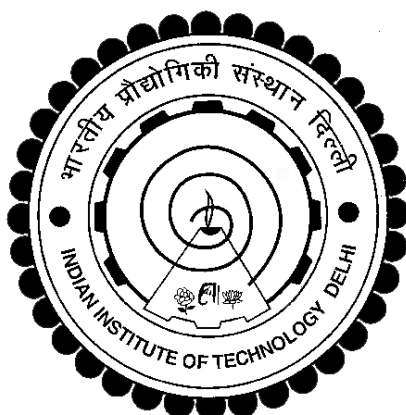


**MODEL-BASED DESIGN AND INTENSIFICATION OF CLEAN-UP
AND CONDITIONING PROCESSES FOR PRODUCTION OF FUEL-
GRADE METHANOL FROM HIGH-ASH COAL**

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DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

JULY 2024

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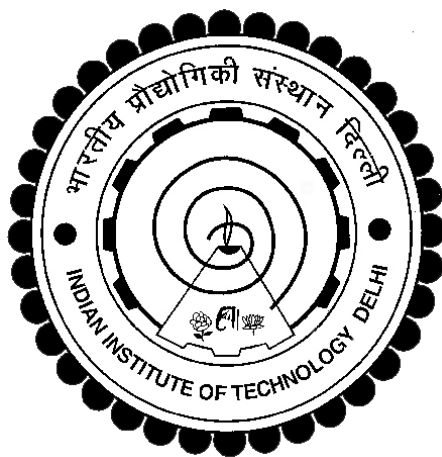
By

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Submitted in the partial fulfilment of the requirements of the degree of

Doctor of Philosophy



to the

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CERTIFICATE

This is to certify that the thesis entitled '**Model-based design and intensification of clean-up and conditioning processes for production of fuel-grade methanol from high-ash coal**' being submitted by **Mr. Pranav V. Kherdekar** to the *Indian Institute of Technology Delhi* for award of **Doctor of Philosophy** is a record of bona fide research work carried out by him under our guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology Delhi. The research report and results presented in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.



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Pranav V. Kherdekar

पूर्णमदः पूर्णमिदं पूर्णात्पूर्णमुदच्यते।

पूर्णस्य पूर्णमादाय पूर्णमेवावशिष्यते॥

- ईशोपनिषद्

”What is visible is the infinite. What is invisible is also the infinite. Out of the Infinite, being the finite has come, yet being infinite, only infinite remains” - īśopaniṣad

ABSTRACT

Gasification of high-ash coal results in a syngas with large concentrations of various contaminants which necessitates a rigorous clean-up and conditioning process to produce syngas suitable for methanol production. As the design of the clean-up and conditioning process has a significant impact on the economy of the coal-to-methanol process, this work addresses intensification of the clean-up and conditioning process for syngas exiting a low-grade coal gasifier. A model-based approach is followed, and numerical simulations of individual units are used to assess their performance.

A one-dimensional model is developed to predict the performance of a pilot-scale bubbling fluidized bed gasifier for low-grade coal gasification. The model is found to predict the outlet composition of the pilot-scale gasifier with reasonable accuracy for different operating conditions. It is shown that the cold gas efficiency of the gasifier exhibits a maximum with the oxygen content of the fluidizing gas. It is also shown that the molar H_2/CO ratio at the gasifier exit can be tailored by altering the steam feed rate. Further, an algorithm is proposed for screening and sequencing of syngas clean-up and conditioning processes. Using a sample syngas composition as the design basis, the feasibility of different sub-process schemes for clean-up and conditioning of syngas is examined by performing process simulations. Simulation of the entire clean-up and conditioning process scheme along with the closed-circuit methanol production unit is then performed and it is shown that the process scheme can yield methanol at 1000 kg/day. While the absorption-based clean-up units can be operated under varying load conditions using an over-design factor, the load-flexibility of the catalytic systems such as the partial water-gas shift unit needs to be ensured. Thus, a dynamic model is developed for a sour water-gas shift reactor and the optimum design and operating parameters are obtained by solving various optimization problems. The reactor designs where the molar H_2/CO ratio at

the reactor exit is governed by equilibrium limitations are found to be dynamically more stable under fluctuating load. The model is extended to examine the possibility of carrying out two reactions: water-gas shift reaction and COS hydrolysis in a single fixed-bed reactor. Techno-economic optimization studies are carried out to propose a heat-integrated multi-functional reactor design for water-gas shift and COS hydrolysis reactions. It is shown that low feed temperatures and high steam flow rates result in high COS conversion at a fixed CO conversion. However, reactor designs with higher feed temperatures eliminate the requirement of hot utility since the products leaving the reactor have sufficient enthalpy to pre-heat the feed syngas.

Ab-initio calculations based on density functional theory are used to establish the dominant reaction pathway for COS hydrolysis on γ -Al₂O₃. Further, optimization of single-pass and closed-circuit methanol production processes involving a multi-tubular reactor is carried out. Maximum CO_x conversion of 70% is obtained in the single-pass process while up to 90% CO_x conversion is obtained in the closed-circuit process. It is shown that the concentrations of inert species in the raw syngas significantly increases the reactor size and recycle processing costs in the closed-circuit process.

The methodology and the results obtained in this work can be used for the design, analysis, and techno-economic optimization of a network of unit processes and unit operations with multiple heating and cooling operations.

सारांश

उच्च-राख कोयले के गैसीकरण से उत्पन्न किए गए वायु, अर्थात् 'सिनगैस' में अनेक दूषणकारी पदार्थ भारी मात्रा में पाए जाते हैं। ऐसी सिनगैस से मेथेनॉल बनाने से पहले सिनगैस से इन दूषणकारी पदार्थों को निकाला जाना एवं सिनगैस के संघटन को मेथेनॉल संश्लेषण हेतु अनुकूल बनाना अनिवार्य होता है। सिनगैस से दूषणकारी पदार्थों को निकालकर उसे मेथेनॉल संश्लेषण हेतु अनुकूल बनाने वाली इस प्रक्रिया का कोयले से मेथेनॉल बनाने की सम्पूर्ण प्रक्रिया की लाभप्रदता पर काफी असर पड़ता है। इसीलिए प्रस्तुत प्रबंध में कम दबाव वाले गैसीफायर से प्राप्त किए गए सिनगैस से दूषणकारी पदार्थों को निकालकर उसे मेथेनॉल संश्लेषण हेतु अनुकूल बनानेवाली प्रक्रिया के गहनीकरण (इन्टेन्सफिकेशन) को संबोधित किया गया है। प्रस्तुत संशोधन में इस गहनीकरण हेतु गणितीय प्रणाली का प्रयोग किया गया है और प्रक्रिया के अलग-अलग भागों के गणितीय प्रतिरूपों की मदद से उन भागों की उपयोगिता जाँची गई है।

इस संशोधन में एक द्रविकृत गैसीफायर की उपयोगिता जाँचने हेतु उस गैसीफायर का एक-आयामी गणितीय प्रतिरूप निर्माण किया गया है। इस गणितीय प्रतिरूप से अनुमानित सिनगैस का संघटन, प्रत्यक्ष मापे गए संघटन से उचित मेल खाता है। प्रतिरूप की मदद से यह दिखाया गया है कि गैसीफायर में प्रवेशित किए गए वायु में ऑक्सीजन के प्रमाण को मध्यम मूल्य पर रखने से निर्मित सिनगैस की ऊर्जा-निर्मिती क्षमता को अधिकतम किया जा सकता है। तत्पश्चात् यह भी दिखाया गया है कि गैसीफायर में प्रवेशित किए गए वायु में भाँप की मात्रा को बदलकर निर्मित सिनगैस में हाइड्रोजन और कार्बन मोनोक्साइड की मात्राओं को संतुलित किया जा सकता है।

सिनगैस से दूषणकारी पदार्थों को निकालकर उसे मेथेनॉल संश्लेषण हेतु अनुकूल बनानेवाली प्रक्रिया के घटकों को छाँटने हेतु तथा उन्हें क्रमित करने हेतु एक कलन विधि (एल्गोरिदम) का निर्माण इस संशोधन

मे किया गया है। प्रक्रिया के घटकों के विविध पर्याय और उनकी उपयोगिता, उन पर्यायों के गणितीय प्रतिरूपों की मदद से जाँचे और चुने गए हैं। सिनगैस से मेथेनॉल बनाने की सम्पूर्ण प्रक्रिया का गणितीय प्रतिरूप बनाकर यह दिखाया गया है की चुने हुए पर्यायों से बनी हुई प्रक्रिया से प्रतिदिन १००० किलोग्राम मेथेनॉल का उत्पादन हो सकता है।

इस प्रक्रिया में मौजूद संप्रेरित रिएक्टरों (catalytic reactors) का गैसीफायर से प्राप्त हुए सिनगैस के संघटन की अनियमितता के प्रति असंवेदनशील होना जरूरी है। इसीलिए इस संशोधन में प्रक्रिया के एक अहम घटक: 'सार वाटर-गैस शिफ्ट' रिएक्टर के लिए एक गतिशील गणितीय प्रतिरूप (dynamic model) का निर्माण किया गया है और उस प्रतिरूप की मदद से रिएक्टर की रचना और संचालन (डिजाइन) का अनुकूलन किया गया है। यह दिखाया गया है की जिन संरचनाओं में रिएक्टर से निकालित वायु का संघटन रासायनिक संतुलन (chemical equilibrium) पर निर्भर करता है, रिएक्टर की वह संरचनाएँ गैसीफायर से प्राप्त हुए सिनगैस के संघटन की अनियमितता के प्रति असंवेदनशील होती हैं। इस गणितीय प्रतिरूप को और विकसित करके एक ऐसे रिएक्टर संरचना का संशोधन किया गया है जिसमें दो अलग संप्रेरित प्रक्रियाएँ: 'सार वाटर-गैस शिफ्ट' और कार्बोनील सल्फाइड (COS) के जलप्रेरित विघटन (hydrolysis) की जा सकें। इस संशोधन में यह पाया गया है की रिएक्टर में प्रवेशित वायु के तापमान को विशिष्ट सीमा तक कम करके, और रिएक्टर में भाँप अधिक मात्रा में प्रवेशित करके कार्बोनील सल्फाइड का परिवर्तन स्तर बढ़ाया जा सकता है। परंतु, तकनीकी एवं आर्थिक अनुकूलन को मध्यनजर रखके यह भी पाया गया है की रिएक्टर में प्रवेशित वायु के तापमान को बढ़ा कर एक ऐसा रिएक्टर संरचित किया जा सकता है जहाँ रिएक्टर से निकालित वायु, रिएक्टर में प्रवेशित वायु का तापमान उचित मात्रा तक बढ़ा सके।

‘डेन्सिटी फंक्शनल थ्योरी’ पर आधारित गणनाओं के आधार पर, गामा अल्युमिना पर कार्बोनील सल्फाइड (COS) के जलप्रेरित विघटन (hydrolysis) में अणु-स्तर पर होने वाली प्रक्रियाओं का अभ्यास भी इस संशोधन में किया गया है। मेथेनॉल संश्लेषण के लिए उपयोग किए जाने वाले बहुनलिका रिएक्टर की दो अलग संरचनाओं का अनुकूलन भी इस संशोधन में किया गया है। पहली संरचना में रिएक्टर से निकालित गैस पुनः चक्रित नहीं की जाती, और गैस में मौजूद ७०% कार्बन आक्साइड्स (CO_x), मेथेनॉल में परिवर्तित होती है। दूसरी संरचना में रिएक्टर से निकालित गैस का आंशिक भाग रिएक्टर में पुनः चक्रित किया जाता है और गैस में मौजूद ९०% कार्बन आक्साइड्स (CO_x), मेथेनॉल में परिवर्तित होती है।

इस संशोधन में प्रस्तुत गणितीय प्रतिरूप एवं निरीक्षण ऐसी प्रक्रियाओं के महाजालों की संरचना एवं अनुकूलन में मददगार साबित हो सकते हैं जहां एकाधिक ऊष्मा-विनिमायक आवश्यक हो।

TABLE OF CONTENTS

CERTIFICATE	i
ACKNOWLEDGMENTS	ii
ABSTRACT	v
TABLE OF CONTENTS	x
LIST OF FIGURES	xvii
LIST OF TABLES	xxvii
CHAPTER 1: INTRODUCTION	1
1.1. Background	1
1.2. Avenues for research and intensification	4
CHAPTER 2: LITERATURE REVIEW	6
2.1. Major contaminants present in coal-derived syngas	6
<i>2.1.1. Particulate matter</i>	6
<i>2.1.2. Tars</i>	8
<i>2.1.3. Waxes</i>	13
<i>2.1.4. Sulfur compounds</i>	13
<i>2.1.5. Ammonia and hydrogen cyanide</i>	15
<i>2.1.6. Chlorine compounds</i>	17
<i>2.1.7. Light hydrocarbons</i>	18
<i>2.1.8. Oxygen</i>	18
<i>2.1.9. Trace metals</i>	19
<i>2.1.10. Carbon dioxide</i>	22
2.2. Technologies for syngas clean-up	23
<i>2.2.1. Technologies for particulate removal</i>	23

2.2.2.	<i>Technologies for removal of tars</i>	35
2.2.3.	<i>Technologies for acid gas removal</i>	40
2.2.4.	<i>Technologies for removal of ammonia</i>	58
2.2.5.	<i>Technologies for removal of hydrochloric acid</i>	64
2.2.6.	<i>Removal of light hydrocarbons</i>	66
2.2.7.	<i>Technologies for removal of trace metals</i>	69
2.2.8.	<i>Removal of residual oxygen</i>	74
2.2.9.	<i>Hydrolysis of carbonyl sulfide and hydrogen cyanide</i>	77
2.2.10.	<i>Syngas conditioning by catalytic water-gas shift reaction</i>	81
2.2.11.	<i>Integrated processes for syngas cleanup and conditioning</i>	83
	List of abbreviations	87
CHAPTER 3: DEVELOPMENT OF A TWO-PHASE MODEL FOR A		89
BUBBLING FLUIDIZED BED GASIFIER		
3.1.	Background	89
3.2.	Representative model of the gasifier	93
3.3.	Modelling equations	97
3.3.1.	<i>Calculation of hydrodynamic parameters</i>	97
3.3.2.	<i>Local species balance equations</i>	100
3.3.3.	<i>Local energy balance equations</i>	101
3.3.4.	<i>Kinetic model discrimination: Homogeneous reactions</i>	106
3.3.5.	<i>Kinetics of heterogeneous reactions</i>	111
3.3.6.	<i>Overall balances and convergence schemes</i>	113
3.3.7.	<i>Devolatilization of coal</i>	118
3.3.8.	<i>Computational procedures</i>	118
3.4.	Results and discussion	119

3.4.1.	<i>Kinetic model discrimination</i>	119
3.4.2.	<i>Comparison of model predictions with experimental data</i>	121
3.4.3.	<i>Axial variation of molar flow rates and rates of reactions</i>	122
3.4.4.	<i>Effect of oxygen content of feed air</i>	130
3.4.5.	<i>Effect of steam flow rate</i>	131
3.5.	Conclusions	133
	List of symbols	134
	List of abbreviations	140
CHAPTER 4: SCREENING, SEQUENCING AND SIMULATION OF		142
CLEAN-UP AND CONDITIONING PROCESSES FOR LOW-GRADE		
COAL-DERIVED SYNGAS		
4.1.	Background	142
4.2.	Methodology	147
4.2.1.	<i>Design basis</i>	147
4.2.2.	<i>Algorithm for process selection and sequencing</i>	149
4.2.3.	<i>Process simulation</i>	163
4.3.	Results and discussion	164
4.3.1.	<i>Process screening and sequencing</i>	164
4.3.2.	<i>Process simulation</i>	168
4.3.3.	<i>Simulation of the overall process</i>	195
4.4.	Conclusions	200
	List of symbols	202
	List of abbreviations	203

CHAPTER 5: DYNAMIC MODELING AND OPTIMIZATION OF A FIXED-BED REACTOR FOR PARTIAL WATER-GAS SHIFT REACTION	204
5.1. Background	204
5.2. Methodology	209
5.2.1. <i>Model development</i>	209
5.2.2. <i>Solution of equations</i>	213
5.2.3. <i>Multi-objective optimization</i>	214
5.2.4. <i>Dynamic stability analysis</i>	218
5.3. Results and discussion	219
5.3.1. <i>Optimization</i>	219
5.3.2. <i>Dynamic stability analysis</i>	232
5.4. Conclusions	238
List of symbols	239
CHAPTER 6: TECHNO-ECONOMIC OPTIMIZATION OF FIXED-BED CATALYTIC REACTOR SYSTEMS FOR WATER-GAS SHIFT AND COS HYDROLYSIS REACTIONS	243
6.1. Background	243
6.2. Methodology	248
6.2.1. <i>Model formulation for a single-tube fixed-bed reactor</i>	248
6.2.2. <i>Solution of equations</i>	251
6.2.3. <i>Calculation of capital and operating costs</i>	251
6.2.4. <i>Multi-objective optimization</i>	256
6.3. Results and Discussion	262
6.3.1. <i>CASE 1: Optimization of the conventional system</i>	262

6.3.2.	<i>CASE 2: Two-objective optimization of a multi-functional fixed-bed reactor</i>	266
6.3.3.	<i>Three-objective optimization of the multi-functional fixed-bed reactor</i>	271
6.3.4.	<i>Discussion</i>	277
6.4.	Conclusions	280
	List of symbols	281
CHAPTER 7: EXPLORING THE ENERGETICS OF HYDROLYSIS OF CARBONYL SULFIDE ON γ-ALUMINA (110) SURFACE BY AB-INITIO SIMULATIONS		287
7.1.	Background	287
7.2.	Methodology	292
7.2.1.	<i>Analysis and description of reaction steps and pathways</i>	292
7.2.2.	<i>Computational methods</i>	294
7.2.3.	<i>Model for dehydrated catalyst surface</i>	297
7.2.4.	<i>Models for hydroxylated catalyst surfaces</i>	298
7.3.	Results and discussion	301
7.3.1.	<i>Adsorption of COS on dehydrated and hydroxylated surfaces</i>	301
7.3.2.	<i>Formation of the hydrogen thiocarbonate species</i>	303
7.3.3.	<i>Direct pathway</i>	308
7.3.4.	<i>HCO₃-mediated pathway</i>	312
7.3.5.	<i>Reaction energetics</i>	317
7.3.6.	<i>Degree of rate control (DORC) analysis</i>	319
7.4.	Conclusions	326

List of symbols	327
List of abbreviations	329
CHAPTER 8: MODEL-BASED DESIGN AND OPTIMIZATION OF THE CATALYTIC PROCESS FOR METHANOL PRODUCTION FROM COAL-DERIVED SYNGAS	330
8.1. Background	330
8.2. Methodology	335
8.2.1. <i>System description and model assumptions</i>	335
8.2.2. <i>1D+1D model for multi-tubular reactor</i>	338
8.2.3. <i>Modelling of the gas-liquid separator</i>	343
8.2.4. <i>Modelling of the multi-stage compressor</i>	343
8.2.5. <i>Multi-objective optimization</i>	344
8.3. Results and discussion	349
8.3.1. <i>Optimization of methanol production process with once-through reactor operation (Case 1)</i>	349
8.3.2. <i>Analysis of selected chromosomes on Pareto-optimal front: Once-through operation</i>	358
8.3.3. <i>Optimization of a closed-circuit methanol production process (Case 2)</i>	363
8.3.4. <i>Analysis of chromosomes for the closed-circuit process</i>	370
8.3.5. <i>Discussion</i>	375
8.4. Conclusions	377
List of symbols	378
List of abbreviations	383

CHAPTER 9: SUMMARY, CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK	384
9.1. Summary and conclusions	384
9.2. Scope for future work	391
APPENDIX A: STRUCTURES AND REACTION ENERGY DIAGRAMS FOR VARIOUS STEPS INVOLVED IN COS HYDROLYSIS ON γ-ALUMINA (110) SURFACE	395
A1. Optimized structures of COS adsorbed on dehydrated and hydroxylated surfaces	395
A2. Formation of hydrogen thiocarbonate (HTC) species: Initial, transition, final state structures, and reaction energy diagrams	398
A3. Bond rotation and isomerization of HTC ₁ species: Initial, transition, final state structures, and reaction energy diagrams	404
A4. Surface proton extraction and formation of H ₂ S and CO ₂ : Initial, transition, final state structures, and reaction energy diagrams	408
A5. Reaction between H ₂ O and surface HTC ₂ species leading to formation of H ₂ S and surface HCO ₃ species: Initial, transition, final state structures, and reaction energy diagrams	412
A6. Decomposition of surface bicarbonate species: Initial, transition, final state structures, and reaction energy diagrams	416
BIBLIOGRAPHY	419
BIO-DATA	470

LIST OF FIGURES

Fig. 2.1.	Cyclone separator	25
Fig. 2.2.	Westinghouse particulate removal system	26
Fig. 2.3.	Schematic of a downflow fixed bed granular filter	30
Fig. 2.4.	Cross-flow moving bed filter	33
Fig. 2.5.	Outline of the OLGA tar removal process	38
Fig. 2.6.	Schematic of a chemical solvent-based acid gas removal process	42
Fig. 2.7.	Schematic of the hot potassium carbonate process	47
Fig. 2.8.	Schematic of the single circulating loop caustic scrubbing process	51
Fig. 2.9.	Schematic of the dual-stage Rectisol unit	53
Fig. 2.10.	Schematic of the dual-stage Selexol process	55
Fig. 2.11.	General process scheme of wet-scrubbing process for ammonia removal	59
Fig. 2.12.	Process scheme for adsorbent-based NH ₃ removal	63
Fig. 2.13.	A representative cold syngas cleanup and conditioning process for IGCC application	84
Fig. 2.14.	Block diagram of the syngas cleanup process proposed by Chandran et al.	85
Fig. 2.15.	Block diagram of warm syngas clean-up and conditioning process	87
Fig. 3.1.	Representative model of the gasifier: (a) Bubbling fluidized bed configuration, (b) Equivalent model, (c) Modes of heat losses from the gasifier	95
Fig. 3.2.	Procedure for discrimination of global kinetic models for homogeneous reactions	110

Fig. 3.3.	Iterative scheme for the calculation of char conversion (Loop L1)	115
Fig. 3.4.	Iterative scheme for the calculation of solid temperature (Loop L2)	117
Fig. 3.5.	Fig. 3.5. Discrimination of global kinetic models for homogeneous reactions (a) TOPSIS scores for different combinations, and (b-e) Prediction of rates of production (ROP) of different species by the selected combination of global kinetic models	120
Fig. 3.6.	Comparison of model-predicted syngas composition with experimental data (a) Pilot-scale gasifier operated by a major commercial organization, and (b) Pilot-scale gasifier reported by Kumar et al.	122
Fig. 3.7.	Model predictions for gasification of low-grade coal in a pilot-scale coal gasifier (a) Convergence outer loop (L2) for the calculation of T_s , (b) Comparison of model-predicted results with measured data, (c) Axial variation of temperatures, (d) Axial variation of molar flow rates	123
Fig. 3.8.	Axial variation of rates of reactions: (a) Heterogeneous reactions, (b) Homogeneous reactions in emulsion phase, (c) Homogeneous reactions in bubble phase, (d) Comparison of predicted composition of syngas with equilibrium composition in emulsion phase, and (e) Comparison of predicted composition of syngas with equilibrium composition in bubble phase	126
Fig. 3.9.	Effect of oxygen content of air on gasifier performance: (a) Variation of T_s and X_C with w_{O_2} , and (b) Variation of component flow rates and cold gas efficiency with w_{O_2}	130
Fig. 3.10.	Effect of steam flow rate on gasifier performance: (a) Variation of T_s and X_C with steam flow rate, (b) Variation of component flow rates and cold gas efficiency with steam flow rate	132

Fig. 4.1.	Flowchart for the calculation of penalty P1	156
Fig. 4.2.	Flowchart for the calculation of penalty P2	157
Fig. 4.3.	Flowchart for calculation of penalty P3	159
Fig. 4.4.	Flowchart for calculation of penalty P4	160
Fig. 4.5.	Flowchart for calculation of penalty P5	161
Fig. 4.6.	Procedure for the calculation of number of stages and required solvent flow rates	164
Fig. 4.7.	Optimal process sequences identified using two-level optimization (a) Sequence 1, (b) Sequence 2, and (c) Sequence 3	165
Fig. 4.8.	Simulation of particulate removal system: (a) Flowsheet of the particulate removal system, (b) Efficiency of cyclone separator, and (c) Efficiency of candle filtration system	168
Fig. 4.9.	Graphical method calculations for wet scrubbing of ammonia using water (a) Number of stages and solvent flow rate for absorption of ammonia in pure water, (b) Variation in the number of stages with ammonia concentration in the lean solvent, (c) Equilibrium and operating lines for different ammonia concentrations in the lean solvent	172
Fig. 4.10.	Closed-loop wet scrubbing process for ammonia removal (a) Flowsheet, (b) Variation of performance with purge fraction	173
Fig. 4.11.	Closed-loop acid wash process using a packed bed absorption column (a) Flowsheet, (b) Extent of removal of different contaminants, and (c) Extent of removal of light tar compounds	176
Fig. 4.12.	Closed-loop acid wash process using a spray tower (a) Flowsheet (b) Extent of removal of different contaminants, and (c) Extent of removal of tar compounds	178

- Fig. 4.13.** Process simulation for the removal of tars (a) Graphical method **181**
calculations for absorption column, (b) Variation of number of stages
with benzene concentration in lean solvent, (c) Graphical method
calculations for stripping column, (d) Variation of number of stages
with xylene concentration in rich solvent, and (e) Flowsheet for closed-
loop process
- Fig. 4.14.** Process simulation of the WGS and COS hydrolysis reactors in series **184**
(a) Flowsheet, (b) Variation of CO, H₂, CO₂ concentrations and
temperature along the length of the WGS reactor (WGSRS2), (c)
Variation of COS and HCN concentrations along the length of the WGS
reactor (WGSRS2), and (d) Variation of COS concentration along the
length of the hydrolysis reactor (HYDS2)
- Fig. 4.15.** Process simulation of the hydrolysis and WGS reactors in parallel: (a) **186**
Flowsheet, (b) Axial variation of COS and HCN concentrations for
hydrolysis reactor (HYDP1) (c) Axial variation of CO, H₂, CO₂
concentrations and temperature for water-gas shift reactor (WGSRP1),
and (d) Variation of COS and HCN concentrations and reactor
temperature along the length of the water-gas shift reactor (WGSRP1)
- Fig. 4.16.** Process simulation of amine-based acid gas removal process, (a-c) **191**
Graphical method calculations for absorption of acid gas compounds in
aqueous 30% MDEA solution: (a) Absorption of CO₂ from CO₂+N₂
mixture, (b) Absorption of H₂S from H₂S+N₂ mixture, (c) Absorption
of H₂S from a H₂S+CO₂+N₂ mixture, (d) Flowsheet for acid gas
removal from syngas, and (e) Variation of temperature and heat flow
along the length of the absorption column

Fig. 4.17.	Simulation of the methanol production unit: (a) Flowsheet, and (b) Variation of composition and reactor temperature along the length of the reactor	195
Fig. 4.18.	Flow sheet of syngas clean-up and conditioning unit and methanol production unit	196
Fig. 4.19.	Heating and cooling requirements of the different units in the syngas to methanol conversion process (a) Heating requirement, and (b) Cooling requirement	200
Fig. 5.1.	Simulink model used for dynamic stability analysis	218
Fig. 5.2.	Results for the two-objective optimization of case 1 (a) Pareto-optimal set, (b-k) Decision variables associated with the chromosomes of the Pareto-optimal set, and (l) Correspondence between catalyst weight and inlet gas temperature	221
Fig. 5.3.	Pressure drop for the chromosomes of case 1 Pareto set	223
Fig. 5.4.	Results for the two-objective optimization of case 2 (a) Pareto-optimal set, and (b-g) Decision variables associated with the chromosomes of the Pareto-optimal set	226
Fig. 5.5.	Operating costs for the chromosomes of Case 2 Pareto set	228
Fig. 5.6.	(a) Contour plot representation of the Pareto-optimal front for the three-objective optimization problem, (b-g) Decision variables corresponding to the chromosomes of the Pareto set	230
Fig. 5.7.	Effect of temporal variations in feed flow rates on H_2/CO ratio for selected reactor designs	233
Fig. 5.8.	(a) Axial temperature and (b) CO conversion profiles for chromosome A during the startup period	235

Fig. 5.9.	(a) Axial CO conversion and (b) temperature profiles for chromosome B during the startup period	236
Fig. 5.10.	Effect of temporal variations in temperature on H ₂ /CO ratio for selected reactor designs	237
Fig. 6.1.	Conventional process scheme for water-gas shift reaction, COS hydrolysis, and acid-gas removal	245
Fig. 6.2.	Catalytic reactor systems considered for optimization (a) Conventional system comprised of two reactors in parallel, and (b) Single multi-functional reactor	258
Fig. 6.3.	Optimization of the conventional system for water-gas shift and COS hydrolysis reactions (a) Pareto-optimal fronts for different split fractions, and (b-j) Variation of objective functions with decision variables	264
Fig. 6.4.	Optimization of a multi-functional fixed-bed reactor system for water-gas shift and COS hydrolysis reactions (a) Pareto-optimal front, (b-d) Variation of objective functions with decision variables	267
Fig. 6.5.	Conversion and temperature profiles for chromosomes A and B obtained during optimization of the multi-functional reactor (Case 2)	270
Fig. 6.6.	Techno-economic optimization of a multi-functional fixed-bed reactor system for water-gas shift and COS hydrolysis reactions (a) Pareto-optimal front, (b) Variation of objective functions with T _{g,in} , (c) Grand composite curve for chromosome C, (d) Hot and cold composite curves for chromosome C, and (e) Variation of objective functions with (S/CO) _m	273

- Fig. 6.7.** Techno-economic optimization of a multi-functional fixed-bed reactor 276
system for WGS and COS hydrolysis reactions (a) Variation of OBJ_3 with d_p , (b) Variation of OBJ_1 and OBJ_2 with d_p , (c) Variation of OBJ_3 with d_p , (d) Variation of OBJ_3 with W_{cat} , and (e) Variation of OBJ_1 and OBJ_2 with W_{cat}
- Fig. 7.1.** Slab model for $\gamma\text{-Al}_2\text{O}_3$ (110) surface (a) Lateral view (b) Atoms in the 298
top layer of the oxygen terminated surface
- Fig. 7.2.** Top layers of optimized slab models of hydroxylated $\gamma\text{-Al}_2\text{O}_3$ (110) 300
surfaces; OH coverage: (a) 3 OH/nm², (b) 8.9 OH/nm², (c) 11.8 OH/nm²
- Fig. 7.3.** Formation of hydrogen thiocarbonate (HTC) species (a) Initial, 304
transition and final states for formation of HTC_1 species on Al(III) site at OH coverage of 11.8 OH/nm², (b) Initial, transition and final states for formation of HTC_2 species on Al(III) site at OH coverage of 11.8 OH/nm²
- Fig. 7.4.** Formation of hydrogen thiocarbonate (HTC) species (a) Variation of 307
activation energy with reaction energy (HTC_1 species), and (b) Variation of activation energy with reaction energy (HTC_2 species)
- Fig. 7.5.** Initial, transition and final states for intramolecular transformation 308
of HTC_1 species at Al(III) site on hydroxylated $\gamma\text{-Al}_2\text{O}_3$ (110) surface at OH coverage of 11.8 OH/nm²
- Fig. 7.6.** Initial, transition and final states for extraction of surface proton by 311
transformed HTC species on Al(III) site of the hydroxylated $\gamma\text{-Al}_2\text{O}_3$ (110) surface at OH coverage of 11.8 OH/nm²

Fig. 7.7.	Initial, transition, and final states for reaction of surface HTC_2 species with gas-phase H_2O on Al(III) site of hydroxylated $\gamma\text{-Al}_2\text{O}_3$ (110) surface (OH Coverage: 11.8 OH/nm^2)	313
Fig. 7.8.	Initial, transition and final states for decomposition of surface bicarbonate species on Al(III) site of hydroxylated $\gamma\text{-Al}_2\text{O}_3$ (110) surface (OH Coverage: 11.8 OH/nm^2)	315
Fig. 7.9.	Reaction energy diagram for COS hydrolysis on hydroxylated $\gamma\text{-Al}_2\text{O}_3$ (110) surface (OH coverage= 11.8 OH/nm^2) (a) Direct pathway, (b) HCO_3 -mediated pathway	318
Fig. 7.10.	Reaction pathway analysis for COS hydrolysis reaction on Al(IV#) site of $\gamma\text{-Al}_2\text{O}_3$ (110) surface (a) generation/ consumption rates of gaseous species, (b) variation of turnover frequency and degree of rate control with temperature	323
Fig. 8.1.	Process for coal to methanol production	330
Fig. 8.2.	(a) Schematic of the system under consideration, and (b) Internal configuration of the Lurgi-type reactor	336
Fig. 8.3.	Process flow configuration for Case 1: Single-pass configuration	348
Fig. 8.4.	Process flow configuration for case 2: Configuration with recycle and purge	349
Fig. 8.5.	Results for the optimization of the multi-functional reactor for Case 1 (a) Pareto-optimal front, and (b-f) Dependence of methanol production rate on various decision variables	351
Fig. 8.6.	Results for optimization of the reactor for Case 1: (a) Conversion of CO_x , (b) CO/CO_2 ratio and S_N at reactor inlet and outlet, (c) Variation of water flow rate with x_{WGS} and CO_2 content in feed, and (d) Variation	355

of outlet gas and coolant temperatures with coolant flow rate and methanol production rate

Fig. 8.7. Total CO₂ equivalent for *Case 1*: (a) Variation of the total CO₂ 357
equivalent with the methanol production rate, and (b) Contribution of
various factors to the CO₂ equivalent

Fig. 8.8. Variation of properties along reactor length for chromosome A. (a) 359
Component flow rates, (b) gas and coolant temperature, (c) reaction
rates, (d) CO₂ and H₂O flow rates, and (e) Contribution of CO₂
hydrogenation reaction to the net rate of production of methanol

Fig. 8.9. Variation of properties along reactor length for chromosome B (a) 362
Component flow rates, (b) Gas and coolant temperature, (c) Reaction
rates, and (d) Contribution of CO₂ hydrogenation reaction to the net rate
of production of methanol

Fig. 8.10. Results for the optimization of the closed-circuit process (*Case 2*) and 364
comparison with *Case 1* (a) Pareto-optimal front and, (b-i) effect of
decision variables.

Fig. 8.11. Results for optimization of the closed-circuit process (*Case 2*) (a) 368
Conversion of CO_x and comparison with *Case 1*, (b) Variation of the
recycle to feed ratio with CO₂ content, (c) variation of exit H₂O flow
rate with x_{WGS} and CO₂ content in feed, and (d) Variation of outlet
coolant temperature with coolant flow rate and methanol production
rate

Fig. 8.12. Total CO₂ equivalent for *Case 2*: (a) Variation of the total CO₂ 370
equivalent with the methanol production rate, and (b) Contribution of
various factors to the CO₂ equivalent

Fig. 8.13. Variation of properties along reactor length for chromosome P (a) 372
Component flow rates, (b) Gradients of flow rates of reactants, (c)
Reaction rates, and (d) Gas and coolant temperature

Fig. 8.14. Variation of properties along reactor length for chromosome Q (a) 374
Component flow rates, (b) Gas and coolant temperature, and (c) Rates
of heterogeneous reactions

LIST OF TABLES

Table 2.1.	Classification of chemical solvents for acid gas removal	41
Table 3.1.	Global kinetic models for homogeneous reactions	107
Table 3.2.	Case study inputs for screening of global kinetic models for homogeneous reactions	111
Table 3.3.	Rate expressions and parameters for heterogeneous reactions	113
Table 4.1.	Composition of the coal-derived syngas at the gasifier outlet used as design basis	148
Table 4.2.	Removal and tolerance compatibility matrix (RTCM) used for screening and sequencing of processes	151
Table 4.3.	Process-temperature range matrix (PTRM)	152
Table 4.4.	Process-pressure range matrix (PPRM)	153
Table 4.5.	Process-environmental impact compatibility matrix	154
Table 5.1.	Composition of syngas before the WGS reactor	210
Table 5.2.	Details of chromosomes selected for dynamic stability analysis	232
Table 6.1.	Composition of raw syngas before the catalytic reactor	256
Table 6.2.	Decision variables for chromosomes A and B	269
Table 7.1.	COS adsorption energy on hydroxylated γ -Al ₂ O ₃ slabs	302
Table 7.2.	Activation energies for formation of hydrogen thiocarbonate species (HTC ₁ and HTC ₂) on hydroxylated γ -Al ₂ O ₃ (110) surface	305
Table 7.3.	Activation energies for intramolecular transformation of HTC ₁ species on hydroxylated γ -Al ₂ O ₃ (110) surface	310
Table 7.4.	Activation energies for surface proton extraction by transformed HTC ₁ species on hydroxylated γ -Al ₂ O ₃ (110) surface	312

Table 7.5.	Activation energies for H ₂ O-mediated conversion of HTC ₂ species on hydroxylated γ -Al ₂ O ₃ (110) surface	314
Table 7.6.	Activation energies for decomposition of surface bicarbonate species on hydroxylated γ -Al ₂ O ₃ (110) surface.	316
Table 7.7.	Combined mechanism of COS hydrolysis on γ -Al ₂ O ₃ (110) surface	320
Table 7.8.	Rate parameters for COS hydrolysis on hydroxylated γ -Al ₂ O ₃ (110) surface	321
Table 8.1.	Fixed parameters for the methanol production process	337
Table 8.2.	Kinetic parameters for refitted Graff's model	340
Table 8.3.	Decision variables and respective bounds	347
Table 8.4.	Details of chromosomes chosen for detailed analysis of reactor operation: <i>Case 1</i>	358
Table 8.5.	Details of chromosomes chosen for detailed analysis of reactor operation: <i>Case 2</i>	371