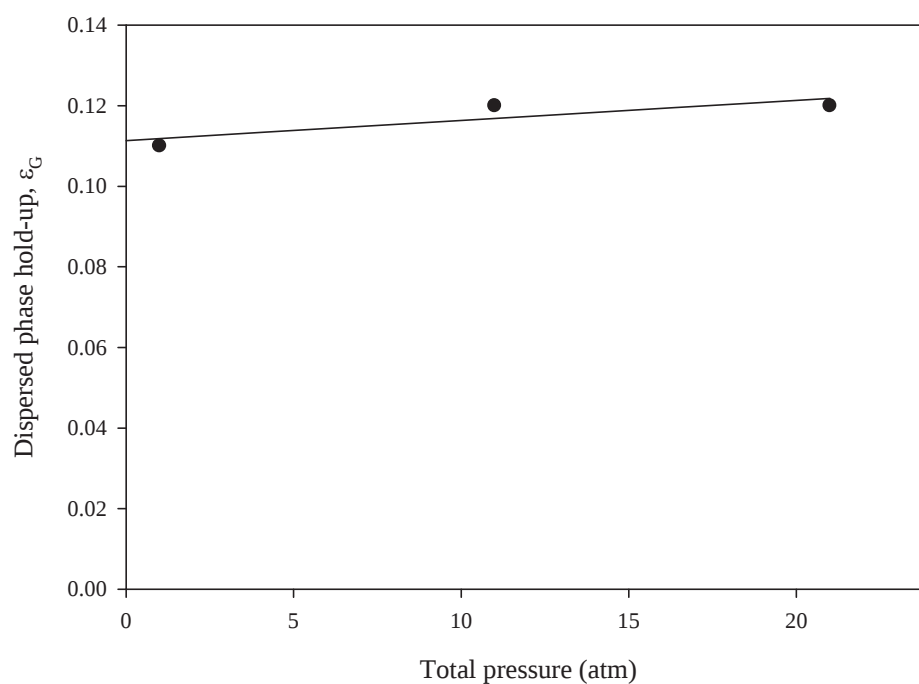


Figure 7.18 Dispersed phase hold-up as function of total pressure for reaction conditions: $T = 498\text{K}$, and syngas with $\text{H}_2:\text{CO}$ ratio = 2:1

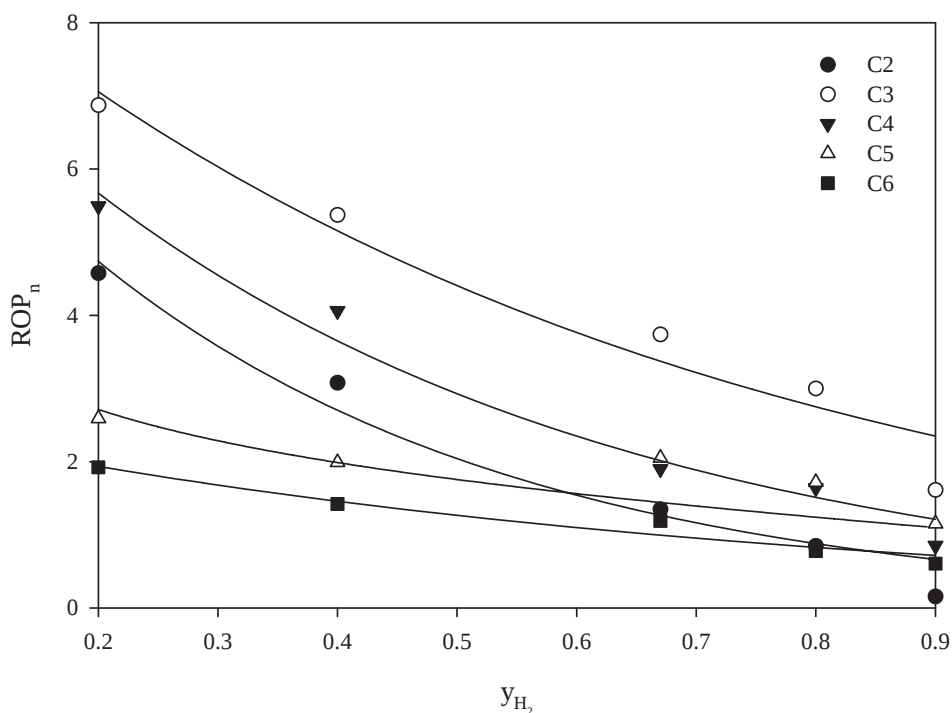


Figure 7.19 ROP_n as function of feed composition, y_{H_2}

While, Figure 7.19 illustrates the trend in olefin-to-paraffin ratio, ROP, for each carbon number with respect to feed composition. The decreasing ROP with increased feed H_2 mole fraction is a reflection of the fact that nearly identical surface H:C ratio is required for the formation of olefins and paraffins as the chain carbon number increased.

Cooper *et al* [3] had previously shown that external transport and pore diffusional limitations may be avoided in the same FT reactor using impeller speed in excess of 600 rpm and average particle size smaller than 425 μm .

7.7.5. Dispersed phase hold-up evaluation

The dispersed phase hold-up, ε_D , was determined from the instantaneous tomograms (permittivity data) taken over the vessel cross-sectional area using the Maxwell equation [21] as given as Equation (3.12) in Chapter 3.

Figure 7.20 shows typical tomograms obtained from the reactor during a run. Since the ECT sensor cannot discriminate between a solid particle

and a gas bubble, the dispersed phase hold-up, ε_D is a combination of the gas phase hold-up (ε_G) and the solid phase hold-up (ε_S).

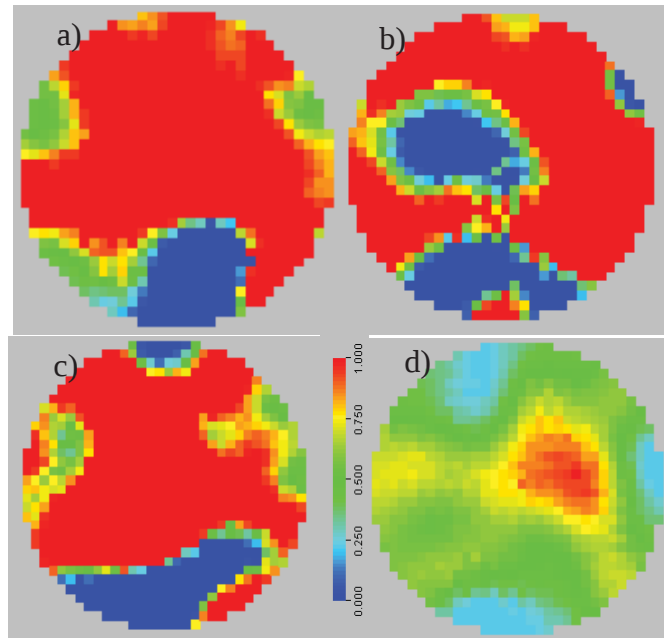


Figure 7.20 Tomography images at different temperature a) 473 K b) 493 K c) 513 K and d) 533 K. Operating conditions: Pressure: 21 atm, catalyst loading: 10 g L^{-1} stirring speed: 1200 rpm

It would therefore seem that there was no significant change in the electrical permittivity of the alumina particles and the paraffin oil (used as the reaction medium) with temperature since the dispersed phase hold-up was constant. However, the data for the gas-inducing impeller demonstrated that the dispersed phase hold-up increased monotonically with temperature. The increased dispersed phase hold-up for the gas-inducing stirrer may be attributed to a change only in the gas phase hold-up (consistent with the earlier results from Figure 6.20) which may be associated with volume increase due to gas expansion with increasing temperature.

Given that the coefficient of expansion at constant pressure for a gas is,

$\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$, which is simply the reciprocal of the absolute temperature for

an ideal gas, then the change witnessed in gas phase hold-up over the temperature range used, may be given as, $\frac{V_2}{V_1} = \frac{T_2}{T_1} = \frac{\varepsilon_{G_2}}{\varepsilon_{G_1}}$ which is about

1.8 with T_1 and T_2 as 293 and 530 K respectively, in agreement with a doubling of the dispersed phase hold-up within the same temperature window in Figure 7.8. Indeed, a fit of the dispersed (gas) phase hold-up data for the gas-inducing impeller to an Arrhenius expression yielded a low activation energy of 5.81 kJ mol⁻¹ indicative of a purely physical process such as gas diffusion or solubility in liquids. As a result of these initial considerations, changes in dispersed phase hold-up during isothermal FTS reaction may be readily decoupled from thermal expansion effects,

The influence of total operating pressure on the dispersed phase hold-up was also examined. Figure 7.18 evinces a linear, albeit gentle, increase in dispersed phase hold-up with increased operating pressure. The behaviour is readily captured by;

$$\varepsilon_D = \varepsilon_{D_0,P} + \lambda P \quad (7.28)$$

where,

$\varepsilon_{D_0,P}$ is the dispersed phase hold-up at atmospheric conditions

P is the total operating gauge pressure

λ an empirical constant for the syngas in paraffin oil

Linear regression gave ε_{D_0} and λ as 0.112 and 5×10^{-4} atm⁻¹ respectively.

7.7.6. ECT-based reaction evaluation

FTS runs were performed at different temperatures and at a constant pressure of 21 atm using syngas with H₂:CO ratio of 2:1. The rise in dispersed (gas) phase hold-up (since the contribution due to the alumina supported catalyst particles has been previously determined to be temperature-insensitive) with temperature seemed to level off at higher temperature as may be seen in Figure 7.21, Hence, the behaviour was described by;

$$\varepsilon_G = \varepsilon_{G_0} + b_0 [1 - \exp(-b_1 \theta)] \quad (7.29)$$

where θ is the dimensionless temperature ($\theta = T - T_0 / T_0$), with T_0 as the room temperature ($T_0 = 295$ K). Nonlinear regression of the data provided, $\varepsilon_{G0} = 0.04 \pm 0.0013$, $b_0 = 19.54 \pm 0.047$ and $b_1 = 0.0048 \pm 0.0002$. The change in gas phase hold-up over the reaction temperature range employed is more than what was expected due to mere gas volume expansion (6% from 493 to 523 K) since ε_G increased by more than 19% over the same temperature range, suggesting that extant liquid phase properties as product accumulation continued were probably responsible for the large variation in gas hold-up with temperature. This finding is in line with the original proposition of reaction-induced change in hydrodynamic attributes. Clearly, the sensible change in gas phase hold-up due to product accumulation would also affect mixing characteristics and thus, reaction rate. Indeed, this increase in gas hold-up with temperature was also reported by others [3, 21] due to decreased liquid viscosity and surface tension. On the other hand, it is evident from Figure 7.21 that the reaction rate followed the expected Arrhenius behaviour with b_2 estimated as the Arrhenius number, $E/RT_0 = 26.58$, for the FT reaction at T_0 and hence, an activation energy, E , of 65.2 kJ mol⁻¹.

$$(-r_{rxn}) = r_0 \exp\left(-\frac{b_2}{(\theta + 1)}\right) \quad (7.30)$$

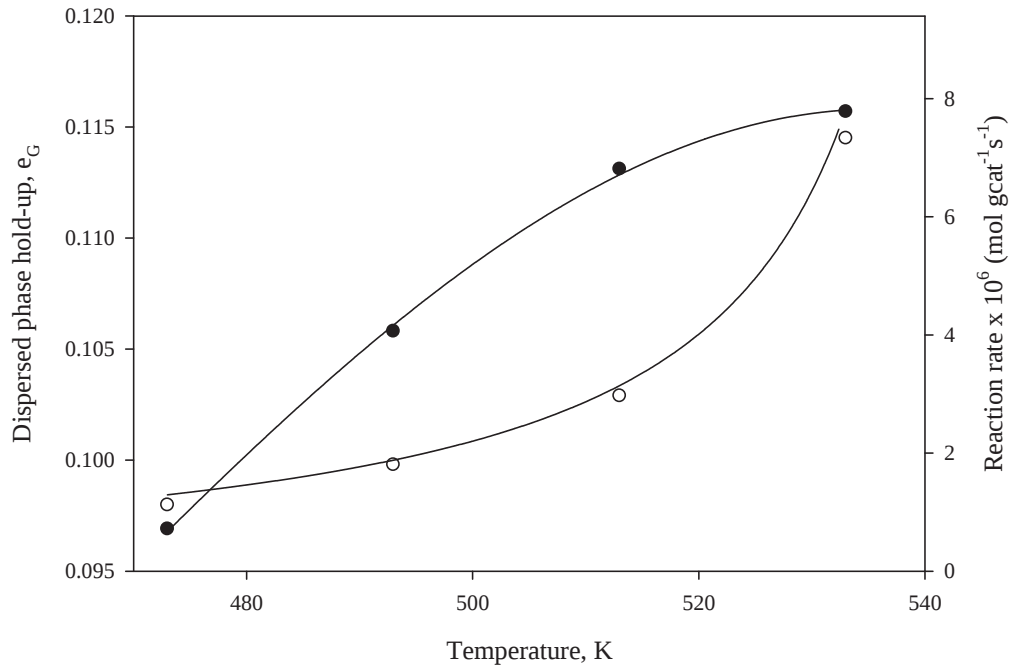


Figure 7.21 Dispersed phase hold-up (●) and reaction rate (○) as functions of temperature

Thus, combining Equations (7.29) and (7.30), the coupling between reaction rate and dispersed phase hold-up may be expressed by;

$$(-r_{rxn}) = r_0 \exp \left[\frac{-b_1 b_2}{b_1 - \ln \left\{ \frac{b_0 - (\varepsilon_G - \varepsilon_{G_0})}{b_0} \right\}} \right] \quad (7.31)$$

The effect of syngas composition on FTS rate is shown in Figure 7.13. The profile is strongly skewed towards the high H_2 mole fraction, y_{H_2} , due to relatively weak adsorption of H_2 on the catalyst surface in the presence of CO.

The latter is reportedly more strongly chemisorbed on the same site as H_2 [3]. Interestingly, the associated gas phase hold-up is practically constant over the feed composition, y_{H_2} , values used as seen on the same plot, regardless of the total pressure. This indicates that the

change in liquid phase properties as a result of product accumulation was probably similar for different syngas concentrations.

7.8. FT Transient Evaluation

7.8.1. FT time constant and solubility analysis

The slurry phase FT reaction has an important intrinsic reaction transient for pseudo-saturation of the initial liquid medium with products. Typically, the solvent used is a paraffinic liquid. In this study, the average chain length of the paraffin oil used was C_{26} . Solubility may play a significant role, especially during start up at high pressure. Solubility may affect chain length of reaction products by reducing the production rate due to longer transient time for higher hydrocarbons.

Time constant, τ_n , for the transient chain length, n , is given by,

$$\tau_n = \frac{\sigma_n(t)m_l}{r_n(t)m_{cat}MW_n} \quad (7.32)$$

where, σ_n = mass solubility (g_n/g_l) of product of chain length n , in liquid medium, as a function of time

r_n = reaction rate (mol g_{cat}⁻¹ s⁻¹) of product, n , as a function of time

m_l = mass of liquid medium (g)

m_{cat} = mass of catalyst added (g)

MW_n = molecular weight of product n , (g mol⁻¹)

τ_n = time constant for transient of product n , (s)

The transient partial pressure of species i , assuming a first order response approximation (valid for a stirred tank reactor) is given as

$$P_i(t) = P_i^\infty + (P_i^0 - P_i^\infty)e^{-bt} \quad (7.33)$$

where, $P_i(t)$ = partial pressure of component, i , as a function of time, t ,
 P_i^0, P_i^∞ = partial pressure of component, i , at start of transient, and at infinite time, or steady state composition, b = inverse of first order time constant, τ .

Equation (7.33) can be simplified for the case of primary reaction run, $P_i^0 = 0$ in terms of normalized reaction rate as,

$$\frac{r_i(t)}{r_i^{ss}} = 1 - \exp\left(-\frac{t}{\tau}\right) \quad (7.34)$$

where r_i^{ss} is the reaction rate of i at steady state, and the time constant, τ , is the inverse of the constant, b , given by Boelee [22],

Transient time, τ_{TR} , is the paramount parameter in transient analysis in a slurry stirred tank reactor. Pinna et al. [23] estimated the transient time of slurry FT synthesis in a stirred tank reactor. For such a system, which was very similar to this study, τ_{TR} needed to achieve 99% of true steady state was $4.6\tau_{TR}$. Since this is a rigorous estimate of the transient duration, and also highly conservative in most cases, it is necessary to make a practical estimate of the time needed to achieve pseudo steady-state conditions.

Thus Table 7.6 provides the solubility coefficients and the theoretical transient time constants for the slurry stirred tank reactor under studied.

Table 7.6. Solubility and theoretical time constant at different carbon number, reaction conditions: 498 K, 2.0 MPa, 20 g L⁻¹, 9:1 (H₂:CO), 1200 rpm

Carbon number, n	Solubility coefficient, $s_i(\text{m}^3\text{L}/\text{m}^3\text{G})$	Theoretical time constant, $\tau(\text{h})$	Theoretical transient time, $\tau_{\text{TR}}=4.6\tau$
1	2.354	0.3839	1.766
2	1.352	0.4467	2.055
3	0.777	0.5560	2.557
4	0.446	0.7462	3.433
5	0.256	1.077	4.956
6	0.147	1.654	7.608

By adopting the approach from Pinna *et al* [23] and applying Equation (7.34) the theoretical normalised reaction rate constant is depicted in Figure 7.22. This theoretical behaviour of transients is in excellent agreement with the experimental results (cf. Figure 7.24 (a and b)) for fresh start-up medium. However, in practices, the changes in process conditions and liquid paraffin properties would have changed the transient time. Nonetheless, the 36 h time on stream allowed stabilisation of any change in the process conditions.

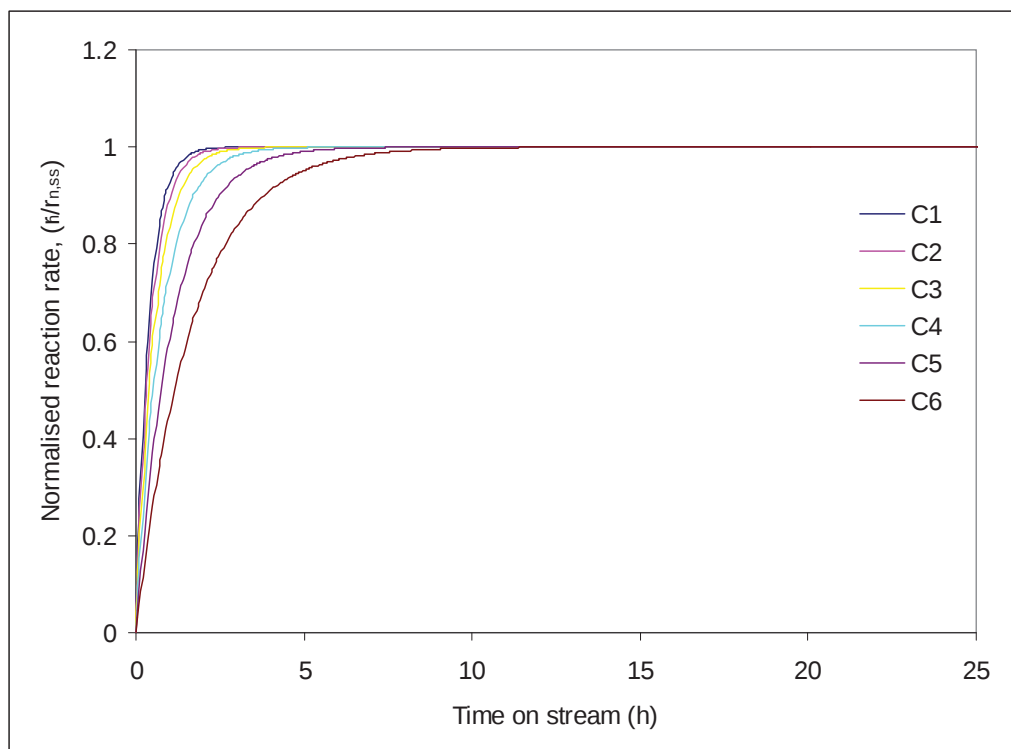


Figure 7.22. Theoretical normalized reaction rate transient, C₁-C₆, Reaction condition: 498 K, 21 atm, $y_{H_2}=0.9$, $N_s=1200$ rpm

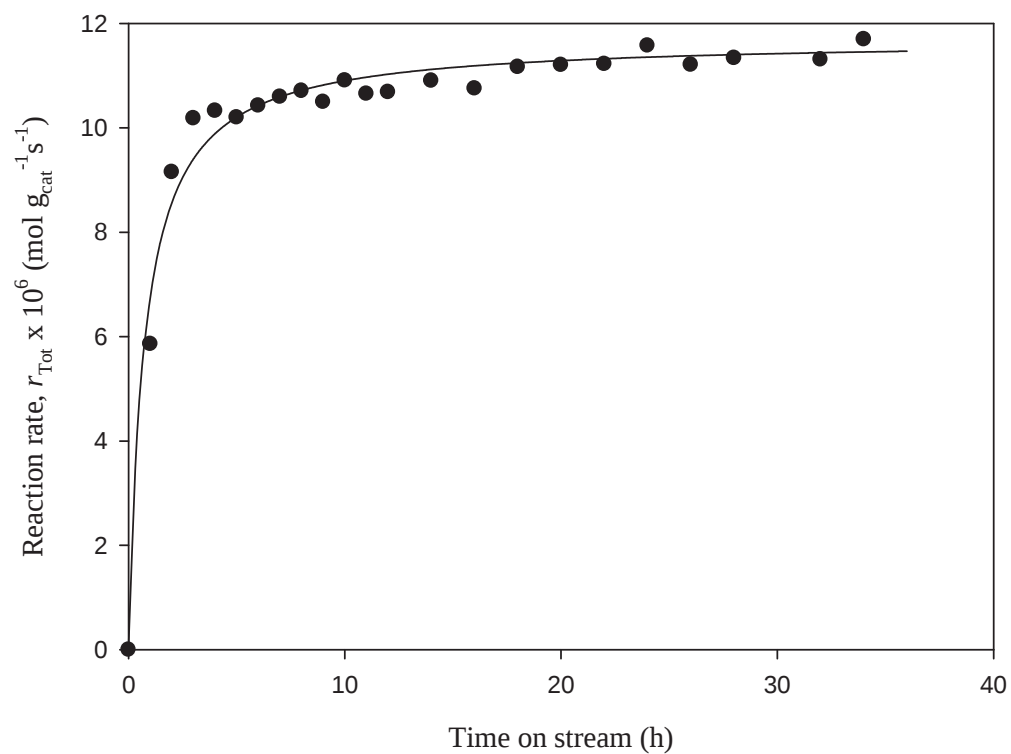


Figure 7.23 Reaction rate profile with time-on-stream at 498 K, 21 atm using feed with $H_2:CO=9:1$.

Figure 7.23 shows that the total hydrocarbon synthesis rate followed a 1st order exponential rise to a final steady-state value with time-on-stream. Although this behaviour is similar to the stirred reactor dynamics under non-reactive conditions a difference in time-constants was evident when data in Figures 4.6 (refer to chapter 4) & 7.23 were individually fitted to the expression:

$$y_P = y_P^{SS} [1 - \exp(-t / \tau_P)] \quad (7.35)$$

where y_P is the time-dependent response of the operation P to a step-change in y and y_P^{SS} is the final or ultimate value of y at steady-state while τ_P is the time-constant for the particular operation. Nonlinear regression of the data in both plots to Equation (7.35) provided τ_P for the non-reactive conditions as 26 mins while the reaction rate has a corresponding value of 1.28 hours. This clearly suggests that the net reaction relaxation time constant (a hybrid of the surface relaxation time constants for all elementary steps) during FTS is larger than the resistance due to mixing. The data in Figure 4.6 (cf. chapter 4), also showed an initial transport lag of about 6 mins. A mixing time constant of 26 mins confirms that the reaction dynamics (monitored for about 36 hours) was not disguised by fluid phase hydrodynamics or mixing.

Interestingly, the plots in Figure 7.24 (a & b) reveal that the individual hydrocarbon species also experienced similar reaction dynamics albeit characterized by different formation time-constants (reciprocal of the surface rate velocity) when the production rate data were fitted to Equation (7.35). These estimates are summarised in Table 7.7 below.

Table 7.7 Estimation of time-constant, τ_P , (hours) for individual hydrocarbons from Equation (7.35)

	C1	C2	C3	C4	C5	C6
Paraffins	1.09	1.40	2.27	3.27	4.42	5.64
Olefins	-	0.48	1.22	1.54	2.23	2.43

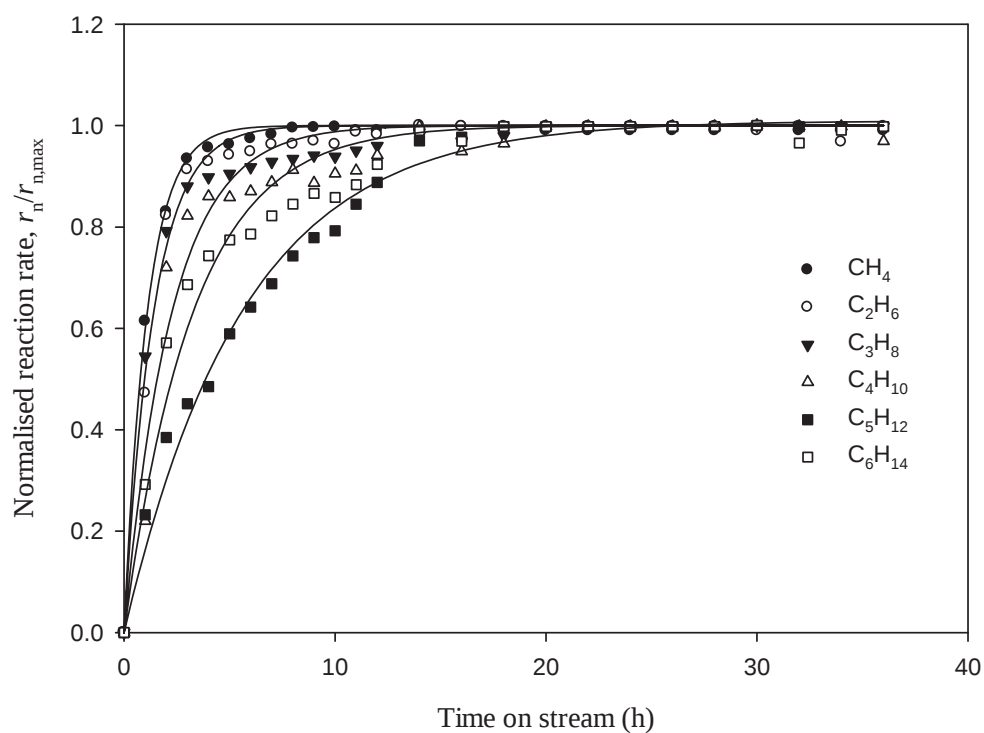


Figure 7.24a. Normalised reaction rate history of individual paraffinic species at $T = 498$ K, and 21 atm with a feed $H_2:CO$ ratio= 9:1

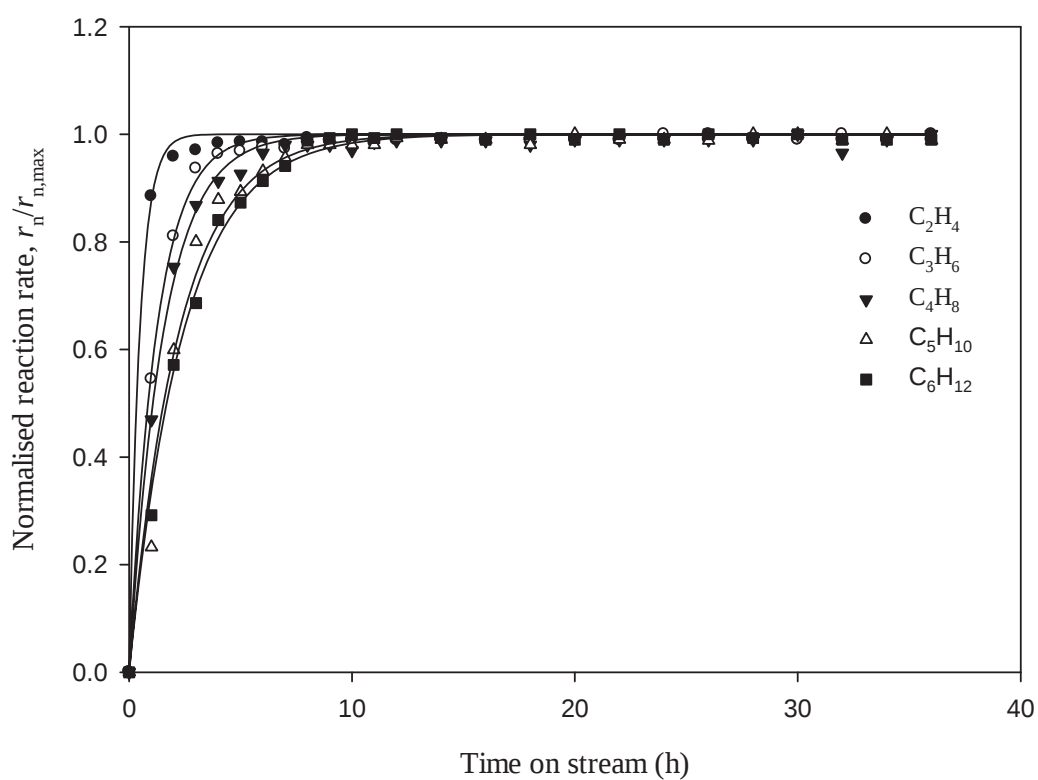


Figure 7.24b. Normalised reaction rate history of individual olefinic species at $T = 498$ K, and 21 atm with a feed $H_2:CO$ ratio= 9:1

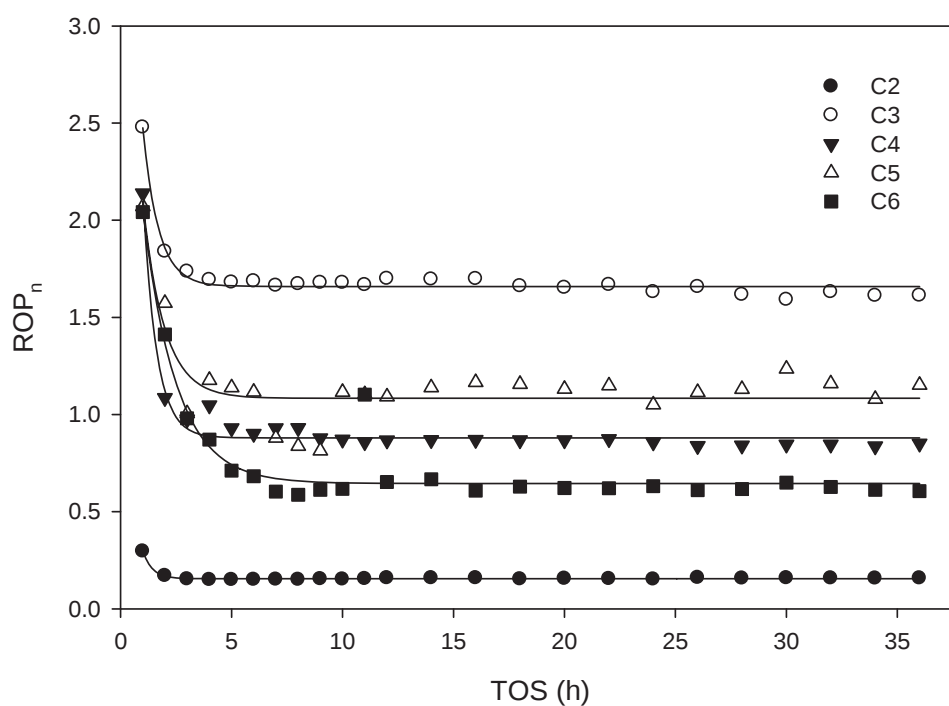


Figure 7.24c ROP as a function of time-on-stream, $T=498$ K, $y_{H_2}=0.9$

Figure 7.24c suggests that the ROP value initially dropped with time-on-stream (TOS) but reached an essentially constant value after about 10 hours for all hydrocarbon species. Even so, it is apparent that the time to complete this initial drop increased with carbon number.

7.8.2. Influence of FT reaction conditions over Time-On-Stream (TOS)

The role of temperature and time-on-stream on dispersed phase hold-up is shown in Figure 7.25. The transient profile has a characteristic sigmoid shape at all temperatures and thus, the thermotemporal behaviour may be expressed as:

$$\varepsilon_D = \varepsilon_{D_0} + \varepsilon_{D_1} \left[1 - \exp(-\zeta t) \right]^\upsilon \quad (7.36)$$

where $\varepsilon_{D,0}$ is the initial dispersed hold-up, $\varepsilon_{D,1}$ is the deviation between the ultimate dispersed phase hold-up (at infinite time) and the initial value, ζ is the time constant for the dispersed phase and υ is an empirical exponent..

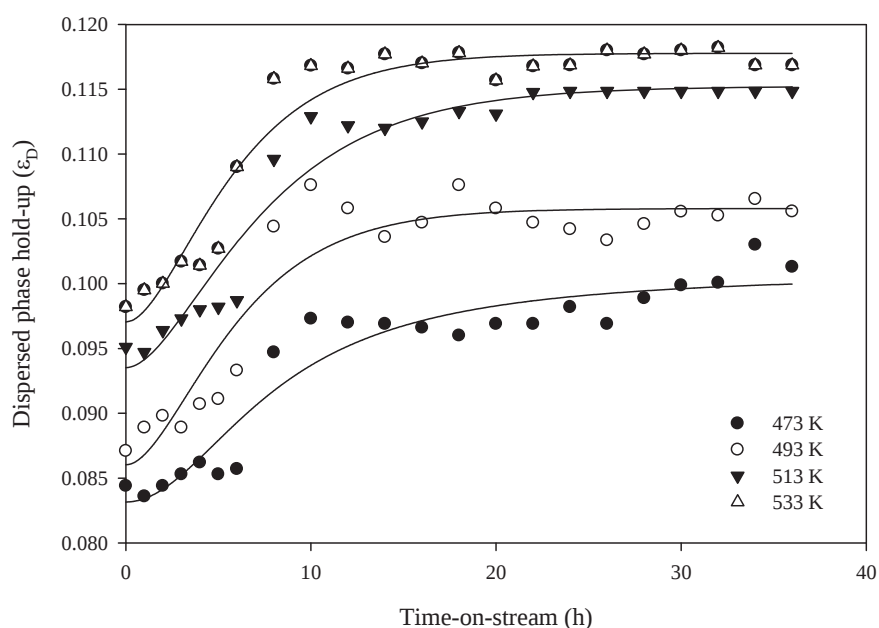


Figure 7.25 Dispersed phase hold-up as a function of TOS at different temperatures. Reaction conditions: $\text{H}_2:\text{CO} = 2:1$ at total pressure of 21 atm,

Table 7.8 Estimates of parameters of Equation (7.36)

Temperature	ε_{D0}	ε_{D1}	ζ	ν
473 K	0.0830 ± 0.0021	0.0168 ± 0.0004	0.1566 ± 0.0040	2.0
493 K	0.0860 ± 0.0017	0.0199 ± 0.0004	0.2276 ± 0.0046	2.0
513 K	0.0922 ± 0.0023	0.0222 ± 0.0006	0.2300 ± 0.0058	2.0
533 K	0.0970 ± 0.0030	0.0339 ± 0.0010	0.2333 ± 0.0071	2.0

Table 7.8 displays the estimates from nonlinear regression of the data. It is apparent that all the model parameters (with the exception of ν estimated as 2.0) are temperature-sensitive. In particular, while ε_{D0} reflects essentially the contribution due to thermal expansion of the gas phase, ε_{D1} is indicative of a reaction-induced involvement.

Interestingly, an Arrhenius treatment of the data provided an activation energy, E_{D0} of 5.6 kJ mol^{-1} (symptomatic of a physical process and in

agreement with the activation energy, i.e. 5.8 kJ mol^{-1} , found for the data in Figure 7.8 under non-reactive conditions) for the initial dispersed phase hold-up, ε_{D0} and a corresponding, but larger, value, E_{D1} of 23 kJ mol^{-1} for ε_{D1} confirming its association with a reaction-controlled step. The empirical exponent represents the number of dispersed phase entities involved in any interaction occasioning a change in the hold-up with time-on-stream. A value of 2.0 for ν suggests that at least 2 gas bubbles are implicated in the bubble-bubble interaction.

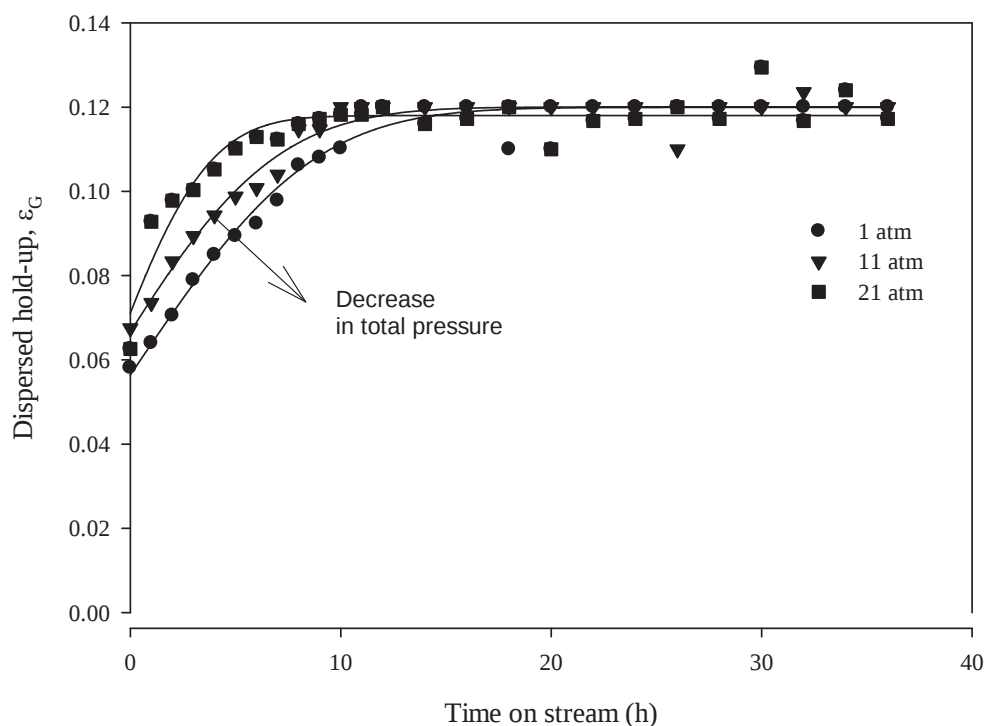


Figure 7.26 Transient profile of the dispersed phase hold-up at different total pressures, reaction condition: $\text{H}_2:\text{CO}=9:1$, Temperature = 498 K

As may be seen in Figure 7.26, the effect of total operating pressure on the dispersed phase hold-up with time-on-stream also followed a first-order exponential rise to an ultimate value. Consequently, a model structurally similar to Chapman-Richards model may be used to represent the behaviour, namely;

$$\varepsilon_{D,P} = \varepsilon_{D_0,P} + \varepsilon_{D_1,P} [1 - \exp(-\zeta_P t)] \quad (7.37)$$

The resulting parameter estimates are provided in Table 7.4 below.

Table 7.9 Values of the model estimate in Equation (7.37)

Pressure (atm)	$\varepsilon_{D_0,P}$	$\varepsilon_{D_1,P}$	ζ_P
1	0.0533±0.0008	0.0682±0.0010	0.1712±0.0026
11	0.0641±0.0013	0.0567±0.0011	0.2129±0.0043
21	0.0673±0.0035	0.0510±0.0026	0.4068±0.0209

Consistent with earlier findings (cf. Figure 7.18) on the relatively mild influence of pressure (compared to temperature) on dispersed phase hold-up, the results here reinforce the modest role of operating pressure on gas hold-up during reaction. Even so, there is a discernible trend in the values of the model parameters with increased pressure.

These estimates revealed that for any carbon number, olefin has a shorter relaxation surface time constant than paraffin indicating that it is more reactive and serves as the precursor to paraffin. Additionally, the relationship between τ_P and carbon number, n , for both homologous series seemed to be adequately captured by;

$$\tau_P = \phi n^\xi \quad (7.38)$$

with the pair ϕ and ξ as 0.91 and 0.95 for paraffins and 0.20 and 1.47 for olefins. The power-law dependency of the relaxation time constant on carbon chain length is consistent with the polymerization nature of the FT reaction [20].

The associated chain growth probability with time-on-stream is also shown in Figure 7.27. The data suggests an initial regime (within the first 5 hours –Region I) where the chain growth factor increased linearly with TOS followed by a longer period of about 25 hours (Region II) during which α_{FT} was essentially constant and a final stage (Region III) where another linear increase with TOS was experienced. However, the chain growth factor was somewhat insensitive to temperature. This behaviour has also been observed in previous studies [3, 24]. In particular, the relation between α_{FT} and temperature, T may be written as;

$$\alpha_{FT} = \frac{r_p}{r_p + r_t} = \frac{A_p f_p \exp(-E_p / RT)}{A_p f_p \exp(-E_p / RT) + A_t f_t \exp(-E_t / RT)} \quad (7.39)$$

$$= \frac{1}{1 + \frac{A_t f_t}{A_p f_p} \exp\{-(E_t - E_p) / RT\}}$$

where both A_p and A_t are the propagation and termination rate frequency factors respectively with f_p and f_t as associated functions of feed composition i.e. H_2 and CO partial pressures for the propagation and termination steps respectively. It is apparent that for a given composition, the variation of α with increasing temperature may either show a decreasing ($E_t > E_p$) or increasing ($E_t < E_p$) trend or be somewhat insensitive or even diffused depending on the relative magnitude of E_p and E_t and the ratio $\frac{A_t f_t}{A_p f_p}$. This explains the reason of different effects of

temperature has been reported in the literature [25]. These changes implicate an ongoing interaction between the physicochemical properties of the reaction medium and reaction metrics and hence, the transient behaviour observed in the dispersed phase hold-up as reaction progressed. While the initial rise in α value in Region I is a reflection of the intrinsic propagation step in hydrocarbon synthesis on the catalyst surface, the plateau in Region II suggests an equilibration between the liquid phase and the gas phase individual hydrocarbon composition. These two regimes parallel the behaviour seen in the dispersed phase

hold-up with time-on-stream. The trend seen in Region III may, however, be due to the production of hydrocarbons from the breakdown of waxy deposit (which had accumulated in the previous two regions). Although gas phase CO conversion would remain constant in this regime, hydrocarbon production would be a combination of the intrinsic FT propagation step as well as the cracking of waxy deposit on the catalyst surface and hence, a rejuvenative increase in α_{FT} -value. Intuitively, Region III itself would attain a new climax and then level off, although the 2-day run period was probably insufficient to realize this proposed stage. The dispersed phase hold-up would not be affected in Region III since the same hydrocarbon species were produced but only in greater amounts and hence, no discernible variation in the physicochemical properties of the liquid phase composition.

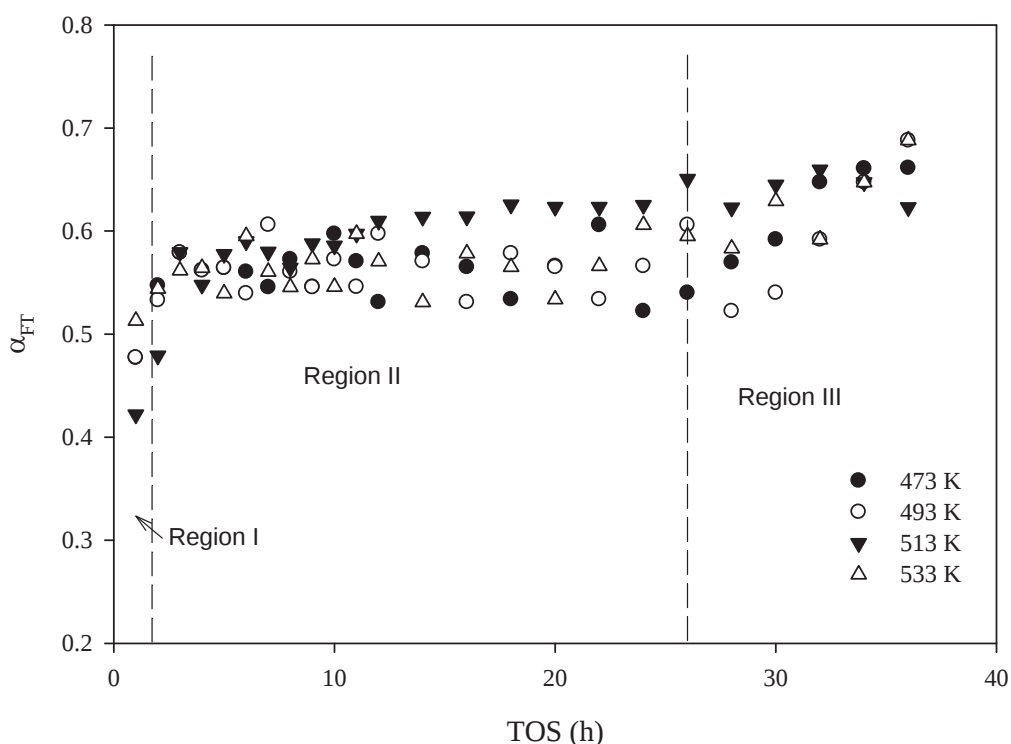


Figure 7.27 ASF chain growth factor as function of time-on-stream (TOS), P=21 atm

Figure 7.28 below indeed confirms that CO conversion also rose to a final steady-state value consistent with the individual hydrocarbon production history.

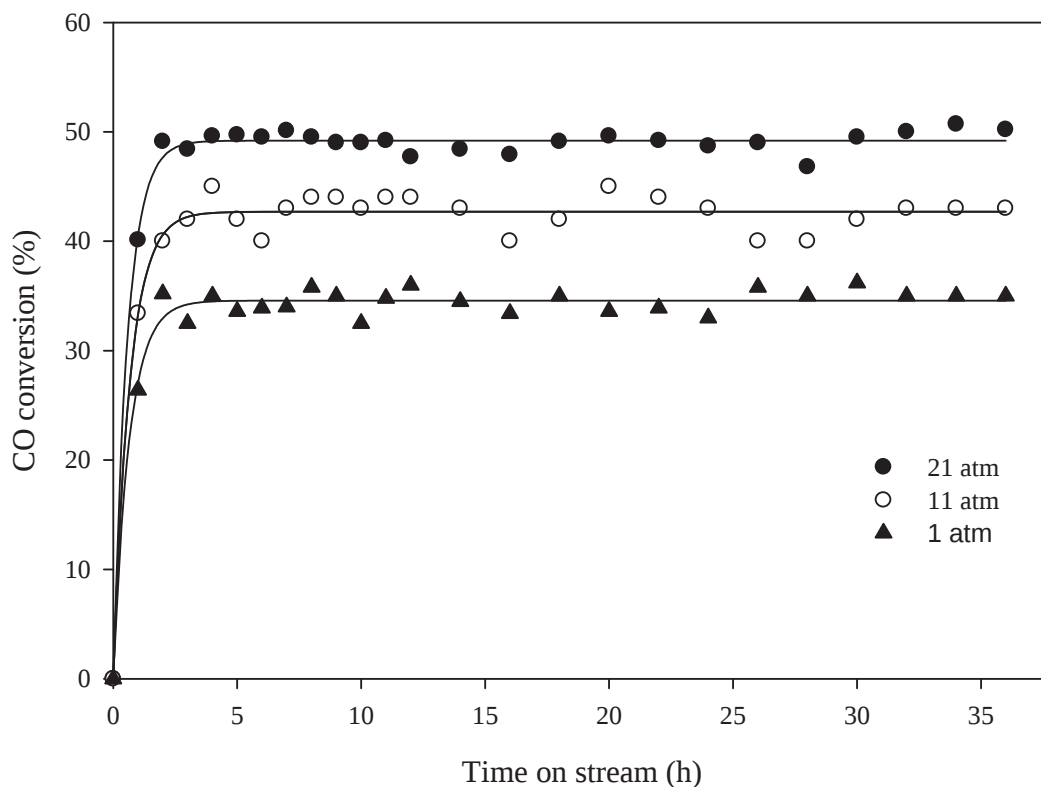


Figure 7.28 CO conversion history for FTS at $T = 498$ K, and syngas ratio $H_2:CO = 9:1$.

7.9. Conclusions

The non-invasive monitoring of an FTS slurry reactor using electrical capacitance tomography has shown that the multiphase hydrodynamic attributes such as dispersed phase hold-up (and by inference solid recirculation rate and distribution) are intimately intertwined with the reaction metrics (rate, product selectivity, etc). This coupling is due to the changing physicochemical properties of the liquid phase medium as product accumulation continues in the course of the reaction. This phenomenon is especially important in FTS operation since it can help to

unlock some of the peculiar reaction performance (evolution of chain growth factor, α_{FT}) observed over a long run time. This dynamic feedback between transport and reaction processes has not been previously unambiguously identified. However, the present analysis has provided, for the first time, a quantitative relation between reaction rate and dispersed phase hold-up. Furthermore, the data demonstrated that under non-isothermal conditions, changes in gas phase hold-up could not be accounted for by simple thermal expansion. Indeed, the sigmoid-shaped thermotemporal relationship for the dispersed phase hold-up in the slurry FT reactor was also derived and shown to be a combination of volumetric expansion and a reaction-controlled increment. Although the gas phase hold-up increased linearly with operating total pressure, the accompanying improvement was relatively small compared to thermal or reaction-induced effects. Analysis of the FT reaction rate data showed that the olefin-to-paraffin ratio, ROP, has a maximum at carbon number between 3 and 4. Moreover, ROP is also a strong function of the hydrogen composition in the feed mixture and this was confirmed by the dependency of the parameters of the proposed ROP model on feed $H_2:CO$ ratio. The approach taken in this study (tomographical analysis and empirical modelling) represents a new paradigm in the treatment of reaction rate data from a gas-solid-liquid reactor and over time, would help elucidate some of the apparent anomalous or pathological behaviour observed in slurry reactor systems. The ECT-based models developed may also be reliably employed for process simulation and optimization as well as providing additional insights into the fundamental nature of the reaction chemistry.

7.10. References

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8 ■ Conclusions and Recommendations

8.1. Conclusions

To a large extent, the objectives of this research project have been achieved. In short, the hydrodynamics and mass transfer study performed in a non-reactive multiphase gas-inducing stirred tank reactor (GIST) by changing various operating conditions demonstrated improved performance over the conventional gas-sparged stirred reactor, both economically and theoretically, using a non-intrusive tool i.e. ERT and ECT. In FT operation similar to industrial conditions, we successfully elucidated some of the peculiar reaction behaviour due to changing physicochemical properties of the liquid phase medium as product accumulation continues in the course of the reaction.

The following is a summary of conclusions which can be drawn from this study:

1. In gas-liquid systems, mixing intensity affects both the gas hold-up and mass transfer coefficient in stirred tank reactors. Gas hold-up and k_La achieved a sigmoidal increase with increasing Re_i .
2. The radial gas phase hold-up distribution was practically flat between $0 \leq r/R \leq 0.86$ at $Re_i = 4.2 \times 10^4$, while as expected, the gas phase hold-up plummeted to nearly zero value at the wall (behind the baffle) due to the formation of a relatively unperturbed liquid layer.
3. GIST shows an increase of 9% in mass transfer coefficient, k_La , as compared to the conventional gas-sparged system, indicating

efficient and sufficient mass transfer without need of external sources. In this regard, GIST is economically better than conventional systems.

4. Three distinct mixing regimes have been identified in GIST namely; laminar, transition and churn-turbulent, indicating the existence of a radial transport gradient within the vessel in gas-liquid systems.
5. The gas phase hold-up radial profiles in the gas-liquid system went through a minimum at the shaft ($r=0$) for $Re_l < 4.2 \times 10^4$ while the curves exhibited a maximum at the same location for $Re_l > 4.2 \times 10^4$.
6. Mean bubble size in GIST decreased gradually with Re_l .
7. From ERT data, gas phase hold-up is highly concentrated near the impeller zone which contrasts near the wall. It is expected that low gas hold-up was found behind the baffle due to the presence of the baffle itself as an obstacle for the gas bubbles to pass through. The existence of a boundary layer near the tank wall also may have contributed to low gas volume fraction in this region.
8. Favourable comparisons between CFD and tomographic data were established thus justifying the usefulness of an unsteady-state 3D CFD model for scale-up and optimization purposes, especially for industrial related applications.
9. In CFD, radial velocity profile shows a maximum at the centre ($r/R=0$), within the impeller region ($0 \leq r/R < 0.5$) and dropped rapidly towards the vessel wall.
10. CFD simulation confirmed the flow dynamics postulated in chapter 5.

11. The behaviour of gas dispersion in gas-liquid GIST was successfully modelled in CFD based on common Laguerre equation.
12. The switch from maximum to minimum radial gas phase hold-up profile ($600 \text{ RPM} < N_s < 800 \text{ RPM}$) at Ta exceeding 1700 suggests that gas flow in the liquid phase changed from predominantly laminar to axial flow. This indicated that vorticity in the gas-liquid system was responsible for the switch from a minimum to a maximum radial gas hold-up profile between 600 and 800 RPM.
13. Transient profiles for gas phase hold-up derived from CFD simulations can be adequately described by Laguerre's equation applied to dynamics of birth, growth, and death of bubble populations in the liquid phase.
14. Although the liquid phase was in turbulent flow ($Re_l > 10^4$), both gas and solid flows went through different hydrodynamic regimes and experienced radial hold-up gradients over the range of impeller speed employed.
15. The behaviour of solid phase hold-up for both solid loading and particle size can be explained using the Chapman-Richards model which reveals that the maximum solid hold-up (ε_{S1}) and particle clustering activity (ξ) are dependent on particle size and solid loading.
16. Again the behaviour of dispersed phase hold-up (mixture with solid and gas bubbles) can be explained using a 3-parameter model. This behaviour implicates a three-step system, namely; *birth* (bubbles and solid particles initiation into the liquid medium), *growth* (bubble-particle propagation and dispersion) and finally, *maturity* (attainment of maximum gas volume fraction and solid particles homogeneity).
17. The behaviour of solid phase hold-up exhibited a sigmoid-shape with respect to Re_l , suggesting three possible solid suspension

regimes, viz: off-bottom suspension, incomplete suspension, and homogenous (uniform) suspension.

18. The dispersed phase (solid and gas) hold-up profiles for the three-phase system were all characterised by a maximum at the centre ($r/R=0$).
19. Dispersed phase hold-up at $r/R=0$ increased with stirring speed suggesting the solid particles were concentrated in the impeller region irrespective of the impeller speed.
20. The degree of mixing, $1-\chi$, was strongly correlated to the impeller Reynolds number (Re_i). It confirmed the previous proposition that the hydrodynamic behaviour over the range of operating conditions traversed three regimes for solid phase hold-up.
21. Statistical treatment of the tomographical data also showed that regardless of particle size, uniform solid-liquid mixing was achieved at rotational speeds higher than 850 RPM ($Re_i > 1.5 \times 10^4$).
22. Based on the data analysis, the dispersed phase hold-up increased with size of alumina particle.
23. However, dimensionless particle time constant (τ_{spp}) and initial solid phase hold-up ($\varepsilon_{s,0}$) are found to be independent of particle size and stirring speed.
24. It appears that an incomplete solid suspension prevailed for $Re_i < 20800$ but not below N_{js} (≈ 52 RPM).
25. As Re_i increased beyond 20800, all alumina particles were displaced into the liquid phase with the extent of dispersion increasing with impeller speed.
26. A reasonably good agreement was found between the proposed correlations and the experimental data.
27. In the 3-phase system, $k_L a$ increased with stirring speed albeit the solid loading showed no improvement on $k_L a$ values.

28. It is revealed that at low concentration of solid particles, k_La value decreased less compared to high concentration. This suggests that the alumina particles act as an attenuating factor on k_La in the 3-phase system.
29. In the 3-phase system, gas-inducing impeller exhibits practical advantage over conventional stirrer at $Re_r > 9088$.
30. Empirical correlation of power consumption in the 3-phase system is proposed as a function of both stirring speed and solid loading.
31. The non-invasive monitoring of an FTS slurry reactor using ECT has shown that the multiphase hydrodynamic attributes such as dispersed phase hold-up (and by inference solid recirculation rate and distribution) are intimately intertwined with the reaction metrics (rate, product selectivity, etc)
32. This dynamic feedback between transport and reaction processes has not been previously unambiguously identified. However, the present analysis has provided, for the first time, a quantitative relation between reaction rate and dispersed phase hold-up.
33. The data demonstrated that under non-isothermal conditions, changes in gas phase hold-up could not be accounted for by simple thermal expansion. Indeed, the sigmoid-shaped thermo-temporal relationship for the dispersed phase hold-up in the slurry FT reactor was also derived and shown to be a combination of volumetric expansion and a reaction-controlled increment.
34. Although the gas phase hold-up increased linearly with operating total pressure, the accompanying improvement was relatively small compared to thermal or reaction-induced effects.
35. Analysis of the FT reaction rate data showed that the olefin-to-paraffin ratio, ROP, has a maximum at carbon number between 3 and 4.

36. ROP exhibits a strong correlation with the hydrogen composition in the feed mixture and this was confirmed by the dependency of the parameters of the proposed ROP model on feed H₂:CO ratio.
37. The approach taken in this study (tomographical analysis and empirical modelling) represents a new paradigm in the treatment of reaction rate data from a gas-solid-liquid reactor and over time, could help elucidate some of the apparent anomalous or pathological behaviour observed in slurry reactor systems.

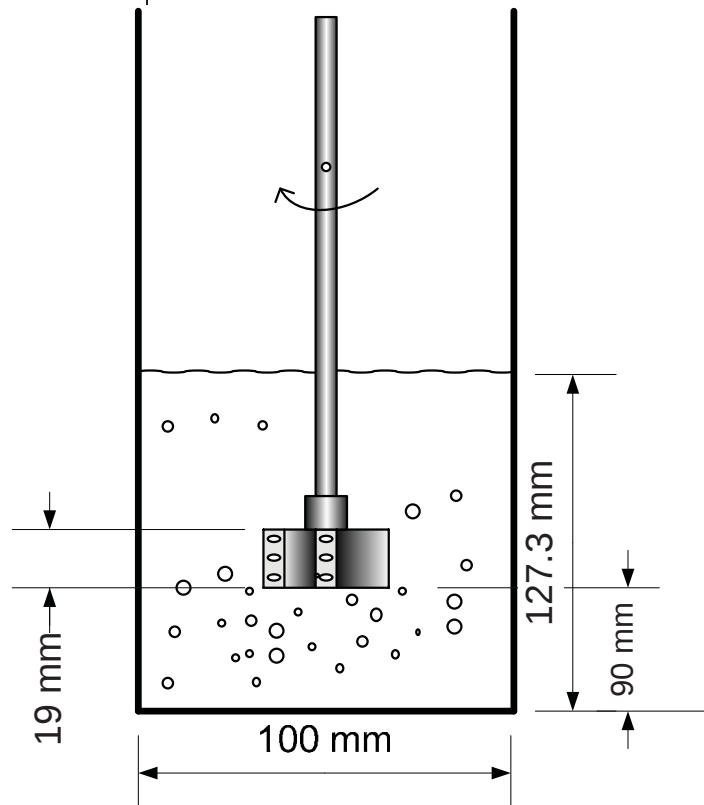
8.2. Recommendations

Although this study has achieved most of the objectives set in the Introduction chapter, the results and discussion presented are by no means comprehensive. The following are recommendations for further investigation:

1. In this study, one design of gas-inducing impeller was extensively investigated. Different designs of gas-inducing impeller would possibly behave differently.
2. The mechanism of mass transfer study in reactive systems such as Fischer-Tropsch synthesis is not well established in gas-inducing stirred tank reactors. Thus, a study needs to be carried out to determine the mechanism in a stirred slurry FT reactor, in particular a reactor equipped with gas-inducing impeller.
3. Different solid particles such as zirconia, magnesia, and titania would be likely to behave differently to alumina in terms of hydrodynamics and mass transfer as they belong to different class of groups in periodic table of elements.
4. Hydrodynamics study of the 3-phase system in GIST should be extended using CFD.

Appendix 1

Calculation on Critical Impeller Speed, N_{cs}



Based on N_{cs} proposed by Sawant and Joshi [1], and given as,

$$\frac{N_{cs}^2 D_I^2}{gh} \left(\frac{\mu}{\mu_w} \right)^{-0.11} = 0.21 \quad (\text{A1.40})$$

where, h is the impeller submersion depth, D_I = impeller diameter, μ is the liquid phase viscosity, μ_{water} is the water viscosity while g is the

acceleration due to gravity. For the present stirred tank arrangement, $h = 18.3$ mm, $D_I = 50$ mm and the liquid phase was water, $\mu/\mu_{water} = 1$, Equation (A1.1) yields,

$$N_{sc} = \frac{\sqrt{0.21gh}}{D_I} \quad (A1.2)$$

From our system, $h=18.3$ mm, $g=9810$ mm s⁻² and substitute into Equation (A1.2),

$$N_{sc} = \frac{\sqrt{0.21 \times 9180 \times 18.3}}{50}$$

$$N_{cs} = 3.883 \text{ s}^{-1}$$

$$= 233 \text{ RPM}$$

However, this N_{sc} only valid if speed loss coefficient lie between 0 and 1 ($0 < K < 1$). In order to prove this, Bernoulli equation is used as a basis given as;

$$gh + \frac{P_2}{\rho_L} = \frac{P_2}{\rho_L} + \frac{u_1^2}{2} + gh_{f1} \quad (A1.3)$$

where, u is a relative velocity between gas outlet and the liquid and given as $u = \pi D_I N_s K$.

where,

N_s = impeller stirring speed (rps)

K = impeller speed loss coefficient

h_{f1} = energy loss in the turbulent field

D_I = the impeller diameter at gas outlet orifices

Thus,

Rearrange equation (A1.3), yields

$$\frac{P_2 - P_1}{\rho_L} = \frac{1}{2}(\pi D_i N K)^2 + h_{f1} - gh \quad (A1.4)$$

For gas to flow from the headspace to the liquid at the gas outlet orifice, $P_2 - P_1 \geq 0$, thus at critical impeller speed, $N_s = N_{cs}$, thus $P_2 = P_1$ and equation (A1.4) becomes;

$$N_{cs} = \frac{\sqrt{2(gh - h_{f1})}}{\pi D_i K} \quad (A1.5)$$

In the case of turbulent flow, $h_{f1} \leq gh$. Thus, $gh - h_{f1} \approx gh$. Therefore, Equation (A1.5) reduced to,

$$N_{cs} = \frac{\sqrt{2gh}}{\pi D_i K} \quad (A1.6)$$

We can estimate the impeller speed loss coefficient as

$$K = \frac{\sqrt{2gh}}{\pi D_i N_{cs}} \quad (A1.7)$$

In our cases,

$K=0.98$, Thus confirming $0 < K < 1$.

Reference

1. Sawant, S.B. and J.B. Joshi, *Critical impeller speed for the onset of gas induction in gas-inducing types of agitated contactors*. The Chemical Engineering Journal, 1979. **18**(1): p. 87-91.

Appendix 2

Rate of Gas Induction

Based on Bernoulli equation,

$$\frac{P_1}{\rho} + \frac{u_1^2}{2} + gh_1 = \frac{P_2}{\rho} + \frac{u_2^2}{2} + gh \quad (\text{A2.41})$$

where,

P_1, P_2 = pressure at location 1 and 2

u_1, u_2 = fluid velocity at location 1 and 2

h_1, h_2 = static head at location 1 and 2

ρ = density of the dispersed phase, in this case the gas phase

g = gravitational acceleration (9.81 m s^{-1})

In agitated tank reactor, the rate gas induction can be estimated once the N_{CS} is attained, thus the Bernoulli equation becomes;

$$\frac{P_1}{\rho_G} + \frac{1}{2} \left(\frac{Q_G}{A_{\text{orifice}}} \right)^2 + gh_{f2} = \frac{P_2}{\rho_G} \quad (\text{A2.2})$$

where,

Q_G = gas volumetric flowrate

A_{orifice} = gas outlet orifice area

ρ_G = gas phase density

h_{f2} = energy loss during gas flow through the impeller shaft
from inlet to exit

Substitute Equation (A2.2) into (A2.1), yields;

$$Q_G = 2A_{orifice}^2 \left(\frac{P_2 - P_1}{\rho_G} - h_{f2} \right) \quad (A2.3)$$

Where $P_2 - P_1$ can be known from Equation (A1.4) from appendix 1 and replace the liquid density, ρ_L , by the density of the 2-phase mixture, ρ_M , as

$$\rho_M = (1 - \varepsilon_G) \rho_L + \varepsilon_G \rho_G \quad (A2.4)$$

Substituting Equations (A1.4) and (A2.4) into equation (A2.3) gives,

$$Q_G = A_{orifice} \sqrt{\left[\frac{\rho_L (1 - \varepsilon_G)}{\rho_G} + \varepsilon_G \right]} \left[(\pi D_i N_s K)^2 + 2h_{f1} - 2gh \right] - 2hf_2 \quad (A2.5)$$

Neglecting h_{f1} and h_{f2} for turbulent flow,

Equation (A2.5) becomes,

$$Q_G = A_{orifice} \sqrt{\left[\frac{\rho_L (1 - \varepsilon_G)}{\rho_G} + \varepsilon_G \right]} \left[(\pi D_i N_s K)^2 - 2gh \right] \quad (A2.6)$$

For our experimental conditions,

$$\rho_L = 998.1 \text{ kgm}^{-3}$$

$$\rho_G = 1.2 \text{ kgm}^{-3}$$

$$A_{orifice} = 7.917 \times 10^{-6} \text{ m}^2$$

$$\rho_L / \rho_G = 832$$

Thus, estimates of Q_G are tabulated in Table A2.1 below

Table A2.1 Values of gas volumetric flowrate based on Equation (A2.6)

$N_s(\text{rpm})$	$N_s(\text{rps})$	ε_G	$Q_s \times 10^4 \text{ m}^3 \text{ s}^{-1}$	Re_G
			1	
400	6.67	0.0275	1.89	132.5

600	10.00	0.05	3.17	222.5
800	13.33	0.05	4.38	307.9
1000	16.67	0.055	5.56	390.4
1200	20.00	0.07	6.67	468.7

Appendix 3

ITS M3000-ERT System Specification

This Appendix provides the specifications for the M3000-ERT system as detailed in the ITS Manual [1].

Parameter	Specification
Number of electrodes	16
Current injection method	Normal adjacent
Image reconstruction algorithm	Linear back projection
Property of interest	conductivity
Microcontroller	DSP microcomputer ADSP-2181 with 3 operations per cycle

Clock speed	33 MHz
Memory	1MB EPROM, 80K bytes of on-chip RAM
Sinewave generator	DDS AD7008 with 32bit in zero order hold staircase wave
Oscillator	20 MHz
ADC frequency	1 MHz
Current injection frequency	Programmable up to 15kHz (normal in 10kHz)
Injecting current	Up to 40mA(ad-ad)
Measurement range	-10 V (pp) to +10 V (pp)
Sensitivity	2 x 4.88 uV @ gain ×1000
CMRR	> -70 db @ 53.6 kHz
Measurement Accuracy	± 1% (@10 kHz)
Mode of measurement	Sequential

Type of demodulation	Phase sensitive demodulation
Phase shift compensation	0.7° to 180°
Communication interface	USB 2.0
Power consumption	DC 24 V 60W (power adapter output o DAS, +5V, +15V, -15V)
Power input from mains supply	100-240 V a/c, 50/60 Hz 1.5A

Reference

1. Industrial Tomography Systems, *M 3000 Multi-modal Tomography System* v2.9. 2007, Industrial Tomography Systems Ltd.: Manchester, UK.

Appendix 4

ITS M3000-ECT System Specification

This Appendix provides the specifications for the M3000-ECT system as detailed in the ITS Manual [1].

Parameter	Specification
Number of electrodes	12
Current injection method	Normal adjacent
Image reconstruction algorithm	Linear back projection
Property of interest	Permittivity (ϵ)
Microcontroller	DSP microcomputer ADSP-2181 with 3 operations per cycle
Clock speed	33 MHz

Memory	1MB EPROM, 80K bytes of on-chip RAM
Sinewave generator	DDS AD7008 with 32bit in zero order hold staircase wave
Oscillator	50 MHz
ADC frequency	1 MHz
Current injection frequency	Programmable up to 15kHz (normal in 10kHz)
Injecting voltage	18 V (peak-peak)
Measurement range	0.001 +10 V (pp) with 80mV increment
Sensitivity	0.81 V/pF @ 5 fF change of 4.05mV
CMRR	> -120 db @ 1 MHz
Relative Accuracy measurement range	≈ 0.01-1 pF with one plane sensor
Signal to noise ratio (SNR)	56 dB
Mode of measurement	Sequential

Measurement stability at V_{output}	+/- 0.6mV
Type of demodulation	Phase sensitive demodulation
Speed of acquisition for one frame	20 mS/F (digital demodulation @ 500 kHz for 12 electrodes)**
Phase shift compensation	0° to 360° with 0.09° resolution
Communication interface	USB 2.0
Power consumption	DC 24 V 70W (power adapter output into DAS, +5V, +15V, -15V)
Power input from mains supply	100-240 V a/c, 50/60 Hz 1.5A

** Based on theoretical calculation on 100 uS transient time of the capacitance measurement circuits

References

1. Industrial Tomography Systems, *M 3000 Multi-modal Tomography System* v2.9. 2007, Industrial Tomography Systems Ltd.: Manchester, UK.

Appendix 5 Catalyst Preparation Calculation

Cobalt supported alumina catalyst was prepared using wet impregnation technique. Mettler-Toledo T90 titration system was used to ensure the homogeneity of slurry during catalyst preparation. The actual mass of the metal and amount of precursor needed are calculated as follows;

$$m_i = m_{cat} f_i \quad (A5.42)$$

and

$$m_{i,p} = m_i \frac{MW_{i,p}}{MW_i n_{i,m-p}} \quad (A5.43)$$

where,

m_i = actual mass of the metal i .

m_{cat} = total mass of catalyst

f_i = desired fraction (wt/wt) of active metal i in catalyst sample

$m_{i,p}$ = actual mass of precursor compound for metal i to be added

MW_i = molecular mass of metal i

$MW_{i,p}$ = molecular mass precursor for metal i

$n_{i,m-p}$ = number of atoms of metal i in the precursor compound

The precursor used for Co was Cobalt nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Table A5.1 summarises the molecular mass of Cobalt and its precursor. While, Table A5.2 tabulates the mass of precursor for Cobalt catalyst formulation in preparing 10 g of catalyst sample (10wt%Co/ Al_2O_3).

Table A5.8.1 Molecular mass Co and its precursor

Species	Molecular mass, MW_i (g mol^{-1})
Co	58.9322
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	291.0348

Table A5.8.2 Precursor loading for preparing 10 g of catalyst sample (metal-only basis)

Catalyst	Metal	f_i	m_i (g)	$m_{i,p}$ (g)
10Co	Co	0.1	1.0	4.9384

Appendix 6

Selected Experimental Results

A6.1 Hydrodynamics study

Table A6.1.1 Global gas-phase hold-up in gas-inducing stirred tank reactor

Stirring speed (rpm)	Re_i 10^{-4}	α 0 gL ⁻¹	10 gL ⁻¹	20 gL ⁻¹	30 gL ⁻¹	40 gL ⁻¹
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
200	1.0417	0.0000	0.0150	0.0159	0.0140	0.0198
400	2.0833	0.0276	0.0460	0.0569	0.0646	0.0765
600	3.1250	0.0487	0.0671	0.0780	0.0859	0.1011
800	4.1667	0.0505	0.0809	0.0943	0.1013	0.1191

1000	5.2083	0.0553	0.0887	0.1086	0.1165	0.1290
1200	6.2500	0.0672	0.0976	0.1145	0.1272	0.1469

TableA6.1.2 Radial distribution of gas phase hold-up without any alumina present

Radial position (r/R)	50 rpm	200 rpm	400 rpm	600 rpm	800 rpm	1000 rpm	1200 rpm
-0.9564	0.0000	0.0000	0.0097	0.0159	0.0160	0.0245	0.0281
-0.8647	0.0000	0.0000	0.0265	0.0353	0.0314	0.0445	0.0547
-0.7618	0.0000	0.0000	0.0252	0.0337	0.0316	0.0458	0.0574
-0.6422	0.0000	0.0000	0.0253	0.0359	0.0338	0.0477	0.0626
-0.4928	0.0000	0.0000	0.0221	0.0333	0.0351	0.0504	0.0701
-0.2464	0.0000	0.0000	0.0115	0.0272	0.0357	0.0550	0.0823
0.2464	0.0000	0.0000	0.0115	0.0272	0.0357	0.0550	0.0823
0.4928	0.0000	0.0000	0.0221	0.0333	0.0351	0.0504	0.0701
0.6422	0.0000	0.0000	0.0253	0.0359	0.0338	0.0477	0.0626

0.7618	0.0000	0.0000	0.0252	0.0337	0.0316	0.0458	0.0574
0.8647	0.0000	0.0000	0.0265	0.0353	0.0314	0.0445	0.0547
0.9564	0.0000	0.0000	0.0097	0.0159	0.0160	0.0245	0.0281

Table A6.1.3 Radial distribution of dispersed phase hold-up at 10 gL⁻¹

Radial position (r/R)	400 rpm	600 rpm	800 rpm	1000 rpm	1200 rpm
-0.9564	0.0221	0.0378	0.0479	0.0583	0.0628
-0.8647	0.0289	0.0479	0.0558	0.0686	0.0794
-0.7618	0.0321	0.0512	0.0593	0.0759	0.0872
-0.6422	0.0393	0.0591	0.0681	0.0825	0.0964
-0.4928	0.0447	0.0651	0.0739	0.0925	0.1100
-0.2464	0.0495	0.0703	0.0889	0.1013	0.1309

0.2464	0.0495	0.0703	0.0889	0.1013	0.1309
0.4928	0.0447	0.0651	0.0739	0.0925	0.1100
0.6422	0.0393	0.0591	0.0681	0.0825	0.0964
0.7618	0.0321	0.0512	0.0593	0.0759	0.0872
0.8647	0.0289	0.0479	0.0558	0.0686	0.0794
0.9564	0.0221	0.0378	0.0479	0.0583	0.0628

Table A6.1.4 Radial distribution of dispersed phase hold-up at 20 gL⁻¹

Radial position (r/R)	400 rpm	600 rpm	800 rpm	1000 rpm	1200 rpm
-0.9564	0.032646	0.04986	0.065913	0.078071	0.082473
-0.8647	0.034521	0.054376	0.070273	0.08285	0.094219
-0.7618	0.035254	0.069726	0.082796	0.098101	0.109699

-0.6422	0.038642	0.07859	0.098917	0.11203	0.128089
-0.4928	0.04204	0.089154	0.109809	0.123817	0.143327
-0.2464	0.04831	0.098301	0.12314	0.142033	0.169802
0.2464	0.04831	0.098301	0.12314	0.142033	0.169802
0.4928	0.04204	0.089154	0.109809	0.123817	0.143327
0.6422	0.038642	0.07859	0.098917	0.11203	0.128089
0.7618	0.035254	0.069726	0.082796	0.098101	0.109699
0.8647	0.034521	0.054376	0.070273	0.08285	0.094219
0.9564	0.032646	0.04986	0.065913	0.078071	0.082473

Table A6.1.5 Radial distribution of dispersed phase hold-up at 30 gL⁻¹

Radial position (r/R)	400 rpm	600 rpm	800 rpm	1000 rpm	1200 rpm
-0.9564	0.039265	0.078093	0.085928	0.094096	0.098101

-0.8647	0.042521	0.080755	0.090128	0.103599	0.114713
-0.7618	0.043525	0.082901	0.094843	0.110203	0.121834
-0.6422	0.048642	0.090286	0.101975	0.117085	0.131906
-0.4928	0.05204	0.093243	0.113128	0.1297	0.14925
-0.2464	0.05831	0.102329	0.132158	0.151801	0.17922
0.2464	0.05831	0.102329	0.132158	0.151801	0.17922
0.4928	0.05204	0.093243	0.113128	0.1297	0.14925
0.6422	0.048642	0.090286	0.101975	0.117085	0.131906
0.7618	0.043525	0.082901	0.094843	0.110203	0.121834
0.8647	0.042521	0.080755	0.090128	0.103599	0.114713
0.9564	0.039265	0.078093	0.085928	0.094096	0.098101

Table A6.1.6 Radial distribution of dispersed phase hold-up at 40 gL⁻¹

Radial	400 rpm	600 rpm	800 rpm	1000 rpm	1200 rpm
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position					
(r/R)					
-0.9564	0.040826	0.089303	0.111659	0.120157	0.123237
-0.8647	0.042515	0.095103	0.117088	0.131655	0.141978
-0.7618	0.045353	0.103127	0.127294	0.141519	0.153486
-0.6422	0.049686	0.113127	0.142775	0.156289	0.172928
-0.4928	0.05202	0.123276	0.152859	0.168003	0.18709
-0.2464	0.060983	0.137813	0.173591	0.193826	0.22141
0.2464	0.060983	0.137813	0.173591	0.193826	0.22141
0.4928	0.05202	0.123276	0.152859	0.168003	0.18709
0.6422	0.049686	0.113127	0.142775	0.156289	0.172928
0.7618	0.045353	0.103127	0.127294	0.141519	0.153486
0.8647	0.042515	0.095103	0.117088	0.131655	0.141978

0.9564	0.040826	0.089303	0.111659	0.120157	0.123237
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Table A6.1.7 Radial distribution of solid phase hold-up at 10 gL⁻¹

Radial position (r/R)	400 rpm	600 rpm	800 rpm	1000 rpm	1200 rpm
-0.9564	0.01239	0.02242	0.0342	0.03387	0.03459
-0.8647	0.00240	0.0126	0.0144	0.0134	0.0248
-0.7618	0.00698	0.0175	0.0277	0.0300	0.0297
-0.6422	0.0140	0.0232	0.0343	0.0348	0.0338
-0.4928	0.0226	0.0318	0.0388	0.0421	0.0400
-0.2464	0.0339	0.0426	0.0538	0.0538	0.0537
0.2464	0.0339	0.0426	0.0538	0.0538	0.0537
0.4928	0.0226	0.0318	0.0388	0.0421	0.0400
0.6422	0.0140	0.0232	0.0343	0.0348	0.0338
0.7618	0.00240	0.0175	0.0277	0.0300	0.0297

0.8647	0.00698	0.0126	0.0244	0.0241	0.0248
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0.9564	0.01239	0.02242	0.0342	0.03387	0.03459
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Table A6.1.8 Radial distribution of solid phase hold-up at 20 gL⁻¹

Radial position (r/R)	400 rpm	600 rpm	800 rpm	1000 rpm	1200 rpm
-0.9564	0.022935	0.033964	0.05399	0.053537	0.054354
-0.8647	0.00803	0.0191	0.0389	0.0383	0.0395
-0.7618	0.0101	0.0360	0.0512	0.0523	0.0523
-0.6422	0.0134	0.0427	0.0651	0.0644	0.0655
-0.4928	0.0199	0.0559	0.0748	0.0734	0.0733
-0.2464	0.0313	0.0637	0.0840	0.0840	0.0840
0.2464	0.0313	0.0637	0.0840	0.0840	0.0840
0.4928	0.0199	0.0559	0.0748	0.0734	0.0733
0.6422	0.0134	0.0427	0.0651	0.0644	0.0655
0.7618	0.0101	0.0360	0.0512	0.0523	0.0523
0.8647	0.00803	0.0191	0.0389	0.0383	0.0395
0.9564	0.022935	0.033964	0.05399	0.053537	0.054354

Table A6.1.9 Radial distribution of solid phase hold-up at 30 gL⁻¹

Radial position (r/R)	400 rpm	600 rpm	800 rpm	1000 rpm	1200 rpm
-0.9564	0.24683	0.25591	0.26365	0.271043	0.27521
-0.8647	0.0160	0.0455	0.0588	0.0591	0.0600
-0.7618	0.0184	0.0492	0.0632	0.0644	0.0644
-0.6422	0.0234	0.0544	0.0682	0.0694	0.0693
-0.4928	0.0299	0.0600	0.0781	0.0793	0.0792
-0.2464	0.0407	0.0715	0.0926	0.0927	0.0927
0.2464	0.0407	0.0715	0.0926	0.0927	0.0927
0.4928	0.0299	0.0600	0.0781	0.0793	0.0792
0.6422	0.0234	0.0544	0.0682	0.0694	0.0693
0.7618	0.0184	0.0492	0.0632	0.0644	0.0644
0.8647	0.0160	0.0455	0.0588	0.0591	0.0600
0.9564	0.24683	0.25591	0.26365	0.271043	0.27521

Table A6.1.10 Radial distribution of solid phase hold-up at 40 gL⁻¹

Radial position (r/R)	400 rpm	600 rpm	800 rpm	1000 rpm	1200 rpm
-0.9564	0.0291	0.07341	0.09868	0.09810	0.09928
-0.8647	0.0160	0.0598	0.0857	0.0872	0.0873
-0.7618	0.0202	0.0694	0.0957	0.0957	0.0961
-0.6422	0.0244	0.0773	0.1090	0.1086	0.1103
-0.4928	0.0299	0.0900	0.1178	0.1176	0.1170
-0.2464	0.0395	0.0981	0.1338	0.1339	0.1339
0.2464	0.0395	0.0981	0.1338	0.1339	0.1339
0.4928	0.0299	0.0900	0.1178	0.1176	0.1170
0.6422	0.0244	0.0773	0.1090	0.1086	0.1103
0.7618	0.0202	0.0694	0.0957	0.0957	0.0961
0.8647	0.0160	0.0598	0.0857	0.0872	0.0873
0.9564	0.0291	0.07341	0.09868	0.09810	0.09928

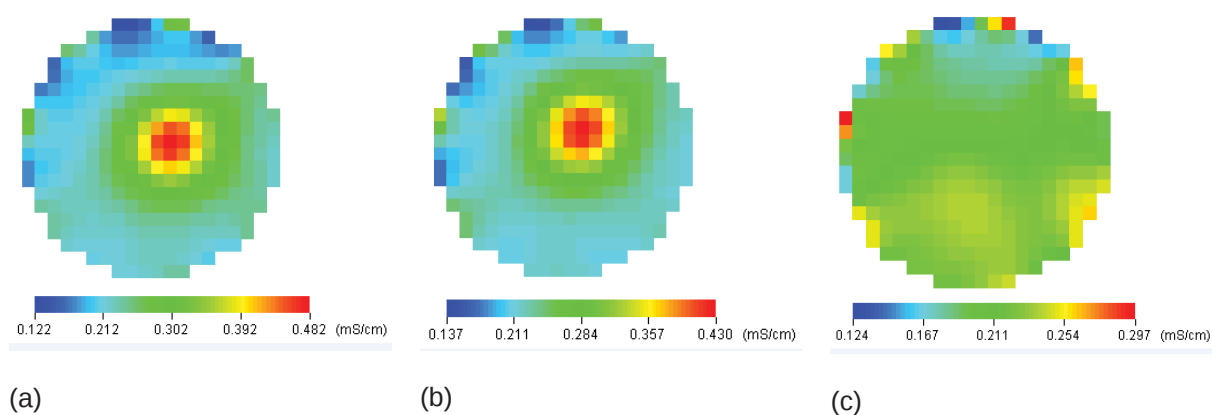


Figure A6.1: ERT tomograms at various impeller positions with stirring speed of 400 rpm (a) 30 mm (b) 60 mm (c) 90 mm from the bottom of the stirred vessel

It is evident that an axial impeller location of 90 mm from the bottom, gave negligible effect on the electrical field caused by stainless steel shaft and brass impeller blade. The red colour signifies the presence of high conductivity material in stirred tank reactor.

Table A6.1.11 The dispersed phase hold-up for gas and non gas inducing impeller at different catalyst loading

Catalyst loading (g L ⁻¹)	Non-gas inducing impeller	Gas inducing impeller
0	0	0
2	0.0107	0.0185
4	0.0301	0.0374
6	0.0480	0.0588
8	0.0734	0.0826

10	0.0913	0.1045
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A6.2 Mass Transfer Study

Table A6.2.1 Mean bubble size as function of stirring speed for case a-c

Stirring speed (rpm)	$Re_i \times 10^{-4}$	Case (mm)	a Case (mm)	b Case c (mm)
0	0.0000	2.8093	-	2.8186
200	1.0417	2.7886	-	2.7514
400	2.0833	2.3064	2.6079	2.7250
600	3.1250	2.2829	2.2543	2.1955
800	4.1667	2.2279	2.1264	1.8964
1000	5.2083	1.9779	2.0057	1.6943
1200	6.2500	2.0014	1.8664	1.7057

Note: Gas inducing impeller starts dispersed gas at $Re_i > 200$ rpm

Table A6.2.2 Degree of gas mixing ($1-\sigma$) as function of Re_i for case a-c

Stirring speed (rpm)	$Re_i \times 10^{-4}$	Case a (dimensionless)	Case b (dimensionless)	Case c (dimensionless)
0	0.0000	0.0000	-	0.0110
200	1.0417	0.0890	-	0.2004
400	2.0833	0.3339	0.2736	0.5520

600	3.1250	0.7135	0.6740	0.7451
800	4.1667	0.8373	0.7903	0.8380
1000	5.2083	0.8627	0.8253	0.8035
1200	6.2500	0.9098	0.8731	0.8609

Table A6.2.3 Sauter mean bubble size as function of Re_l for case a-c

Stirring speed (rpm)	$Re_l \times 10^{-4}$	Case a (mm)	Case b (mm)	Case c (mm)
0	0.0000	3.7938	-	3.6781
200	1.0417	3.8855	-	3.6555
400	2.0833	3.6129	3.7070	3.4136
600	3.1250	3.4036	3.5346	3.2333
800	4.1667	3.1840	3.3592	3.1457
1000	5.2083	3.2509	3.2458	3.0009
1200	6.2500	3.2438	3.2402	2.9916

Table A7.2.4 Sherwood number based on Sauter bubble diameter as function of Re_l

Stirring speed (rpm)	$Re_l \times 10^{-4}$	Case a	Case b	Case c
0	0.0000	0.0898	-	0.0844
200	1.0417	0.0942	-	0.0834
400	2.0833	0.0815	0.0858	0.0727

600	3.1250	0.0825	0.0780	0.0653
800	4.1667	0.0732	0.0704	0.0618
1000	5.2083	0.0660	0.0658	0.0562
1200	6.2500	0.0657	0.0655	0.0559

Table A6.2.5 Specific interfacial area as function of Re_i

Stirring speed (rpm)	$Re_i \times 10^{-4}$	Case a (m^{-1})	Case b (m^{-1})	Case c (m^{-1})
0	0.0000	0.9489	-	0.4894
200	1.0417	2.3163	-	1.9696
400	2.0833	9.6776	12.7865	50.9731
600	3.1250	52.5332	51.6036	90.9297
800	4.1667	76.7166	160.7512	259.2094
1000	5.2083	102.6166	345.6746	434.0707
1200	6.2500	101.3426	370.3426	459.0288

Table A6.2.6 Volumetric mass transfer coefficient ($k_L a$) as function of Re_i

Stirring speed (rpm)	$Re_i \times 10^{-4}$	Case a (s^{-1})	Case b (s^{-1})	Case c (s^{-1})
0	0.0000	6.0000E-4	3.0000E-4	3.0000E-4
200	1.0417	1.0000E-3	2.0000E-4	2.0000E-4
400	2.0833	1.2000E-3	5.0000E-4	5.0000E-4

600	3.1250	1.3570E-3	1.5000E-3	6.0000E-4
800	4.1667	1.5000E-3	1.5000E-3	1.2000E-3
1000	5.2083	5.2000E-3	7.9000E-3	0.0290
1200	6.2500	0.0340	0.0304	0.0490

Table A6.2.7 Liquid side mass transfer coefficient (k_L) as function of Re_l

Stirring speed (rpm)	$Re_l \times 10^{-4}$	Case a ($\times 10^4 \text{ m s}^{-1}$)	Case b ($\times 10^4 \text{ m s}^{-1}$)	Case c ($\times 10^4 \text{ m s}^{-1}$)
0	0.0000	6.3230	-	6.1302
200	1.0417	6.4758	-	6.0925
400	2.0833	5.3732	6.1784	5.6893
600	3.1250	6.4721	5.8911	5.3888
800	4.1667	6.1408	5.5987	5.2429
1000	5.2083	5.4182	5.4097	5.0015
1200	6.2500	5.4064	5.4004	4.9860

A6.3 Fischer-Tropsch reaction study

Table A6.3.1 The reaction rate for 10%Co at 523 K for different total pressure (atm)

y_{H_2}	Reaction rate for product carbon number $\times 10^7$ $\text{mol g}_{\text{cat}}^{-1}\text{s}^{-1}$		
	1 atm	11 atm	21 atm
0.00	0.00	0.00	0.00
0.20	0.11	0.75	1.00
0.40	0.35	1.74	2.69
0.67	0.46	3.02	4.26
0.80	1.27	6.12	9.43
0.90	2.74	9.72	20.85
1.00	0.00	0.00	0.00

Table A6.3.2 ROP as function of feed composition, y_{H_2} at different carbon number

Feed composition, y_{H_2}	Carbon number, n				
	C2	C3	C4	C5	C6
0.2	4.5780	6.8717	5.4906	2.5893	1.9240
0.4	3.0780	5.3717	4.0600	1.9900	1.4240
0.67	1.3490	3.7375	1.9000	2.0500	1.1899
0.8	0.8490	3.0000	1.6400	1.7177	0.7800
0.9	0.1577	1.6124	0.8505	1.1515	0.6059

Table A6.3.3 Normalised transient reaction rate for paraffins (T = 498 K, and 21 atm, $y_{H_2}=0.9$)

Time (h)	Normalised reaction rate, $r_n/r_{n,max}$ (dimensionless)					
	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1	0.6140	0.4719	0.5445	0.2196	0.2323	0.2917
2	0.8300	0.8222	0.7920	0.7200	0.3847	0.5711
3	0.9340	0.9130	0.8800	0.8220	0.4511	0.6860
4	0.9560	0.9290	0.8980	0.8600	0.4851	0.7430
5	0.9620	0.9415	0.9048	0.8580	0.5890	0.7740
6	0.9740	0.9483	0.9181	0.8700	0.6420	0.7861
7	0.9820	0.9626	0.9286	0.8880	0.6880	0.8220
8	0.9950	0.9630	0.9344	0.9123	0.7430	0.8450

9	0.9960	0.9690	0.9410	0.8864	0.7790	0.8660
10	0.9970	0.9629	0.9387	0.9047	0.7923	0.8581
11	0.9900	0.9870	0.9510	0.9110	0.8450	0.8830
12	0.9900	0.9820	0.9600	0.9410	0.8880	0.9230
14	0.9900	1.0000	0.9800	0.9980	0.9700	0.9900
16	0.9980	0.9980	0.9690	0.9490	0.9770	0.9690
18	0.9900	0.9980	0.9790	0.9640	0.9980	0.9980
20	0.9900	0.9980	0.9980	0.9980	0.9980	0.9980
22	0.9900	0.9980	0.9980	0.9980	0.9980	0.9980
24	0.9900	0.9980	0.9980	0.9980	0.9980	0.9980
26	0.9900	0.9980	0.9980	0.9980	0.9980	0.9980
28	0.9900	0.9980	0.9980	0.9980	0.9980	0.9980

30	0.9980	0.9900	1.0000	1.0000	1.0000	1.0000
32	0.9900	0.9980	0.9980	0.9980	0.9980	0.9655
34	0.9900	0.9676	0.9980	0.9980	0.9980	0.9905
36	0.9900	0.9980	0.9980	0.9690	0.9980	0.9980

Table A6.3.4 . Normalised transient reaction rate for olefins (T = 498 K, and 21 atm , $y_{H_2}=0.9$)

Time (h)	Normalised reaction rate, $r_n/r_{n,max}$ (dimensionless)				
	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}
0	0.0000	0.0000	0.0000	0.0000	0.0000
1	0.8847	0.5445	0.4697	0.2323	0.2917
2	0.9580	0.8099	0.7530	0.5990	0.5711
3	0.9700	0.9360	0.8680	0.8000	0.6860
4	0.9830	0.9630	0.9130	0.8780	0.8404
5	0.9850	0.9680	0.9260	0.8930	0.8730
6	0.9850	0.9750	0.9650	0.9310	0.9130
7	0.9800	0.9730	0.9800	0.9560	0.9410
8	0.9930	0.9900	0.9800	0.9800	0.9880

9	0.9880	0.9880	0.9800	0.9800	0.9930
10	0.9880	0.9900	0.9700	0.9800	1.0000
11	0.9830	0.9880	0.9850	0.9800	0.9930
12	0.9880	0.9900	0.9880	0.9930	1.0000
14	0.9900	0.9900	0.9880	0.9900	0.9930
16	0.9880	0.9880	0.9880	0.9900	0.9900
18	0.9900	0.9900	0.9800	0.9800	1.0000
20	0.9900	0.9900	0.9900	1.0000	0.9900
22	0.9880	0.9900	0.9900	0.9900	1.0000
24	0.9900	1.0000	0.9900	0.9900	0.9900
26	1.0000	0.9900	0.9900	0.9880	1.0000
28	0.9900	0.9900	0.9900	1.0000	0.9930

30	0.9900	0.9900	1.0000	1.0000	1.0000
32	0.9900	1.0000	0.9650	0.9880	0.9900
34	0.9880	0.9900	0.9900	1.0000	0.9900
36	1.0000	0.9900	1.0000	0.9880	0.9900

Table A6.3.5 Dispersed phase hold-up at different temperature

Time (h)	Dispersed phase hold-up (ϵ_D)			
	473 K	493 K	513 K	533 K
0	0.0844	0.0871	0.0951	0.0982
1	0.0836	0.0889	0.0947	0.0995
2	0.0844	0.0898	0.0964	0.1000
3	0.0853	0.0889	0.0973	0.1017
4	0.0862	0.0907	0.0980	0.1014
5	0.0853	0.0911	0.0982	0.1027
6	0.0857	0.0933	0.0987	0.1090
7	0.0947	0.1044	0.1096	0.1158
8	0.0973	0.1076	0.1129	0.1168

9	0.0970	0.1058	0.1122	0.1166
10	0.0969	0.1036	0.1120	0.1177
11	0.0966	0.1047	0.1125	0.1170
12	0.0960	0.1076	0.1133	0.1178
14	0.0969	0.1058	0.1131	0.1157
16	0.0969	0.1047	0.1148	0.1168
18	0.0982	0.1042	0.1149	0.1169
20	0.0969	0.1033	0.1149	0.1180
22	0.0989	0.1046	0.1149	0.1177
24	0.0999	0.1055	0.1149	0.1180
26	0.1001	0.1053	0.1149	0.1182
28	0.1030	0.1065	0.1149	0.1169

30	0.1013	0.1056	0.1149	0.1169
32	0.1029	0.1054	0.1150	0.1170
34	0.1012	0.1055	0.1152	0.1170
36	0.1010	0.1056	0.1148	0.1169

Table A6.3.6 Transient dispersed phase hold-up at different total pressure, $T=493\text{ K}$, $y_{\text{H}_2}=0.9$

Time (h)	Dispersed phase hold-up (ε_{D})		
	1 atm	11 atm	21 atm
0	0.0581	0.0675	0.0626
1	0.0640	0.0735	0.0928
2	0.0705	0.0834	0.0978
3	0.0789	0.0894	0.1003
4	0.0849	0.0943	0.1052
5	0.0894	0.0988	0.1102
6	0.0923	0.1008	0.1129
7	0.0978	0.1040	0.1123
8	0.1062	0.1147	0.1160

9	0.1080	0.1147	0.1172
10	0.1102	0.1200	0.1182
11	0.1200	0.1200	0.1182
12	0.1200	0.1200	0.1200
14	0.1200	0.1200	0.1160
16	0.1200	0.1200	0.1172
18	0.1100	0.1200	0.1200
20	0.1200	0.1200	0.1100
22	0.1200	0.1200	0.1167
24	0.1200	0.1200	0.1172
26	0.1200	0.1100	0.1200
28	0.1200	0.1200	0.1172

30	0.1200	0.1200	0.1294
32	0.1200	0.1236	0.1167
34	0.1200	0.1200	0.1240
36	0.1200	0.1200	0.1172

Table A6.3.7 ASF chain growth factor at different temperature

Time (h)	ASF chain growth probability, α_{FT}			
	473 K	493 K	513 K	533 K
0	0	0	0	0
1	0.4770	0.4774	0.4220	0.5130
2	0.5470	0.5330	0.4790	0.5440
3	0.5790	0.5791	0.5793	0.5616

4	0.5620	0.5616	0.5478	0.5642
5	0.5640	0.5642	0.5776	0.5395
6	0.5603	0.5395	0.5900	0.5950
7	0.5455	0.6060	0.5797	0.5603
8	0.5726	0.5603	0.5644	0.5455
9	0.5459	0.5455	0.5878	0.5726
10	0.5973	0.5726	0.5857	0.5459
11	0.5705	0.5459	0.5973	0.5973
12	0.5310	0.5973	0.6098	0.5705
14	0.5782	0.5705	0.6137	0.5310
16	0.5651	0.5310	0.6139	0.5782
18	0.5337	0.5782	0.6255	0.5651

20	0.5661	0.5651	0.6233	0.5337
22	0.6058	0.5337	0.6234	0.5661
24	0.5222	0.5661	0.6253	0.6058
26	0.5400	0.6058	0.6504	0.5950
28	0.5694	0.5222	0.6226	0.5830
30	0.5917	0.5400	0.6449	0.6290
32	0.6471	0.5917	0.6595	0.5917
34	0.6607	0.6471	0.6471	0.6471
36	0.6612	0.6880	0.6231	0.6880

Table A6.3.8 Transient carbon monoxide conversion (%) at 493 K, $y_{H_2}=0.9$

Time (h)	CO conversion (%)		
	1 atm	11 atm	21 atm
0	0.0	0.0	0.0
1	26.4	33.4	40.1
2	35.2	40.0	49.1
3	32.5	42.0	48.4
4	35.0	45.0	49.6
5	33.6	42.0	49.7
6	33.9	40.0	49.5
7	34.0	43.0	50.1
8	35.8	44.0	49.5
9	35.0	44.0	49.0

10	32.5	43.0	49.0
11	34.8	44.0	49.2
12	36.0	44.0	47.7
14	34.5	43.0	48.4
16	33.4	40.0	47.9
18	35.0	42.0	49.1
20	33.6	45.0	49.6
22	33.9	44.0	49.2
24	33.0	43.0	48.7
26	35.8	40.0	49.0
28	35.0	40.0	46.8
30	36.2	42.0	49.5

32	35.0	43.0	50.0
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34	35.0	43.0	50.7
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36	35.0	43.0	50.2
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Appendix

7

Internal (Intra-particle)
Mass Transport

Criterion set by Hudgins 1968 [1] is commonly employed to ensure the system is free from the internal (intra-particle) mass transport resistance as given:

$$\frac{r_{\text{exp}} d_p^2 |r'(C_0)|}{D_{\text{eff}} r(C_0)} < 3 \quad (\text{A7.44})$$

$r_{\text{exp}} = 2.17 \times 10^{-6} \text{ mol g}_{\text{cat}}^{-1} \text{ s}^{-1}$ at $T=533 \text{ K}$, $y_{\text{H}_2}=0.67$. Density of the paraffin oil is 0.804 g cm^{-3} , hence the reaction rate per unit volume of catalyst particle gives, $r_{\text{exp}} = 1.744 \times 10^{-6} \text{ mol cm}^3 \text{ s}^{-1}$.

$$d_p = 75 \times 10^{-4} \text{ cm}$$

with D_{AB} being the diffusivity of gas CO at 533 K and 21 atm (assuming the effect of pressure is negligible). The value of D_{AB} was $0.651 \text{ cm}^2 \text{ s}^{-1}$ at 298 K [2], thus $D_{AB}^{533\text{K}}$ may be estimated from;

$$\frac{D_{AB}^{533\text{K}}}{D_{AB}^{298\text{K}}} = \left(\frac{T_{533}}{T_{298}} \right)^{1.5} \quad (\text{A7.45})$$

$$\therefore D_{AB}^{533K} = 0.651 \times \left(\frac{533}{298} \right)^{1.5} = 1.56 \text{ cm}^2 \text{ s}^{-1}$$

To estimate the r'_{CO} value, we are assumed that the CO reaction rate may be expressed by an empirical expression given as;

$$r_{CO} = k P_{CO}^a P_{H_2}^b \quad (\text{A7.46})$$

Equation (A7.3) may be re-arranged by assuming partial pressure of FT product is negligible at low conversion,

$$r_{CO} = k P_{CO}^a (P - P_{CO})^b \quad (\text{A7.47})$$

Thus, the gas phase concentration of CO may be given as;

$$C_{CO} = \frac{n_{CO}}{V} = \frac{P_{CO}}{RT} \quad (\text{A7.48})$$

$$\text{where, } C = \frac{n}{V} = \frac{P}{RT}$$

$$\therefore P_{CO} = \frac{C_{CO}}{C} P \quad (\text{A7.49})$$

by combining Equations (A7.4) and (A7.6) gives;

$$r'_{CO} = k \left(\frac{P}{C} \right)^{a+b} \left[a C_{CO}^{a-1} (C - C_{CO})^b + b C_{CO}^a (C - C_{CO})^{b-1} \right] \quad (\text{A7.50})$$

Hence,

$$\frac{r'_{CO}}{r_{CO}} = \frac{a}{C_{CO}} + \frac{b}{C - C_{CO}} \quad (A7.51)$$

where,

$$C = \frac{n}{V} = \frac{P}{RT} = \frac{1}{82.06 \times 533} = 2.29 \times 10^{-5} \text{ mol cc}^{-1}$$

and

$$C_{CO} = \frac{0.5}{82.06 \times 533} = 1.14 \times 10^{-5} \text{ mol cc}^{-1}$$

A nonlinear regression of experimental data to Equation (A7.3) gives a and b values of 0.75 and 2.14 respectively. Therefore,

$$\frac{r'_{CO}}{r_{CO}} = \frac{0.75}{1.14 \times 10^{-5}} + \frac{2.14}{2.29 \times 10^{-5}} = 1.59 \times 10^5$$

where D_{eff} is the effective diffusivity = $\frac{D_{AB}}{10}$ [3], thus

$$\therefore D_{eff} = 1.2 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$$

Hence,

$$\frac{r_{exp} d_p^2 |r'(C_0)n|}{D_{eff} r(C_0)} = \frac{1.744 \times 10^{-6} \times (75 \times 10^{-4})^2 \times 1.59 \times 10^5}{1.56} n = 1.0 \times 10^{-5} n$$

The typical order of reaction in any system, $n=3$, thus

$$\therefore 2.98 \times 10^{-5} \ll 3$$

Therefore, the intra-particle resistance is deemed negligible in this system.

References

1. Hudgins, R.R., *A general criterion for absence of diffusion control in an isothermal catalyst pellet*. Chem. Eng. Sci., 1968. **23**(1): p. 93-94.
2. Perry, R.H., D.W. Green, and J.O. Maloney, *Perry's chemical engineers' handbook 7th Ed.* 1997: McGraw-Hill Sydney.
3. Satterfield, C.N., *Mass transfer in heterogeneous catalysis*. MIT Press, 1970.

Appendix 8

Experimental Error Estimation

FT reaction rate is estimated using the following equation given:

$$r_i = \frac{y_i F}{m S_m} \quad (\text{E8.52})$$

where,

y_i = mole fraction of component, i , in product stream

F = total molar feed flowrate (mol s^{-1})

M = mass of catalyst used (g)

r_i = reaction (production) rate of species, i

S_m = metallic surface area determined by chemisorption analysis ($\text{m}^2 \text{g}^{-1}$)

Generally, the propagation error can be written as [1, 2];

$$\left(\frac{\Delta y}{y} \right)^2 = \sum_{i=1}^N \left(\frac{d \ln y}{dx_i} \right)^2 \left(\frac{\Delta x_i}{x_i} \right)^2 \quad (\text{E8.53})$$

In logarithmic form, Equation (E8.1) can be re-written as;

$$\ln r_i = \ln y_i + \ln F - \ln m - \ln S_m \quad (\text{E8.54})$$

Thus,

$$\frac{d \ln r_i}{d \ln y_i} = \frac{d \ln r_i}{d \ln F_i} = \frac{-d \ln r_i}{d \ln m} = \frac{-d \ln r_i}{d \ln y_i} = 1$$

and

by applying Equation (E8.2), it gives;

$$\left(\frac{\Delta r_i}{r_i} \right)^2 = \left(\frac{\Delta y_i}{y_i} \right)^2 + \left(\frac{\Delta F}{F} \right)^2 + \left(\frac{\Delta m}{m} \right)^2 + \left(\frac{\Delta S_m}{S_m} \right)^2 \quad (\text{E8.55})$$

It was assumed that the error range for these parameters as following:

$$\frac{\Delta y_i}{y_i} = 1 - 4\%$$

$$\frac{\Delta F}{F} = 1 - 4\%$$

$$\frac{\Delta m}{m} = 0.5 - 2\%$$

$$\frac{\Delta S_m}{S_m} = 1 - 4\%$$

Hence, the overall errors range of these parameters is 0.018-0.0721 (2-7%)

References

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