FLUIDIZED BED MEMBRANE REACTOR FOR STEAM REFORMING OF HIGHER HYDROCARBONS

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

The Faculty of Graduate Studies

(Chemical & Biological Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA (Vancouver)

July 2010

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ABSTRACT

With growing demand for hydrogen in the industrial and energy sectors, research on novel hydrogen production processes is gaining importance. Fluctuations in price and availability of different hydrocarbons emphasize the need to diversify feedstock options beyond natural gas, the major source for hydrogen. Traditional steam reformers for making hydrogen from hydrocarbons suffer from low catalyst effectiveness factors, poor heat transfer and limited hydrogen yield due to thermodynamic equilibrium constraints.

A fluidized bed membrane reactor (FBMR) was designed, fabricated, installed with close attention to safety and operated with methane, propane and heptane as feedstocks at average bed temperatures up to 550°C and pressures up to 800 kPa. When operated without membranes, near-equilibrium conditions were achieved inside the reactor with fluidized catalyst due to the fast reforming reactions. Installation hydrogen permselective Pd₇₇Ag₂₃ membrane panels inside the reactor to extract pure hydrogen shifted the reaction towards complete conversion of the hydrocarbons, including methane, the key intermediate when propane and heptane were the feed hydrocarbons. Reforming of higher hydrocarbons was found to be limited by the reversibility of the steam reforming of this methane. To assess the performance due to hydrogen *in situ* withdrawal, experiments were conducted with one and six membrane panels along the reactor. The results demonstrated that the FBMR could produce pure hydrogen from higher hydrocarbon feedstocks at moderate operating temperatures of 475-550°C.

A two-phase fluidized bed reactor model was developed, with gas assumed to be in plug flow in both the bubble and dense phases. Diffusional mass transfer, as well as bulk convective flow between the phases, was incorporated to account for concentrations changing due to reactions predominantly in the dense phase, and due to increased molar flow due to reaction. Membranes withdraw hydrogen from both the dense and bubble phases.

These studies show that an FBMR can provide compact reactor system with favourable hydrogen yield, and high purity. The model predicted feedstock flexibility capabilities achieved by the experiments, with the higher hydrocarbon feedstock rapidly producing methane and the non-permeate mixture approaching chemical equilibrium.

TABLE OF CONTENTS

ABSTRACT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	viii
LIST OF FIGURES	ix
NOMENCLATURE	xiv
ACKNOWLEDGEMENTS	xviii
DEDICATION	xix
CO-AUTHORSHIP STATEMENT	XX
CHAPTER 1. INTRODUCTION	1
1.1 Thesis Overview	1
1.1.1 Research objectives	1
1.1.2 Thesis outline	2
1.2 Hvdrogen Demand	
1.2.1 Climate change and the hydrogen economy	
1.2.2 Industrial uses of hydrogen	4
1.3 Manufacture of Hvdrogen	5
1.3.1 Processes for hydrogen from hydrocarbons	6
1.3.2 Steam reforming for hydrogen production	8
1.3.3 Steam reforming of higher hydrocarbons	9
1.3.4 Industrial hydrogen producing units using steam reforming process	10
1.4 Steam Reforming Catalysts	13
1.4.1 Common steam reforming catalysts	13
1.4.2 Coke formation and catalyst deactivation	
1.4.3 Promotion of steam reforming catalysts	14
1.5 FBMR for Steam Reforming of Hydrocarbons	15
1.5.1 Limitations of fixed bed steam reformer	15
1.5.2 Hydrogen removal using permselective membranes	
1.5.3 Fluidization of catalysts	18
1.5.4 Fluiuizeu deu memorane reformer	18
1.6 FBMR for Steam Reforming of Higher Hydrocarbons	
1.6.1 Previous studies	
1.0.2 Uurrent research	19
1.7 References	

CHAPTER 2. PILOT SCALE EXPERIMENTAL SETUP FOR HYDROGEN PRODUCTION FROM HIGHER HYDROCARBONS: SAFETY CONSIDERATIONS AND IMPLEMENTATION

AND IMPLEMENTATION	44
2.1 Introduction	44
2.2 Pilot Plant Lavout	45
2.2 Front Fund Dayout	
2.2.1 Fluidized Bed Membrane Reactor (FBMR)	
2.2.2 Findalized Ded Membrane Reactor (FDMR)	53
2.2.4 Reformer gas withdrawal section	53
2.2.5 Gas sampling	
2.3 Objectives of Experimental Setup	53
2.4 Toxicological and Safety Information of Materials Encountered	54
2.5 Safety Considerations during FBMR Operation	55
2.5.1 Temperature control	55
2.5.2 Pressure control	
2.5.3 Prevention of backflow	56
2.5.4 Hazardous gas leakage	57
2.5.5 Air ingress into hydrogen permeate section	57
2.5.6 Gas sampling	58
2.5.7 Trips and emergency shutdown	58
2.5.8 Catalyst handling	59
2.5.9 Insulation	59
2.5.10 Electrical safety	59
2.5.11 Safety apparel	59
2.5.12 Safe working habits	60
2.5.13 Process control for FBMR operation	60
2.6 Conclusions	60
2.7 References	
CHAPTER 3. STEAM REFORMING OF PROPANE IN A FLUIDIZED BED	
MEMBRANE REACTOR FOR HYDROGEN PRODUCTION	
3.1 Introduction	
3.1.1 Background	
3.1.2 Equilibrium compositions in steam reforming of propane	
3.1.3 Steam reforming of propane: Industrial practice	
3.1.4 Fluidized bed membrane reactor (FBMR)	
3.2 Catalysts for Steam Reforming of Propane	88
3.2.1 Catalyst selection	88
3.2.2 Micro-reactor testing of RK-212 catalyst particles	89
3.3 Experimental Set-up and Procedure	
3.3.1 Selective hydrogen removal	
3.3.2 Heat supply to the reactor	91
3.3.3 Experiments	91
3.4 Experimental Results	

3.5	Discussion	
3.6	Conclusions	
3.7	References	118
CHAPT MEMBI	ER 4. STEAM REFORMING OF HEPTANE IN A FLUIDIZED BED	123
4.1 1 1	Introduction	123
4.1.	Catalyst issues in steam reforming of higher hydrocarbons	123
4.1.	3 Naphtha steam reforming: Industrial practice	
4.1.	4 Thermodynamics of n-heptane steam reforming	127
4.2	FBMR for Steam Reforming of Heptane	127
4.2.	1 FBMR experimental set-up	127
4.2.	2 Experimental plan and performance characterization	128
4.3	Results and Discussion	129
4.3.	FBMR experiments	129
4.3.	2 Influence of key operating parameters	130
4.3.	3 Hydrogen purity	
4.3.	4 Discussion	134
4.4	Conclusions	135
4.5	References	
	neger ences	
CHAPT HYDRO	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS	R FOR S 162
CHAPT HYDRO 5.1	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS Introduction	R FOR S 162 <i>162</i>
CHAPT HYDRO <i>5.1</i> 5.1.	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBON <i>Introduction</i> Hydrogen from higher hydrocarbons feedstock	R FOR S 162 <i>162</i> 162
CHAPT HYDRO 5.1 5.1. 5.1.	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS <i>Introduction</i> I Hydrogen from higher hydrocarbons feedstock	R FOR S 162 162 162 163
CHAPT HYDRO 5.1 5.1. 5.1. 5.2	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS <i>Introduction</i> 1 Hydrogen from higher hydrocarbons feedstock. 2 Fluidized Bed Membrane Reactors (FBMR) <i>Description</i> .	R FOR S 162 162 163 164
CHAPT HYDRO 5.1 5.1. 5.1. 5.2 5.2 5.2.	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOF GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS <i>Introduction</i> Hydrogen from higher hydrocarbons feedstock Fluidized Bed Membrane Reactors (FBMR) <i>Description</i> Reactions and rate equations	R FOR S 162 162 163 164 164
CHAPT HYDRO 5.1 5.1. 5.1. 5.2 5.2 5.2. 5.2.	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS Introduction 1 Hydrogen from higher hydrocarbons feedstock 2 Fluidized Bed Membrane Reactors (FBMR) 1 Reactions and rate equations 2 Model simplifications	R FOR S 162 162 163 164 164 164
CHAPT HYDRO 5.1 5.1. 5.1. 5.2 5.2. 5.2. 5.2. 5.2.	 ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS <i>Introduction</i> I Hydrogen from higher hydrocarbons feedstock 2 Fluidized Bed Membrane Reactors (FBMR) <i>Description</i> 1 Reactions and rate equations 2 Model simplifications 3 Fluidized bed hydrodynamic model 	R FOR S 162 162 163 164 164 164 165
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.3	 ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS <i>Introduction</i> Hydrogen from higher hydrocarbons feedstock. Fluidized Bed Membrane Reactors (FBMR) <i>Description</i> Reactions and rate equations Model simplifications Fluidized bed hydrodynamic model 	R FOR S 162 162 163 164 164 164 165 170
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.2. 5.3 5.3.	 ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS <i>Introduction</i> Hydrogen from higher hydrocarbons feedstock Fluidized Bed Membrane Reactors (FBMR) <i>Description</i> Reactions and rate equations Model simplifications Fluidized bed hydrodynamic model <i>Model Predictions versus Experimental Results</i> Experimental data for comparison with model predictions 	R FOR S 162 162 163 164 164 164 165 170 170
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.2. 5.3. 5.3. 5.3.	 ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS <i>Introduction</i> I Hydrogen from higher hydrocarbons feedstock. 2 Fluidized Bed Membrane Reactors (FBMR) <i>Description</i> I Reactions and rate equations. 2 Model simplifications 3 Fluidized bed hydrodynamic model. <i>Model Predictions versus Experimental Results</i> 1 Experimental data for comparison with model predictions 2 Membrane effectiveness factor 	R FOR S 162 162 163 164 164 164 164 165 170 170
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.3 5.3. 5.3. 5.3.	 ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOF GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS <i>Introduction</i> Hydrogen from higher hydrocarbons feedstock. Fluidized Bed Membrane Reactors (FBMR) <i>Description</i> Reactions and rate equations Model simplifications Fluidized bed hydrodynamic model <i>Model Predictions versus Experimental Results</i> Experimental data for comparison with model predictions Membrane effectiveness factor Test results with no membrane panels. 	R FOR S 162 162 162 163 164 164 164 164 165 <i>170</i> 170 171 171
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.2. 5.3. 5.3. 5.3.	 ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS <i>Introduction</i> Hydrogen from higher hydrocarbons feedstock. Fluidized Bed Membrane Reactors (FBMR) <i>Description</i> Reactions and rate equations. Model simplifications Fluidized bed hydrodynamic model <i>Model Predictions versus Experimental Results</i> Experimental data for comparison with model predictions Membrane effectiveness factor Test results with no membrane panel present. 	R FOR S 162 162 163 164 164 164 164 165 170 170 171 171 171
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.2. 5.3. 5.3. 5.3.	 ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOF GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS <i>Introduction</i> Hydrogen from higher hydrocarbons feedstock. Fluidized Bed Membrane Reactors (FBMR) <i>Description</i> Reactions and rate equations. Model simplifications Fluidized bed hydrodynamic model. <i>Model Predictions versus Experimental Results</i> Experimental data for comparison with model predictions Membrane effectiveness factor Test results with no membrane panels Test results with six membrane panels 	R FOR S 162 162 162 163 164 164 164 164 165 <i>170</i> 170 171 171 172 173
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.2. 5.3. 5.3. 5.3.	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS Introduction 1 Hydrogen from higher hydrocarbons feedstock 2 Fluidized Bed Membrane Reactors (FBMR) Description 1 Reactions and rate equations 2 Model simplifications 3 Fluidized bed hydrodynamic model Model Predictions versus Experimental Results 1 Experimental data for comparison with model predictions 2 Membrane effectiveness factor 3 Test results with no membrane panels 4 Test results with one membrane panel present 5 Test results with six membrane panels Discussion of Results	R FOR S 162 162 163 164 164 164 164 165 170 170 171 171 173
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.2. 5.3. 5.3. 5.3.	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS Introduction 1 Hydrogen from higher hydrocarbons feedstock. 2 Fluidized Bed Membrane Reactors (FBMR) 2 Fluidized Bed Membrane Reactors (FBMR) 2 Description 1 Reactions and rate equations 2 Model simplifications 3 Fluidized bed hydrodynamic model Model Predictions versus Experimental Results	R FOR S 162 162 163 164 164 164 164 165 170 171 171 173 173
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.2. 5.3. 5.3. 5.3.	 ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS <i>Introduction</i> Hydrogen from higher hydrocarbons feedstock. Fluidized Bed Membrane Reactors (FBMR) <i>Description</i> Reactions and rate equations. Model simplifications Fluidized bed hydrodynamic model. <i>Model Predictions versus Experimental Results</i> Experimental data for comparison with model predictions Membrane effectiveness factor Test results with no membrane panels. Test results with one membrane panel present. Test results with six membrane panels <i>Discussion of Results</i> Comparison between model and experimental data Membrane permeation effectiveness factor 	R FOR S 162 162163164164164164165170170171171172173173174
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.2. 5.3. 5.3. 5.3.	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOF GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS Introduction Hydrogen from higher hydrocarbons feedstock Pluidized Bed Membrane Reactors (FBMR) Description Reactions and rate equations Model simplifications Fluidized bed hydrodynamic model Model Predictions versus Experimental Results Experimental data for comparison with model predictions Membrane effectiveness factor Test results with no membrane panels Test results with six membrane panels Discussion of Results Comparison between model and experimental data Membrane permeation effectiveness factor Two-phase fluidization model	R FOR S 162 162 163 164 164 164 164 164 165 170 171 171 173 173 173 173 174
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.2. 5.3. 5.3. 5.3.	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOF GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS Introduction 1 Hydrogen from higher hydrocarbons feedstock. 2 Fluidized Bed Membrane Reactors (FBMR) Description 1 Reactions and rate equations. 2 Model simplifications 3 Fluidized bed hydrodynamic model. Model Predictions versus Experimental Results 1 Experimental data for comparison with model predictions 2 Membrane effectiveness factor 3 Test results with no membrane panel present. 5 Test results with one membrane panel present. 5 Test results with six membrane panels Discussion of Results. 1 Comparison between model and experimental data 2 Membrane permeation effectiveness factor 3 Two-phase fluidization model.	R FOR S 162 162 163 164 164 164 164 164 165 170 170 171 171 173 173 175 176
CHAPT HYDRO 5.1 5.1. 5.2 5.2. 5.2. 5.2. 5.2. 5.3. 5.3. 5.3.	ER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR GEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS Introduction 1 Hydrogen from higher hydrocarbons feedstock. 2 Fluidized Bed Membrane Reactors (FBMR) Description	R FOR S 162 162 163 164 164 164 164 164 165 170 170 171 171 173 173 174 175 176

CHAP	FER 6. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WO)RK 203
<i>6.1</i>	Conclusions	203
6.2	Limitations of FBMR Steam Reforming	204
6.3	Recommendations for Future Work	205
6.4	Specific Recommendations for Reactor Built in the Current Study	207
6.5	References	208
APPEN FOR H HYDR	IDIX A. KINETIC SIMULATION OF A COMPACT REACTOR SYSTEM YDROGEN PRODUCTION BY STEAM REFORMING OF HIGHER OCARBONS	209
A.1	Introduction	209
A.2	Irreversibility of Steam Reforming of Higher Hydrocarbons	211
A.3	Kinetic Modeling of a Fluidized Bed Membrane Reactor	212
A.	3.1 Model assumptions	212
A.	3.2 Model equations for reactor side	213
A.	3.3 Model equations for separation side	213 214
A A	Rosults and Discussion	214
л. т Л. т	Condusions	214
A.J		210
A.A	Appendices	217
A.	A.2 Hvdrodvnamic equations for the 2-phase model	217
A.6	References	229
		/
APPEN	IDIX B. FBMR OPERATING MANUAL	232
B. 1	Introduction	232
<i>B.2</i>	Steam Reforming Experiments: Reactor Start-up	232
B. 3	During Steam Reforming Experiments	236
B. 4	Keep-Warm Mode of Operation	236
B. 5	Normal Shutdown	237
B.6	Emergency Shutdown	238
APPEN	DIX C. FBMR ASSEMBLY DRAWINGS	239
APPEN	DIX D. CATALYST EVALUATION UNIT	247
APPEN THE F	IDIX E. HYDRODYNAMIC BEHAVIOUR IN A PLEXIGLAS COLUMN A	AND 251
<i>E.1</i>	Fluidizability of the Catalyst Particles	251
<i>E.2</i>	Superficial Gas Velocities in the FBMR	252

<i>E.3</i>	Future Work with Cold Model	
<i>E.4</i>	References	
APPEN	DIX F. MODEL SENSITIVITY ANALYSIS	
<i>F.1</i>	Model Sensitivity to Reaction Rate Constants	
<i>F.2</i>	Model Sensitivity to Interphase Mass Transfer	
<i>F.3</i>	Conclusions	
<i>F.4</i>	References	
APPEN	DIX G. EXPERIMENTAL DATA TABULATION (FBMR)	272

LIST OF TABLES

Table 1.1:	World fertilizer consumption (Calendar year basis)
Table 2.1:	Gases and liquids in FBMR steam reforming process
Table 2.2:	Heaters distribution for the FBMR
Table 2.3:	Micro-GC column information for product gas analysis
Table 2.4:	Controlled parameters for FBMR steam reforming process
Table 2.5:	Performance parameters for FBMR steam reforming process
Table 2.6:	Flammability and safety information of some species encountered
Table 2.7:	Nodes in P&ID and HAZOP worksheet
Table 2.8:	Hazards and Operability Study Worksheet
Table 2.9:	Cause & Effect matrix for actions by the PLC
Table 3.1:	Density of liquid/ liquefied hydrocarbons at ambient pressure 100
Table 3.2:	Composition of RK-212 (catalyst provided by Haldor Topsoe A/S)100
Table 3.3:	Steady-state reactor measurements 101
Table 3.4:	Location of sampling ports, thermocouples and pure hydrogen withdrawal, and
height	intervals of active membrane surface102
Table 3.5:	Experimental runs for steam reforming of propane 103
Tabla 1 1.	Steady state reactor measurements 127
Table 4.1:	Leastion of sampling ports, thermosourles and pure hydrogen with drawal and
Lapie 4.2.	intervals of active membrane surface
Table 4.3	Miero CC column information for product gas analysis
Table 4.5:	Experimental runs for steam reforming of a hontone
1 able 4.4:	Experimental runs for steam reforming of n-neptane
Table 5.1:	Reactor physical details
Table 5.2:	Reaction rate equations
Table 5.3:	Kinetic parameters
Table 5.4:	Experimental conditions for runs where data are compared with model
predic	tions
Table 5.5:	FBMR performance with variations in permeation effectiveness factor 181
	-

 Table A.1: Reactor geometry and base simulation parameters
 219

LIST OF FIGURES

Figure 1.1: H	lydrogen demand and sources	21
Figure 1.2: N	atural range of H ₂ /CO ratio for natural gas	21
Figure 1.3: C	lobal distribution of oil and gas reserves	22
Figure 1.4: N	atural gas price fluctuation	23
Figure 1.5: C	Crude oil price fluctuation	23
Figure 1.6: T	ypical flow-chart configuration of a pre-reformer	24
Figure 1.7: P	re-reformer temperature profiles for different feeds	24
Figure 1.8: R	Reforming section for production of ammonia synthesis gas	25
Figure 1.9: R	Reforming for the production of methanol synthesis gas	25
Figure 1.10:	Relative rates of carbon formation on nickel catalysts	26
Figure 1.11:	Equilibrium methane conversion in steam reforming of methane as a	
function	of temperature and pressure (steam-to-carbon ratio = 3)	26
Figure 1.12:	Enhancement of methane conversion with in-situ hydrogen removal. Stea	m-
to-carbo	n ratio = 3, reactor pressure = 1000 kPa	27
Figure 1.13:	Hydrogen permeabilities of selected metals	27
Figure 1.14:	Pressure-composition isotherms of Pd-H system	28
Figure 1.15:	Equilibrium compositions for heptane steam reforming	29
Figure 1.16:	Circulating fluidized bed membrane reformer configuration for steam	
reformi	ig of heptane	
		30

Figure 2.1: FBN	AR pressure vessel supported on a mobile stand	71
Figure 2.2 (a):	P&ID of pilot plant layout (Supplementary gas feeding section)	72
Figure 2.2 (b):	P&ID of pilot plant layout (Steam and hydrocarbon feeding section)	73
Figure 2.2 (c):	P&ID of pilot plant layout (FBMR)	74
Figure 2.2 (d):	P&ID of pilot plant layout (Gas sampling and Permeate sections)	75
Figure 2.3 (a):	Strength of SA-240 grade 304H plate material as a function of	
temperatu	re	76
Figure 2.3 (b):	MAWP rating of the FBMR pressure vessel	77
Figure 2.4 (a):	Instrumentation ports on a lateral flange cover, also showing a membr	ane
panel insta	lled	78
Figure 2.4 (b):	Membrane panel dimensions	79
Figure 2.5: Pre	ssure transducers arrangement	80

Figure 3.1: Equilibrium compositions (dry gas) in propane steam reforming for steam-to	0-
carbon molar ratio = 5.0: (a) P = 400 kPa; (b) P = 1000 kPa	104
Figure 3.2: Schematic of micro-reactor set-up to study steam reforming of propane	105
Figure 3.3: Propane conversion for steam reforming in micro-reactor, T = 525°C,	
$H_2O = 30 \text{ g/h}$	106
Figure 3.4: The FBMR pressure vessel, showing dimensions of membrane panel, and	
arrangement of ports on each lateral flange cover where membrane panels are	
installed	107
Figure 3.5: Schematic of experimental setup to study steam reforming of propane in an	
FBMR	108

Figure 3.6: Experimental yields and temperature for propane steam reforming without membrane panels at average reactor temperature of 500°C and steam-to-carbon ratio molar ratio of 6.0. Total reactor feed = 0.673 mols/min.....109 Figure 3.7: Parity plot of experimental hydrogen yield without membrane panels against Figure 3.8: Experimental yields and temperature for propane steam reforming at average reactor temperature of 485°C and steam-to-carbon molar ratio 5.0. One membrane panel installed, spanning from 0.95 to 1.16 m above distributor. Total reactor feed = Figure 3.9: Experimental yields and temperature for propane steam reforming at average reactor temperature of 500°C, pressure 600 kPa, and steam-to-carbon molar ratio Figure 3.10: Experimental yields and temperature for propane steam reforming at average reactor temperature of 500°C, permeate pressure 25 kPa, and steam-tocarbon molar ratio 5.0. Six membrane panels installed. Total reactor feeds = 0.410, Figure 3.11: Experimental yields and temperature for propane steam reforming at average reactor temperature of 500°C, pressure 600 kPa, and permeate pressure 25 kPa. Six membrane panels installed. Total reactor feed = 0.614 mols/min.....114 Figure 3.12: Experimental yields and temperature for propane steam reforming at pressure of 600 kPa, permeate pressure 25 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed. Total reactor feeds = 0.635, 0.614, and 0.595 mols/min for 475, 500, and 525°C respectively......115 Figure 3.13: Experimental yields and temperature for propane steam reforming at average reactor temperature of 500°C, pressure 600 kPa, permeate pressure 25 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed......116 Figure 3.14: Parity plot of experimental yields against equilibrium values at local temperatures if there was no hydrogen removal: (a) Hydrogen vield (b) Methane Figure 4.1: Key components in a modern steam reforming plant for hydrogen from higher hvdrocarbon feedstock......141 Figure 4.2: Dry gas equilibrium composition for steam-to-carbon molar ratio of 5.0: Figure 4.3: Dry gas composition for reactor pressure of 400 kPa: (a) Steam-to-carbon molar ratio = 4.0; (b) Steam-to-carbon molar ratio = 6.0. No membranes present.. 143 Figure 4.5: (a) Dimensions of membrane panel. (b) Ports arranged on each side-opening cover where membrane panels are installed......145 Figure 4.6: Schematic of experimental set-up to study steam reforming of n-heptane.....146 Figure 4.7: Experimental yields and temperature for heptane steam reforming without active membrane panels at reactor pressure of 470 kPa and steam-to-carbon ratio molar ratio of 5.0. Total reactor feed = 0.673 and 0.766 mols/min at 520 and 450°C Figure 4.8: Experimental yields and temperature for heptane steam reforming without active membrane panels at average reactor temperature of 520°C and steam-tocarbon ratio molar ratio of 5.0. Total reactor feed = 0.673 mols/min......148

Figure 4.9: Experimental yields and temperature for heptane steam reforming without active membrane panels at average reactor temperature of 520°C and reactor pressure of 725 kPa. Total reactor feed = 0.673 mols/min......149

Figure 4.10: Parity plot of experimental yields without active membrane panels against local equilibrium values: (a) Hydrogen yield (b) Methane yield......150

Figure 4.13: Experimental yields and temperature for heptane steam reforming at average reactor temperature of 500°C, permeate pressure 25 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed. Total reactor feeds = 0.410, 0.614, and 0.819 mols/min for P = 400, 600, and 800 kPa respectively.......153

Figure 4.14: Experimental yields and temperature for heptane steam reforming at average reactor temperature of 475°C, pressure 600 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed. Total reactor feed = 0.635 mols/min...... 154

Figure 4.15: Experimental yields and temperature for heptane steam reforming at average reactor temperature of 500°C, pressure 600 kPa, and permeate pressure 25 kPa. Six membrane panels installed. Total reactor feed = 0.614 mols/min......155

Figure 4.16: Experimental yields and temperature for heptane steam reforming at average reactor temperature of 500°C, pressure 600 kPa, permeate pressure 25 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed...... 156

Figure 5.1: Schematic of reactor geometry18	2
Figure 5.2: Schematic of the FBMR kinetic model	3
Figure 5.3: A cake of catalyst formed around the ROG filter	34
Figure 5.4: Particulate coating formed on the membranes during FBMR operation: (a) A	
fresh membrane before installation (b) the membrane surface covered by the coating	
(c) a view of other side of the same membrane showing a clean shining membrane foil	
exposed after tapping off a part of the coating18	6
Figure 5.5: FBMR performance for experiment Heptane 1.b	57
Figure 5.6: FBMR performance for experiment Propane 1.b	8
Figure 5.7: FBMR performance for experiment Heptane 4.b	9
Figure 5.8: FBMR performance for experiment Propane 2.b	0
Figure 5.9: FBMR performance for experiment Methane 2.c	1
Figure 5.10: FBMR performance for experiment Heptane 5.b	2
Figure 5.11: FBMR performance for experiment Propane 3.c	3
Figure 5.12: FBMR performance for experiment Methane 1.c)4
Figure 5.13: Parity plot for permeate hydrogen yields	95
Figure 5.14: Parity plot for methane vields	6
Figure 5.15: Parity plot for carbon oxides yields	7

Figure 5.16:	Effect of membrane permeation effectiveness factor (Propane Experiment	ıt
3.c)		. 198
Figure A.1:	Equilibrium compositions in n-heptane steam reforming at varying	
tempera	tures and pressures	
Figure A.2:	Schematic diagram of the kinetic model	221
Figure A.3:	Predicted species concentrations in the two phases at 650°C, 10 bars:	
(a) Dens	e phase (b) Bubble Phase	222
Figure A.4:	Predicted methane and hydrogen yields at 650°C, 10 bars: (a) Methane	
(b) Hydı	ogen	. 223
Figure A.5:	Predicted heptane conversions at 650°C, 10 bars	.224
Figure A.6:	Predicted effect of S/C ratios on yields at 650°C, 10 bars: (a) Permeate	
hydroge	n (b) Retentate hydrogen	. 225
Figure A.7:	Reaction zones in FBMR system for higher hydrocarbons: Pre-reforming	5,
reformir	ng and purification in a single unit	. 226
Figure A.8: I	Dependence of hydrogen yields on membrane thickness at 650°C, 10 bars:	
(a) Perm	eate hydrogen (b) Retentate hydrogen	. 227
Figure A.9:	Dependence of hydrogen yields on specific membrane area at 650°C,	
10 bars:	(a) Permeate hydrogen (b) Retentate hydrogen	
Figure C.1:	FBMR assembly: Shell weldment	240
Figure C.2:	FBMR pressure vessel assembly	. 241
Figure C.3:	Typical rectangular cover for side opening	. 242
Figure C.4:	Assembly of rectangular cover and membrane panel	. 243
Figure C.5:	Assembly of inlet head, showing feed distributor	. 244
Figure C.6:	General arrangement of FBMR on reactor stand	. 245
Figure C.7:	Location of band heaters (denoted in brown) mounted on the FBMR	. 246
8		
Eigune D 1.	Catalyst evaluation units Miana reactor feeding system Dart I	240
Figure D.1:	Catalyst evaluation unit: Micro-reactor feeding system, Part I	248
Figure D.2:	Catalyst evaluation unit: Micro-reactor feeding system, Part II	249 250
Figure D.5:	Catalyst evaluation unit: Micro-reactor and gas analysis	. 230
Figure E.1:	Plexiglas column for hydrodynamic studies	. 254
Figure E.2:	Plexiglas column dimensions	. 255
Figure E.3:	Catalyst bed being lifted by the gas	. 256
Figure E.4:	Fresh catalyst particles	. 257
Figure E.5:	Used catalyst particles	. 258
Figure E.6:	Gas superficial velocities for experiment Propane 1.a	. 259
Figure E.7:	Gas superficial velocities for experiment Propane 2.d	. 259
Figure E.8:	Gas superficial velocities for experiment Propane 3.c	. 260
Figure E.9:	Gas superficial velocities for experiment Heptane 1.a	. 260
Figure E.10:	Gas superficial velocities for experiment Heptane 4.d	. 261
Figure E.11:	Gas superficial velocities for experiment Heptane 5.b	. 261

Figure F.1: FBMR performance with variations of reaction rate constants for experiment	t
Propane 3.c	65
Figure F.2: Methane concentrations with variations of reaction rate constants for	
experiment Propane 3.c2	66
Figure F.3: Hydrogen concentrations with variations of reaction rate constants for experiment Propage 3.c	267
Figure F.4: FBMR performance with variations of interphase mass transfer for experiment Propane 3.c	68
Figure F.5: Methane concentrations with variations of interphase mass transfer for experiment Propane 3.c	69
Figure F.6: Hydrogen concentrations with variations of interphase mass transfer for experiment Propane 3.c	70

NOMENCLATURE

a_b	Specific surface area of gas bubbles (m^2/m^3)
A	Cross-sectional area of bed (m ²)
A_P	Membrane permeation area (m)
$A_{P}^{'}$	Membrane permeation area per unit length of membrane (m^2/m)
Ar	Archimedes number (-)
ATR	Autothermal reforming
$C_{i,b}$	Molar concentration of species i per unit volume of bubble phase (mol/m ³)
$C_{i,d}$	Molar concentration of species <i>i</i> per unit volume of dense phase (mol/m ³)
CFD	Computational Fluid Dynamics
$d_{ m b}$	Bubble diameter (m)
$d_{ m bm}$	Maximum bubble diameter (m)
$d_{ m p}$	Mean particle diameter (m)
D_{ie}	Effective molecular diffusivity of component i (m ² /s)
D_{ij}	Binary diffusivity of component <i>i</i> in <i>j</i> , with $i \neq j$ (m ² /s)
E_{H_2}	Activation energy for permeation (J/mol)
$F_{i,b}$	Molar flow rate of species i in bubble phase (mol/s)
$F_{i,d}$	Molar flow rate of species i in dense phase (mol/s)
$F_{i,fb}$	Molar flow rate of species i in freeboard (mol/s)
g	Acceleration due to gravity (m/s^2)
h	Vertical coordinate measured from distributor (m)
h_{fb}	Vertical coordinate measured from dense catalyst bed surface (m)
ΔH	Heat of reaction (kJ/mol)
k_{iq}	Interphase mass transfer component for species i (m/s)
N_C	Number of components
Nor	Number of orifices in distributor
N_R	Number of reactions
O2R	Oxidative reforming
$P_{H2,M}$	Hydrogen partial pressure on permeate side
$P_{H2,R}$	Hydrogen partial pressure on reactor side
Р	FBMR pressure monitored in freeboard (kPa)

P_m	Permeate side pressure (kPa)
P_i	Partial pressure of species <i>i</i> (bar)
$P_i^{'}$	Partial pressure of species <i>i</i> (kPa)
$P_{H_2,b}$	Partial pressure of hydrogen in bubble phase (atm)
$P_{H_2,d}$	Partial pressure of hydrogen in dense phase (atm)
$P_{H_2,p}$	Partial pressure of hydrogen on permeate side (atm)
P_{M0}	Pre-exponential factor for permeation (mole/(m.min.atm ^{0.5}))
POX	Partial oxidation
$Q_{b o d}$	Volumetric balancing cross-flow from bubble to dense phase (m ³ /s)
$Q_{d \to b}$	Volumetric balancing cross-flow from dense to bubble phase (m ³ /s)
$Q_{d,req}$	Flow requirement for dense phase to prevent de-fluidization (m ³ /s)
$Q_{{\it mi},b}$	Permeation rate (molar) of species <i>i</i> per unit length from reactor side to permeate side for
	bubble phase (mol/(m.s))
$Q_{{\scriptscriptstyle m}i,d}$	Permeation rate (molar) of species <i>i</i> per unit length from reactor side to permeate side for
	dense phase (mol/(m.s))
Q_{H2}	Hydrogen diffusion flux through membrane
R	Universal gas constant (J/mol/K)
R_{j}	Rate of j^{th} reaction (mol/kg catalyst/s)
SCR	Steam-to-carbon molar ratio
SMR	Steam methane reforming
Т	Temperature (K)
T_{av}	Bed average temperature (based on temperatures at the six membrane panels or
	dummies) (°C)
U	Superficial gas velocity (m/s)
\mathcal{Y}_i	Mole fraction of component <i>i</i> in gas mixture (-)
Y	Correction coefficient for modified two-phase theory (-)

Greek Letters

$\delta_{\scriptscriptstyle H_2}$	Thickness of hydrogen selective membranes (m)
\mathcal{E}_{mf}	Bed voidage at minimum fluidization (-)
\mathcal{E}_{b}	Volume fraction of catalyst bed occupied by bubble phase (-)

\mathcal{E}_d	Volume fraction of catalyst bed occupied by dense phase (-)
$\pmb{\phi}_b$	Volume fraction of catalyst bed occupied by solid particles in bubble phase (-)
$\phi_{_d}$	Volume fraction of catalyst bed occupied by solid particles in dense phase (-)
$\pmb{\phi}_{fb}$	Volume fraction of freeboard occupied by solid particles (-)
${\gamma}_{ij}$	Stoichiometric coefficient of component i in j^{th} reaction
$ ho_{g}$	Gas density (kg/m ³)
$ ho_p$	Density of catalyst particle (kg/m ³)
μ_{g}	Gas viscosity (kg/m/s)

Subscripts

b	Bubble phase
d	Dense phase
i	Species <i>i</i>
in	Quantity at reactor inlet
j	Reaction j
mf	Minimum fluidization condition

Abbreviations

AAHH	High limit of toxic and combustible gas detectors
BCSA	British Columbia Safety Authority
С	Closed
ESD	Emergency shut down
FAHH	High limit flow alarm
FALL	Low limit flow alarm
FBMR	Fluidized bed membrane reactor
FFDAHH	High limit steam-to-carbon ratio alarm
FFDALL	Low limit steam-to-carbon ratio alarm
FI	Mass flow meter
FICV	Mass flow controller
FO	Fully open
HAZOP	Hazard analysis and operability
HT-BA	Band heaters

HT-CA	Cable heaters
HT-ST	Strip heaters
HTS	High temperature shift
HX	Heater
HYSYS	Commercial process simulation software
LNG	Liquefied natural gas
LPG	Liquefied petroleum gas
LTS	Low temperature shift
MTS	Medium temperature shift
MAWP	Maximum allowable working pressure
MSDS	Material Safety Data Sheet
0	Open
P&ID	Process and instrumentation diagram
РАНН	High limit pressure alarm
PALL	Low limit pressure alarm
PI	Pressure indicator (dial)
PLC	Programmable logic controller
PLOT	Porous layer open tube gas chromatography column
PPU	Porous polymer-U
PSV	Relief valve
РТ	Pressure transducer (gauge or absolute)
PTD	Differential pressure transducer
ROG	Reformer off-gas
SP	Stop
ST	Start
ТАНН	High limit temperature alarm
TALL	Low limit temperature alarm
TIC	Temperature indicator and controller
TLV	Threshold limit value
TT	Thermocouple
TWA	Time weighted average
V	Valve (either needle valve or on/off valve)
VCK	Check valve
XV	Solenoid valve

ACKNOWLEDGEMENTS

All Praise and Glory is to the Almighty who has guided me through this achievement, and for the most precious and green earth he has gifted us all.

I would like to thank all my supervisors, who have guided me throughout this challenging project. Working under Dr. Grace has been one of the most pleasant experiences, not only for my PhD research, but also in my all-round professional development. Continuous follow-up by Dr. Grace and Dr. Lim, while allowing a great degree of independence for a challenging experimental project, developed in me a sense of confidence for tackling future projects. Discussions with Dr. Elnashaie inspired me to look at Chemical Reaction Engineering from a unique way of interpretation.

I express gratitude to Dr. Xiaotao Bi, Dr. Tom Troczynski, and Dr. Tony Boyd for serving as supervisory committee members. A course with Dr. Bi also helped me significantly in understanding fluidization, one of the major topics of my research.

I am grateful to the Natural Sciences and Engineering Research Council (NSERC) and the Canada Foundation for Innovation (CFI) for providing funding for this project. I would like also to acknowledge financial support from NSERC and for recognizing my professional achievements in the form of a 2-year doctoral fellowship.

I would like to thank Alan Keelan, Bahman Ghiasi, Zaid Ahmad, Negar Zakipour, Dr. Hengzhi Chen, and Dr. Hongbo Jiang for helping me in different phases of my experimental program. Technical discussions with fellow graduate students Nabeel Aboghander, and Alexandre Vigneault, helped me in my research analyses.

Assistance of the researchers at Membrane Reactor Technologies, Dr. Tony Boyd, Dr. Anwu Li, and Ali Gulamhusein is gratefully acknowledged. They shared their experiences with FBMR, allowed me to use their instruments, and helped me carry out safety audits for my experimental set-up, a necessity for this kind of research.

I am also grateful for timely input from Darren Johnston from Varian Inc. for sample analysis with the micro-GC, and to Jeff Gomach of Haldor Topsoe for providing valuable literature on industrial practice. I would like to thank the department of Chemical and Biological Engineering for the excellent facilities, and to its staff for providing me help and support whenever I needed.

A number of friends Promod Patil, Praveen Linga, Tumuluru Jayashankar, Sujay Sarkar, Saifur Rahaman, Tabrez Siddiqui, Sharif Zaman, Venkata Tayi, Nagu Daraboina and Mohammad Masnadi - made my PhD studies an enjoyable experience.

I must acknowledge the patience and support of my parents, my wife and my son during this period. I hope their wait is now over!!!!

Dedicated to my Parents,

and

To my wife, and to little Aziz

"Earth provides enough to satisfy every man's need, but not every man's greed"

- 'Mahatma' Mohandas Karamchand Gandhi

CO-AUTHORSHIP STATEMENT

This is a manuscript-based thesis. Drs. John Grace, C. Jim Lim, and Said Elnashaie are my PhD research supervisors, and are co-authors in the manuscripts. During the fabrication and installation of the FBMR, setting up the infrastructure, and ensuring safety procedures in operation, input was received from Tony Boyd and Ali Gulamhusein from Membrane Reactor Technologies Limited, Mark Epp from Jenmar Concepts Inc., and Alan Keelan, then an undergraduate student at the University of British Columbia, who are co-authors in Chapter 2 of this thesis. Bahman Ghiasi conducted catalyst activity and stability tests in a catalyst evaluation unit as a part of his Master of Engineering research project, and is a co-author for Chapter 4. Dr. Yasemin Bolkan was involved during the first year of my research, and is a co-author of the paper included in Appendix A.

My role in the research leading to these manuscripts involved:

- 1. Planning, conceptualization, design, oversight of fabrication, and commissioning of all research equipments relating to the FBMR.
- 2. Planning, building, commissioning of the Catalyst Evaluation Unit.
- 3. Planning, designing, oversight of fabrication of a Plexiglas column for cold hydrodynamic studies.
- 4. Designing and conducting experiments, data collection, modelling and analysis of the FBMR experiments.
- 5. Conducting experiments and guiding Mr. Bahman Ghiasi for experiments with the Catalyst Evaluation Unit for testing activity and stability of steam reforming catalysts.
- 6. Preparing manuscripts, coordinating with co-authors in revising the drafts, corresponding with the publishers for publication of the papers.

The use of these manuscripts is under the permission of all the co-authors.

CHAPTER 1. INTRODUCTION

1.1 Thesis Overview

1.1.1 Research objectives

Growing demand for hydrogen as an energy carrier and a widely used-industrial commodity has intensified research on hydrogen production. Since steam reforming was introduced to industry in the 1930's, it has become the most attractive method for making hydrogen. Over the years, it has seen significant improvements, leading to the development of less costly and more efficient methods of producing synthesis gas and/or hydrogen^{1,2}.

The fluidized bed membrane reactor (FBMR) concept was pioneered at the University of British Columbia (Canada) by a group of researchers³⁻⁵, and commercialized by Membrane Reactor Technologies Ltd.⁶ Since then, the FBMR concept has been studied worldwide for hydrogen production and various other applications. The current research explores feedstock diversification for hydrogen in a fluidized bed membrane reactor, underlining the need for a flexible reformer system to be able to adapt to fluctuating feedstock availability and prices. Specific objectives include:

- 1. Modeling an FBMR for sizing a proof-of-concept reactor.
- 2. Reactor fabrication, installation, and commissioning with proper safety procedures.
- 3. Experimentation with the FBMR for different hydrocarbons heptane, propane and methane representing different categories of the most widely used feedstocks for steam reforming. Heptane is a surrogate for naphtha, which is a liquid under ambient conditions, and a feedstock for hydrogen/ syngas production in many parts of the world. Propane is a key component of LPG, which is gaseous under ambient conditions, but can be easily liquefied at relatively low pressures and abundantly available from refinery operations. Methane is the main component in natural gas, the most widely used steam reforming feedstock worldwide.
- 4. Model verification with requisite improvements and elucidation of the physical phenomena inside the FBMR.

^{*} This chapter presents the background and motivation for the present research. It starts with a statement of the main research objectives, providing an outline of the thesis write-up. Subsequently, a background is offered regarding the demand for hydrogen, methods of hydrogen production, and research trends in the steam reforming process. It ends with a note about the background work done for sizing of the reactor (FBMR) in the form of a modeling work, which has been placed in Appendix A.

1.1.2 Thesis outline

Chapter 1 details the growing demand of hydrogen in various applications, and the techniques for hydrogen production from hydrocarbons. It then describes the steps involved in traditional steam reforming as practiced by industry. This is followed by outlining the key limitations of traditional steam reformers, and considerations in introducing higher hydrocarbon feedstocks. The final section introduces the FBMR concept for higher hydrocarbons as the research focus for the rest of the thesis.

An FBMR was modeled, and designed using a two-phase fluidization model, for steam reforming of heptane. A published paper⁷ with model details and predicted performance is included as Appendix A.

The experiments in this project were conducted at temperatures up to 600°C, at elevated pressures (up to 10 bars), and with hazardous substances (methane, propane, heptane, carbon monoxide, hydrogen, and nickel catalyst powder), requiring close attention to safety issues. Chapter 2 describes the pilot plant layout details, installation, and safety considerations and implementation.

Chapter 3 describes steam reforming of heptane in the FBMR. Experiments were conducted without membranes, with one membrane and with six membranes to assess the effect of membrane area on permeation of hydrogen. Reactor performance was evaluated with variation of temperature, reactor pressure, permeate pressure, steam-to-carbon molar ratio, and superficial velocity. Chapter 4 describes experiments and parametric studies along similar lines for steam reforming of propane in the FBMR.

Chapter 5 presents an FBMR simulation model, with the dense fluidized bed described by a two-phase model, with removal of hydrogen in-situ from both phases. Both phases were treated as in plug flow, with mass exchange between the two phases due to concentration difference of species and maintenance of minimum fluidized conditions in the dense phase. An explanation was provided to the physical phenomena occurring inside the FBMR and the possible reasons for model prediction deviations from experimental data.

Chapter 6 summarizes the conclusions of the thesis with important findings of this research, and proposes recommendations for future research.

1.2 Hydrogen Demand

1.2.1 Climate change and the hydrogen economy

Recently there have been many reports projecting an alarming increase in average global temperature⁸. The effects could be catastrophic, ranging from rise in sea levels⁹, submerging community habitats and already shrinking agricultural lands¹⁰, vanishing of glaciers, unpredictable climatic patterns with severe droughts¹¹ or hurricanes, and even diseases¹².

Global warming has been attributed mainly to the release of greenhouse gases (especially CO_2) due to wide-spread dependence on fossil fuels^{8,13} (which are depleting) as a source of energy. But, at the same time, energy consumption is constantly on the rise due to increase in world population, increasing industrialization, and improved average standards of living. To maintain the balance of demand and supply, new sources of energy need to be investigated and developed, while decreasing greenhouse gas emissions.

For many, the solution lies in a gradual transition to a hydrogen economy^{14,15}, where the main carrier of energy, hydrogen, can be utilized in all parts of this economy. Having the highest gravimetric energy density, and the only product of combustion being water, hydrogen has been projected as an environmentally benign energy carrier. This, however, is not universally accepted, with several severe criticisms about enthusiastic projections of a hydrogen economy¹⁶⁻¹⁸, the main contrary arguments against being:

- 1. Hydrogen is not a clean fuel as is usually claimed to be, since it does not occur naturally, and needs to be derived mainly from fossil fuels, this process releasing large amounts of CO₂.
- 2. Critics describe hydrogen as the most dangerous of all fuels known to man, both in terms of usage, as well as storage.
- 3. Transportation of hydrogen either by pipelines or shipping in liquefied form is not energyefficient, is much more costly than for other fossil fuels, and is subject to leakage.

There is, however, little disagreement to the fact that fossil fuels, especially oil and gas, which currently form the backbone of major economies, are fast depleting. So, alternative sources of energy must be explored, the focus being on carbon-free fuels. While feasibility of a full-fledged hydrogen economy is debatable, hydrogen is already being incorporated into the energy matrix, and its application in the energy domain is continuously expanding^{19,20}. Hydrogen production from alternative sources like biomass or bio-oil, or by utilizing solar energy to generate hydrogen from water is being explored. While these techniques are expected to take

some time to produce hydrogen on large scales, hydrogen from fossil fuels will continue to be important during the transition to a hydrogen economy.

1.2.2 Industrial uses of hydrogen

Hydrogen is one of the most widely used commodities in industry, as a key intermediate for many chemicals and fertilizers.

Hydrogen in refineries

A refinery can be envisioned as a system of processes separating crude oil into products of varying hydrogen contents, and then manipulating the hydrogen distribution among the products to maximize the yield of mid-range products²¹. Thus, in terms of net hydrogen usage, some processes can be classified as hydrogen sinks which consume hydrogen, while some others are hydrogen sources. The main consumers of hydrogen in refineries are hydrocracking and hydrotreating, sometimes referred to together as hydroprocessing. The main process producing hydrogen as a by-product is catalytic reforming, which produces aromatic compounds by cyclization and dehydrogenation processes, to increase the octane number of naphtha²². Hydrogen could also be available by recovery from hydrogen-rich off-gases. With aromatics being increasingly unwanted in reformulated gasoline²³ due to stricter environmental regulations, and with the increasing hydrogen demand for treating increasingly heavy and sour crude oils, refineries are turning from being net producers to net consumers of hydrogen. Using hydrogen pinch analysis techniques, refinery hydrogen management plans have been established to enable an optimum use of available hydrogen "sources" and "sinks"^{22,24,25}. In many cases, however, as an alternative, it may be more cost-effective in the long run to build new hydrogen plants to meet long-term hydrogen requirements²⁶. Canada has huge resources of non-conventional oil in the form of bitumen in oil sands. Large amounts of hydrogen are required for the upgrading of bitumen and heavy oil, since these are deficient in hydrogen, and the hydrogen demand in this sector is on the rise 27,28 .

Hydrogen in fertilizer industries

The world population is growing, increasing the demand for food crops, whereas the available agricultural lands are constrained by growing urbanization, especially in the developing world. Global demand for crop nutrients is steadily on the rise. This is likely to be augmented further by the surging interest in production of bio-fuels, especially U.S. corn, Brazilian sugarcane, and palm oils in Malaysia and Indonesia for bio-diesel production²⁹. Among the major crop nutrients, phosphorus and potassium reserves are usually more or less sufficient in soils, while this is not

the case for nitrogen. Table 1 gives a projection of increasing demand of various nutrients, including nitrogen. More than 99% of the world's nitrogenous fertilizers production is based on ammonia as a raw material³⁰, the basic raw material for which is hydrogen. The global ammonia capacity is projected to increase by about 20% from 181 million metric tons NH₃ in 2008 to 218 million metric tones in 2013, with a third of this from revamping activities, and the rest to be provided by about 55 new units projected to become on-stream worldwide³¹.

Hydrogen in methanol manufacture

Methanol is one of the most widely used commodities in the petrochemical industries, the main applications being production of formaldehyde, dimethyl ether, acetic acid, MTBE and synthetic gasoline. Methanol could also have a significant share as a fuel for fuel cell vehicles. The most widely practiced method of producing methanol requires hydrogen as a raw material. About 90% of methanol is produced globally from natural gas. As of 1995, the worldwide methanol production capacity was 28 million tons/year³², while in 2004, the capacity was 33 million tons³³, and the demand is expected to rise.

Other industrial uses of hydrogen

Hydrogen is also used in manufacture of aldehydes, in Fischer-Tropsch synthesis for producing liquid hydrocarbons from synthesis gas, as a reducing agent in the metallurgical industry^{34,35}, for hydrogenation of unsaturated edible oils in the food industry, etc.³⁶. Synthesis gas, produced as an intermediate stream by the major hydrogen producing technologies, has a wide range of applications in the synthesis of chemicals, as described by Wender³⁷.

Thus there is a huge and growing demand for hydrogen in both the industrial and energy sectors. Figure 1.1 (a)³⁸ shows the global hydrogen consumption pattern, with the main consumers being the fertilizer industry, refineries and methanol production. Currently hydrogen is severely limited as an energy carrier, the only major application being as a rocket fuel.

1.3 Manufacture of Hydrogen

Figure 1.1 (b)³⁹ indicates the main sources of hydrogen on a global basis. Feedstocks can range from sources with no carbon content, e.g. water, to sources with high carbon content, e.g. coal. In fact, carbon can also be looked at as a hydrogen carrier⁴⁰, and usually CO_2 is released while hydrogen is recovered from the carbon skeleton.

Electrolysis of water can be a viable and a renewable path of hydrogen production if the energy used for electrolyzing aqueous solutions is derived from renewable sources like hydroelectricity, wind or solar energy. Hydrogen plants working on the electrolysis technique are located where there is cheap and vast hydro-electric power. The largest water electrolysis plants, with capacities around 30,000 Nm³/h, are located in Norway and the Aswan dam in Egypt⁴¹.

Coal gasification is one of the oldest techniques for syngas and/or hydrogen production⁴². Coal-based fertilizer plants have been phased out over the years with cheaper production costs being achieved by newer technologies based on liquid hydrocarbons and natural gas. However, this process is mainly practiced in places where there are huge deposits of coal, but no oil resources, like South Africa⁴³, where coal is the main feedstock for the country's unique synfuels and petrochemicals industry⁴⁴. Based on the relative abundance of coal compared to other fossil fuels, whose prices fluctuate and increase in unpredictable manners, while coal remains relatively inexpensive⁴⁵, coal-based hydrogen and synthesis gas can be economically competitive in future⁴⁶.

As depicted in Figure 1.1(b), currently the main contenders among the feedstocks for hydrogen manufacture are natural gas and oil (the bulk contribution being in the form of naphtha, and to a smaller extent as fuel oil), all accounting for more than three quarters of the hydrogen produced.

1.3.1 Processes for hydrogen from hydrocarbons

This section outlines the methods for hydrogen production using hydrocarbon feedstocks. All these techniques except hydrocarbon decomposition produce syngas or synthesis gas, which is a mixture of hydrogen, carbon monoxide and carbon dioxide in various proportions.

Steam Reforming

Steam reforming of natural gas is the most widely practiced means of hydrogen production^{23,47}. The major reactions are:

$$CH_4 + H_2O \leftrightarrows CO + 3 H_2$$
 $\Delta H^{\circ}_{298} = 206 \text{ kJ/mol}$ (1.1)

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad \qquad \Delta H^{\circ}_{298} = -41 \text{ kJ/mol} \qquad (1.2)$$

$$CH_4 + 2H_2O \leftrightarrows CO_2 + 4H_2$$
 $\Delta H^{\circ}_{298} = 165 \text{ kJ/mol}$ (1.3)

For higher hydrocarbons⁴⁷⁻⁴⁹,

$$C_n H_m + nH_2 O \to nCO + \left(n + \frac{m}{2}\right) H_2$$
 $\Delta H^0_{298} = 1108 \text{ kJ/mol} \text{ (for n = 7)} (1.4)$

Once H_2 and CO are available by steam reforming of higher hydrocarbons, a reverse steam reforming reaction (reverse of Equation 1.1) produce CH_4 , and thereafter the process proceeds as

simple steam reforming of methane. The steam reforming technique is discussed in more detail below.

CO₂ (Dry) Reforming

$$CH_4 + CO_2 \leftrightarrows 2CO + 2H_2 \qquad \qquad \Delta H^{\circ}_{298} = 247 \text{ kJ/mol} \qquad (1.5)$$

$$C_nH_m + nCO_2 \rightleftharpoons 2nCO + \frac{m}{2}H_2$$
 (1.6)

 CO_2 or dry reforming has the advantage of utilizing greenhouse gases as a feed, and is therefore environmentally attractive. CO_2 reforming of methane produces a syngas with a H₂/CO ratio lower than that from steam reforming, and it is more suitable for specific processes like the Fischer Tropsch synthesis^{47,50-52}. It has also been studied for other hydrocarbons like propane^{53,54} and heptane^{55,56}. However, a major disadvantage is carbon deposition^{51,52}, implying the need for coke-resistant catalysts, or process variants like combination with steam reforming or a reactorregenerator combination. The state-of-the-art for dry reforming of hydrocarbons has been reviewed by Wang et al⁵⁷.

Hydrocarbon Decomposition

$$CH_4 \leftrightarrows C + 2H_2 \qquad \qquad \Delta H^{\circ}_{298} = 75 \text{ kJ/mol} \qquad (1.7)$$

$$C_n H_m \to nC + \frac{m}{2} H_2 \tag{1.8}$$

The biggest attraction of this process is that no greenhouse gases are produced by hydrocarbon decomposition. In addition, pure H₂ can be produced directly without separation of the H₂ from other components in the product gas stream^{58,59}. Special operating conditions for decomposition have also enabled production of nanocarbons which might be attractive as catalyst supports, or in the semi-conductor industry⁶⁰. However, since this process is afflicted by catalyst deactivation, a coke-resistant catalyst is required, in addition to continuous regeneration of the catalysts. In a review paper, Muradov and Veziroglu⁶¹ proposed that the hydrocarbon decomposition process could be important during transition to a hydrogen economy.

Partial Oxidation

Partial oxidation is exothermic and therefore does not need external heat transfer (such as firing in a furnace). The reaction can be written as:

$$CH_4 + \frac{1}{2}O_2 \leftrightarrows CO + 2H_2 \qquad \qquad \Delta H^{\circ}_{298} = -36 \text{ kJ/mol} \qquad (1.9)$$

$$C_n H_m + \frac{n}{2} O_2 \leftrightarrows nCO + \frac{m}{2} H_2$$
(1.10)

Partial oxidation can be conducted with or without catalysts. Catalytic partial oxidation consumes less oxygen than the non-catalytic process. However, the feedstock choice is limited from natural gas to naphtha^{47,62}.

Non-catalytic partial oxidation processes are characterized by their ability to operate with feedstocks ranging from natural gas to heavy fuel oil, regardless of their sulfur content⁴¹. Hence the process can operate with various feedstocks⁴². Also referred to as thermal partial oxidation or gasification, this process is sometimes carried out with steam added to moderate operating temperatures and suppress carbon formation⁶³. Severe operating conditions, like pressures as high as 70 atm and temperatures of 1200 to 1600°C, are used⁶⁴.

Autothermal Reforming

This process consists of combining steam reforming and partial or total oxidation of the hydrocarbon. Part of the hydrocarbon undergoes combustion, thus providing energy for the highly endothermic steam reforming reactions⁶⁵⁻⁷⁰. Optimal control of the operating parameters can make the overall reaction thermally neutral.

In autothermal reforming, air is usually the oxygen source, and nitrogen must be separated from the syngas product mixture, or oxygen from the air (usually cryogenically) before being fed to the syngas reactor. This requirement is critical to avoid nitrogen build-up in the process loop. Usually upstream nitrogen separation from air is more favorable than costly downstream purification, and an oxygen separation plant would be necessary^{71,72}. Since the cryogenic oxygen plant is an expensive section in a reforming process layout, autothermal reforming is economically attractive only for large-scale production⁷³. Studies are being conducted for production of syngas using oxygen-selective ceramic membranes which can introduce oxygen in a distributed fashion along the reactor length, thus avoiding the need for separation of the nitrogen⁷⁴⁻⁷⁷. To be industrially viable, lower cost, high selectivity to oxygen permeation, and a high permeation flux need to be achieved.

The appropriate choice of technology depends on several factors like the nature of downstream applications and product distribution, but in general is dominated by economic considerations. When the goal of the whole exercise is production of hydrogen, steam reforming of hydrocarbons is clearly the preferable choice.

1.3.2 Steam reforming for hydrogen production

Steam reforming of hydrocarbons is the most widely used process for hydrogen production ^{23,47,78}. Its greatest advantage is that hydrogen is extracted not only from the hydrocarbon, but

from steam as well, thereby giving maximum H_2 produced per mole of a certain hydrocarbon. Excess steam in the reaction mixture suppresses the coking reactions, the extent of which depends on the temperature and the type of hydrocarbon. The H_2 /CO ranges⁷⁹ shown in Figure 1.2 for different processes using natural gas as feedstock indicate why steam reforming is preferred for producing hydrogen.

Compared to liquid hydrocarbon feedstocks like naphtha or diesel, natural gas has several operational advantages. The tendency of catalyst deactivation due to carbon formation increases with the average carbon number of the feedstock. Thus, for similar operating conditions of temperature and pressure, a lower steam-to-carbon ratio compared to those required by liquid hydrocarbons can be applied. Natural gas feedstocks tend to be better also in terms of energy efficiency and lower reformer volume requirement. In addition, natural gas needs less desulfurization prior to feeding due to its generally lower sulfur-content.

Currently synthesis gas as well as pure hydrogen is produced from natural gas as the major feedstock. Methane is the major component of natural gas and has the highest hydrogen density per mole of carbon, among all hydrocarbons. Natural gas is widely available worldwide. The overall economics, starting from a generally favorable feedstock pricing to a cheaper cost of hydrogen production, makes it the major feedstock for steam reforming.

1.3.3 Steam reforming of higher hydrocarbons

Countries have varying degrees of availability of natural gas and oil, as depicted in Figure 1.3. In places where natural gas in not available, it may be imported via cross-country pipelines, or the natural gas is compressed and transported in liquefied form. LNG terminals and gasification facilities need to be installed in many instances to gain access to this preferred feedstock. Depending on proximity to sources and the dynamics of feedstock prices, oil-based feedstocks like naphtha may become competitive in some areas⁸⁰.

Even when natural gas is liquefied by compression, its volumetric hydrogen density remains lower than for liquid hydrocarbons, although the H/C ratio of methane is high⁸¹. Therefore, an easily deliverable and safely storable hydrogen source, such as gasoline and diesel, is preferred for mobile applications^{82,83}. On-board hydrogen generation systems prefer liquid hydrocarbon feedstocks, such as gasoline, kerosene and diesel oil, which have higher energy density and a wider distribution network, compared to methanol⁸⁴. Methanol, proposed by some as a feedstock for hydrogen, may not be used widely due to its toxicity and miscibility in water, and due to overall energy efficiency, since hydrogen itself is a major feedstock for methanol

production. In addition to on-board hydrogen generation, for distributed hydrogen generation systems as in hydrogen re-fuelling stations, liquid hydrocarbons have a potential advantage over natural gas, with the ability to utilize existing gasoline/ diesel distribution systems.

Due to fluctuations in supply and market demand, different refinery products may be either scarce or in surplus. Many refineries benefit from flexibility in feedstocks, taking advantage of the surplus of various hydrocarbons in the refinery. With proper desulfurization, it has been possible to convert light gas oils and diesel fuel into syngas with no higher hydrocarbons in the product gas^{23,85}. Feedstock flexibility is therefore an important consideration in refinery hydrogen management as the hydrogen demand soars^{86,87}.

Refinery off-gases, which are high in hydrogen content, constitute a possible substitute for the primary feedstock to the hydrogen plant. Traditionally, these were flared or used as a fuel for firing reactors⁸⁸. Fertilizer plants for ammonia production have often been designed to accept variable feeds, e.g. 100% naphtha, 100% natural gas or intermediate mixtures^{89,90}. Higher hydrocarbons are generally more reactive than methane, with aromatics showing the lowest reactivity, approaching that of methane.

With huge deposits of unconventional oil reserves in the form of oilsands being developed, hydrogen demand for processing them is on the rise in Canada^{27,91}. At the same time, liquid hydrocarbon feedstocks are likely to be available for meeting hydrogen requirement inside refineries or for local hydrogen producing facilities.

Recently, there have been great fluctuations in the price of natural gas⁹² as well as crude oil⁹³, as seen from Figures 1.4 and 1.5. As a result, hydrogen producers favor flexibility of feedstock choices for their reforming units. Hence there is a need to do further research on hydrogen and/or syngas production from a wider range of hydrocarbons like LPG, naphtha, diesel and kerosene.

1.3.4 Industrial hydrogen producing units using steam reforming process

This project investigates a compact reactor configuration for steam reforming of higher hydrocarbons to produce pure hydrogen. In order to understand the merits of the proposed reactor configuration, it is necessary to understand the layout of a traditional hydrogen producing unit. Basic information is outlined in this section, while more detailed information is available elsewhere^{2,94-97}.

<u>Desulfurizer</u>: The hydrocarbon feedstocks first need to be desulfurized, since sulfur poisoning can rapidly and irreversibly deactivate catalysts^{96,98}. In the desulfurizer, the sulfur compounds

are first converted to H_2S by hydrodesulfurization using a Co-Mo catalyst for low sulfur content⁹⁸ or a Ni-Mo catalyst for a high sulfur feedstock like naphtha⁹⁵, and then reactively scrubbed with an adsorbent like ZnO.

$$R-SH + H_2 \rightarrow RH + H_2S \tag{1.11}$$

$$H_2S + ZnO \rightarrow ZnS + H_2O \tag{1.12}$$

<u>Steam Reformer</u>: The sweetened feedstock is then fed to a steam reformer, which consists of hundreds of catalyst-filled vertical tubes, operating in a fixed bed mode, housed inside a furnace. The furnace can be top-fired, side-fired, or of terrace-walled design, depending on the scale of the plant. The side-fired design offers the maximum flexibility, and allows more severe operating conditions⁶⁵, since relatively high average heat flux can be maintained through the tubes without exceeding critical limits ⁷². External heating provides the heat required by the highly endothermic process. In another version, also practiced widely in industry, the reformer is operated autothermally by partially combusting part of the hydrocarbon feed simultaneously^{72,95}. The operating temperature and steam-to-carbon molar ratio in the steam reformer depends on the nature of the hydrocarbon feed. The catalysts employ nickel supported on ceramic supports. Major reactions occurring in the steam reformer:

Higher hydrocarbons steam reforming

$$C_nH_m + nH_2O \rightarrow nCO + (n + \frac{m}{2})H_2$$
 $\Delta H^0_{298} = 1175 \text{ kJ/mol (for n = 7)}$ (1.4)

Methane steam reforming (reverse reaction is methanation)

$$CH_4 + H_2O \leftrightarrows CO + 3 H_2 \qquad \qquad \Delta H^{\circ}_{298} = 206 \text{ kJ/mol} \qquad (1.1)$$

Water gas shift

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad \qquad \Delta H^{\circ}_{298} = -41 \text{ kJ/mol} \qquad (1.2)$$

Methane overall steam reforming

$$CH_4 + 2H_2O \leftrightarrows CO_2 + 4H_2 \qquad \qquad \Delta H^{\circ}_{298} = 165 \text{ kJ/mol} \qquad (1.3)$$

Reactions in the steam reformer are net endothermic, and thus, the hydrocarbon conversion and hydrogen yield are favored at higher temperatures. However, as discussed below, high operating temperatures can lead to catalyst deactivation by carbon formation as well as by sintering. Carbon formation is usually worse for heavier feedstocks⁹⁴. Thus, old-generation steam reformers were designed for specific ranges of feedstock since naphtha steam reformers are operated at lower temperatures and higher steam-to-carbon ratios, compared to natural gas feedstocks.

<u>Pre-reformer</u>: To add flexibility in feedstock for steam reformers, most new reformer systems are equipped with pre-reformer units. A typical pre-reformer installation⁹⁹ is shown in Figure 1.6. A pre-reformer operates almost adiabatically, due to a combination of endothermic steam reforming of higher hydrocarbons (equation 1.1), followed by an exothermic methanation (reverse of equation 1.2). Typical temperature profiles for pre-reformers with different feedstocks are shown in Figure 1.7⁸⁷. The effluent of the pre-reformer is fed to the reformer as a methane-rich gas. With higher hydrocarbons completely converted in the pre-reformer^{23,85}, the reformer can be operated under the same conditions as for natural gas reformers with reduced risk of catalyst deactivation.

<u>Secondary reformer</u>: The steam reformer is referred to as a primary steam reformer when it is followed by a secondary reformer¹⁰⁰. Controlled amounts of air or oxygen are fed when the purpose of the steam reforming process is to generate hydrogen for production of ammonia or methanol, as shown in Figures 1.8 and 1.9⁶⁵.

Water gas shift section: The reforming section is followed by a shift reaction section. Traditionally, a two-step shift process is employed (see reaction (1.2)). With no net change in molar flow due to this reaction, the equilibrium conversion of the shift reaction is independent of pressure, but, being exothermic, is favored at low temperatures. However, to avoid the low kinetic rates at low temperatures, the shift reaction is carried out first in a high-temperature shift (HTS) reactor, followed by a low-temperature shift (LTS) reactor to increase hydrogen yield. The HTS reactor is loaded with an iron-chromium catalyst and operates at ~320-350°C⁹⁵. The exit gas is cooled down, and fed to the LTS reactor operating at ~200-250°C with a copper-zinc-alumina catalyst. The shift reactor section improves the hydrogen yield and reduces the CO concentration. However recent developments have seen a single shift reactor, called a medium temperature shift (MTS) reactor or a HTS reactor with efficient removal of impurities (mainly CO) using efficient Pressure Swing Adsorption (PSA).

<u>Purification section</u>: Downstream of the shift section is the gas purification section, which conventionally included CO_2 removal, followed by a methanation unit to remove residual CO and CO_2 . In modern hydrogen plants, the CO_2 removal and methanation units are replaced by a PSA system to produce high-purity hydrogen (>99.999% purity)¹⁰¹.

1.4 Steam Reforming Catalysts

1.4.1 Common steam reforming catalysts

Attempts to use non-metallic catalysts for steam reforming of hydrocarbons have not had commercial success because of low activity^{47,102}. Metals active for steam reforming include Ni, Co, Pt, Ir, Ru and Rh^{47,94,103}. The specific activities of metals supported on alumina or magnesia have been found to be Rh, Ru > Ni, Pd, Pt > Re > Co¹⁰³.

A common problem with steam reforming catalysts is deactivation, due to various mechanisms such as catalyst poisoning (e.g. due to sulfur in the process stream), coking, or sintering. Ni catalysts present major coking problems because of the formation, diffusion, and dissolution of carbon in the metal. Neither Ru nor Rh dissolves carbon to the same extent and, as a result, carbon formation is less in these systems¹⁰⁴. Pd is the only noble metal that forms carbon, probably because of carbide formation. In addition, in steam reforming, Pd is considerably more active per unit mass than nickel. However, Ni is much cheaper and sufficiently active to be widely used in steam reforming catalysts on an industrial scale ¹⁰⁵. These Ni-based commercial catalysts are supported on refractory materials like Al₂O₃ and SiO₂^{96,106,107}.

1.4.2 Coke formation and catalyst deactivation

In industrial fixed bed steam reformers, operational ills can sometimes lead to excessive rates of coking. The consequences can be catastrophic. Based on the morphology of the carbon deposits, carbon formation on Ni-based catalysts are of three types: encapsulating carbon, pyrolytic carbon, and whisker carbon^{94,108,109}. Only the former two types lead to deactivation of the catalyst. The type of carbon formed depends on several factors such as: (a) Operating temperature, (b) Steam-to-carbon ratio, and (c) Feedstock.

<u>Pyrolytic carbon</u>: Pyrolytic carbon is formed generally by exposure of hydrocarbons to high temperatures^{108,109}, and occurs due to thermal cracking of the hydrocarbon, and subsequent deposition of C precursors on the catalyst. This might lead to encapsulation of the catalyst particle itself, leading to deactivation and an increase in bed pressure drop.

Encapsulating carbon: Metal catalysts may also form carbonaceous gum-type encapsulating carbon deposits on the metal particle resulting in deactivation. These may form during reforming of heavy hydrocarbons with high proportions of aromatic compounds. The deposits consist of thin CH_x films, or layers of graphite covering the nickel particles, resulting in loss of activity^{108,109}. Conditions favouring formation of this type of carbon include: low operating

temperature (<500°C), low steam-to-carbon ratio, low hydrogen-to-hydrocarbon ratio, and high aromatic content in the feed¹⁰⁹.

<u>Whisker Carbon</u>: Nickel catalysts may form whisker carbon in a process where the hydrocarbon or carbon monoxide dissociates into carbon atoms on one side of the metal crystal and a carbon fiber (whisker) nucleates from the opposite side¹¹⁰⁻¹¹³. Thus, the carbon deposits consist of numerous carbon filaments, many with a metal particle at the top. Hence the carbon whisker can grow without deactivation of the active site and progresses without blocking processes responsible for their growth¹¹⁴.

Heavy coking occurs, for example, if the reactor is operated at temperatures higher than designed for, or at steam-carbon ratios lower than a critical value¹⁰⁹. These conditions can lead to large quantities of pyrolytic carbon and carbon filaments. Filamentous carbon plugs catalyst pores and bed voids, pulverizes catalyst pellets, and can bring about process shutdown, all within a few hours, by adversely increasing the pressure drop^{108,109}. Hence whisker carbon has been described as the most destructive form of carbon in steam reforming over nickel catalysts. When carbon forms at the inner perimeter of reforming tubes, this can seriously impair the process since external heat transfer is very important for the endothermic steam reforming reactions. Other than these process difficulties, coking itself might lead to serious loss of active sites of the catalyst, and the catalyst must ultimately be replaced.

Figure 1.10 shows the rate of carbon formation on nickel catalysts from different hydrocarbons based on TGA measurements⁹⁴. The aromatic content is considered to be critical. It has also been found that for a given hydrocarbon, at a given steam-to-carbon ratio, there is a temperature "window", below which gum-type encapsulating carbon formation occurs, while high temperature and whisker carbon formation can occur at the other end⁸⁵.

Olefins content is also critical for steam reforming catalysts, with the rate of carbon formation being several orders of magnitudes higher than for other hydrocarbons. Though not usually present in feedstocks, olefins may form in overheated sections of reformer tubes⁶².

1.4.3 Promotion of steam reforming catalysts

Depending on the hydrocarbon feedstock, steam reformers are operated at different temperatures and steam-to-carbon ratios to minimize catalyst deactivation by carbon formation. Research is also being conducted on catalyst formulation, doping with different promoters to minimize carbon formation by continuously gasifying carbon deposits. Since the acidic nature of the Al_2O_3 support can contribute to carbon formation by promoting hydrocarbon cracking, one approach is to decrease the acidity, e.g. by adding $K_2O^{96,115}$, MgO^{73,116,117} or CaO¹¹⁶. The mechanism of inhibition of carbon formation has been interpreted differently¹¹⁸. The specific activity of the catalyst for steam reforming is reduced as a result of adding promoters^{94,119}. There may also be a slow loss of K₂O over time due to its high volatility⁹⁶. In many industrial steam reforming catalysts, the Al₂O₃ support is replaced by MgAl₂O₄, thereby preventing the formation of NiAl₂O₄, which can render the catalyst inactive¹²⁰. One also avoids MgO which can form Mg(OH)₂, and being bigger in volume than MgO, cause rupture of the catalyst pellet. MgO has a tendency to hydrate in steam at temperatures below 500°C⁹⁸.

1.5 FBMR for Steam Reforming of Hydrocarbons

1.5.1 Limitations of fixed bed steam reformer

The steam reforming process has evolved over decades resulting in less costly and more efficient plants due to better materials for reformer tubes, improved catalysts and closer control of carbon formation limits¹²¹. However, fixed bed reformers are limited by intra-particle diffusional and equilibrium limitations, in addition to high radial temperature and concentration gradients. These gradients become worse as catalyst deactivates due to reduced energy absorption in deactivated zones. To overcome these limitations, we focus on: (1) hydrogen removal using permselective membranes, and (2) fluidization of the catalysts.

1.5.2 Hydrogen removal using permselective membranes

Figure 1.11 shows the thermodynamic limits for steam reforming of methane at a steam-tocarbon ratio of 3 with varying temperature and pressure¹²². Removal of the main products can drive the reaction towards completion, in accordance with Le Chatelier's principle.

In-situ removal of CO₂ from the steam reformer is an attractive method achieving dual targets towards a green economy; enhancing hydrogen yield, as well as concentrating CO₂ for sequestration. Alternatively, CO₂ recovered from steam reforming may be recycled back to the reformer for applications requiring lower H₂/CO ratios⁷⁹. Any required H₂/CO ratio within the natural range⁷⁹ as depicted in Figure 1.2, can be achieved by manipulating the CO₂ recycle. On the other hand, recycling CO₂-lean gas to the reformer can significantly enhance the hydrogen yield^{123,124}. More information about sorption-enhanced steam reforming can be found elsewhere ¹²⁵⁻¹²⁷

Enhancement of hydrogen yield can also be achieved by selectively removing hydrogen. In fact, yield enhancement is more sensitive to hydrogen removal than CO₂ removal ¹²³. Selective hydrogen removal using membranes enhances hydrocarbon conversion by favorably shifting the equilibrium conversion, while also purifying the hydrogen product¹²⁸⁻¹³⁰. Equivalent conversions can be achieved at much lower temperatures with membranes as for much higher temperatures without membranes⁶⁶, as seen in Figure 1.12.

Among the various options available for hydrogen selective membranes, Pd or Pd-alloy membranes theoretically offer infinite selectivity, but are currently expensive and suffer from challenges of structural integrity like hydrogen embrittlement and defects¹³¹⁻¹³⁴. Microporous and dense ceramic membranes show great promise due to their comparatively low cost, and ability to withstand higher temperatures, but permselectivity and permeation flux remain issues to be overcome. Reviews of membranes for hydrogen separation are available^{132,135-138}. Reviews of reaction systems using membranes for selective removal of hydrogen have also been published^{134,139-143}.

1.5.2.1 Dense metallic membranes for hydrogen separation

Figure 1.13 shows the hydrogen permeability of some materials¹³². As seen, metals like niobium, vanadium and tantalum have relatively high hydrogen permeability, but they are difficult to use for hydrogen separation due to formation of oxide layers¹³². Palladium is widely accepted as the most practical material for hydrogen separation membranes¹⁴³, with infinite selectivity and excellent resistance to oxidation and corrosion.

1.5.2.2 Critical temperature for Pd membranes

Below a critical temperature of 298°C, the α and β (sometimes referred to as α) phases of palladium hydrides co-exist¹³⁸. Depending on the composition of the hydride, there can be a transition between the two phases. Figure 1.14 shows hydrogen pressure-composition isotherms for the Pd-H system^{144,145}.

Difference in lattice constants between the two phases causes severe lattice strains during phase transition. After a few cycles of $\alpha \leftrightarrows \beta$ transitions, the palladium membrane becomes brittle¹⁴², and eventually develops micro-cracks. Thus, exposure to hydrogen at conditions where the β phase can form must be avoided, and the reactor must be thoroughly purged with inert gas to desorb hydrogen prior to cooling from high temperature¹⁴⁶. Alloying with other materials like Ag, Cu or Ru decreases the transition temperature significantly. Alloying also improves the
hydrogen flux through the membranes. For example, a $Pd_{77}Ag_{23}$ alloy leads to a 70% gain in permeability compared to pure Pd^{142} .

1.5.2.3 Permeation flux

The mechanism of hydrogen permeation through Pd membranes can be described as follows:

- 1. Dissociative adsorption on the membrane surface.
- 2. Solution of atomic hydrogen in the Pd metal, and diffusion across the membrane in a solid solution to the permeate side.
- 3. Associative desorption from the permeate side.

When diffusion is the rate-limiting step, the hydrogen permeation rate across the membranes follows Sieverts' equation:

$$Q_{H_2} = A_P \frac{P_{M0}}{\delta_{H_2}} \exp\left(\frac{-E_{H_2}}{RT}\right) (\sqrt{P_{H_2,R}} - \sqrt{P_{H_2,M}})$$
(1.13)

1.5.2.4 Membrane reactor for steam reforming of higher hydrocarbons

There has been recent interest in extending steam reforming to higher hydrocarbons for hydrogen production. Steam reforming of higher hydrocarbons has been found to be practically irreversible and complete at industrial steam reforming temperature^{49,85}. It is limited by the thermodynamic equilibrium, as for methane steam reforming⁷, see Figure 1.15. Methane is formed due to methanation reactions as noted above. In principle, selective removal of hydrogen could also enhance the overall hydrocarbon conversion and hydrogen yield.

Few experimental data are available for steam reforming of higher hydrocarbons in membrane reactors. Chen et al^{147,148} studied steam reforming of a synthetic fuel prepared by mixing liquid hydrocarbons (C₄ to C₈) with an average formula of C_{6,43}H_{14,84} with in-situ 4.5 μ m thick Pd membrane supported on a porous α -alumina tube. The feasibility of a one-step process for production of hydrogen was demonstrated, with a permeate hydrogen product purity of 99.5% reported for a fixed bed membrane reactor operating at 450 - 550°C and 200 - 900 kPa. Damle¹⁴⁹ used 25 μ m thick planar Pd-Ag membrane supported on a porous stainless steel frame for hydrogen removal from a small packed bed steam reformer with feedstocks of methanol, butane and Clearite[®], a commercially available sulfur-free grade of kerosene. With the latter as feed and operation at 620°C, 5.84 bars and a steam-to-carbon ratio of 3.5, a hydrogen yield higher than equilibrium prediction was obtained, reasonably matching simulation predictions¹⁵⁰.

1.5.3 Fluidization of catalysts

Steam reforming reactions for hydrocarbons are rapid, making catalysts highly under-utilized due to high intra-particle diffusional resistances in traditional fixed bed reactors. The large catalyst pellets result in effectiveness factors of only 10^{-2} to 10^{-3} in industrial operating conditions^{151,152}.

Elnashaie et al¹⁵³ proposed a fluidized bed reactor with fine catalyst powders suspended in the reaction environment. This enables the reactor to operate with a smaller pressure drop than in a packed bed. Effectiveness factors can also be greatly improved to almost unity in this manner. However, since fluidized bed steam reforming is not practiced on large scales, being instead limited to pilot-scale demonstration units. Fluidizable steam reforming catalysts are also not available commercially. They can be prepared by crushing commercially available catalyst pellets to the required size distribution¹⁵⁴, or prepared in-house^{155,156}. Materials strength is of significant concern for such catalysts which suffer from attrition.

1.5.4 Fluidized bed membrane reformer

Combining catalyst fluidization with a membrane-assisted reforming, Adris et al.^{3,4,157} proposed the fluidized bed membrane reactor (FBMR). Over the years, this concept has been extended to other reaction systems¹⁵⁸⁻¹⁶¹. Grace et al¹⁶² summed up the potential advantages of hydrogen production in a fluidized bed membrane reactor:

- a) higher yields by reducing thermodynamic equilibrium limitations,
- b) process intensification by combining three vessels into one,
- c) reduced temperatures of operation,
- d) countering the adverse effects of pressure on equilibrium conversion,
- e) virtually eliminating intra-catalyst diffusional limitations,
- f) high productivity per unit volume of reformer, and
- g) flexibility in using alternative feedstocks.

1.6 FBMR for Steam Reforming of Higher Hydrocarbons

1.6.1 Previous studies

Chen¹⁶³ and Chen et al.^{48,49,164,165} envisioned and modeled an FBMR for steam reforming of higher hydrocarbons based on heptane as the simulated feedstock, and a circulating fluidized bed configuration, as shown in Figure 1.16. This configuration allowed incorporation of a

regenerator in the loop, where carbon deposited on the catalyst particles could be burned, with the energy generated due to the combustion carried by the hot catalyst particles back to the reformer. By carefully choosing the process parameters, it was shown that an autothermal mode of operation could be achieved. A second autothermal mode was proposed by distributed feeding of oxygen through oxygen-selective membranes immersed in the reformer. However, this configuration has some practical challenges:

- a) Hydrogen permeation flux available with currently commercially available membrane panels remains low. The flux is strongly dependent on the membrane layer thickness. With the current thickness of membranes, a very high height-to-diameter ratio would be required for a reformer operating in the fast fluidized bed regime¹⁶⁶.
- b) Given the high particle velocities in fast fluidized beds, membranes are likely to be subjected to a more erosive environment than in bubbling fluidized beds.
- c) Nickel catalysts would be oxidized in the regenerator while burning off the carbon deposits.

1.6.2 Current research

Rakib et al⁷ investigated a bubbling fluidized bed mode of operation for hydrogen production from heptane, as a surrogate for naphtha. A two-phase bubbling bed model was written, with hydrogen withdrawn selectively through palladium membranes. A practical upper limit temperature of 650°C and a pressure of 10 bars were the base cases for the simulation. It was predicted that the FBMR could be considered as two overlapping zones, a short zone above the distributor where the heptane is fully consumed, and an extended zone where the steam reforming of methane and the water gas shift reaction occur, while pure hydrogen is continuously withdrawn. The FBMR was predicted to provide a compact reactor system for hydrogen production from higher hydrocarbons, by combining the pre-reformer, reformer and hydrogen purification in a single unit.

Simulation results⁷ also showed that thinner membranes could minimize the residual methane and hydrogen in the reformer, and maximize the pure hydrogen yield. The membrane packing factor, expressed as the membrane surface area per unit volume of the reactor, was found to be important, demonstrating that the permeation flux of the currently commercially available membrane panels is a limiting factor. A higher membrane packing factor could significantly reduce the volume of the reactor, but hydrodynamic factors provide practical constraints on the number and spacing of membrane surfaces¹⁶⁷.

Million tons	2008	2009 (estimated)	2013 (forecast)
Nitrogen, N	99.3	101.0	110.4
Phosphorus, P ₂ O ₅	35.9	37.2	43.9
Potassium, K ₂ O	24.8	25.0	31.0
Total	160.0	163.2	185.3

 Table 1.1:
 World fertilizer consumption (Calendar year basis)



Figure 1.1: Hydrogen demand and sources



Figure 1.2: Natural range of H_2 /CO ratio for natural gas⁷⁹.





Crude Oil Reserves: Oil & Gas Journal



1 Includes 173.2 billion barrels of bitumen in oil sands in Alberta, Canada. ² Excludes countries that were part of the former U.S.S.R. See ⁴U.S.S.R.* in Glossary.

Figure 1.3: Global distribution of oil and gas reserves



Eurasia³

Middle

East

Africa

Asia and

Oceania²

Europe²



Crude Oil Reserves: World Oil



0.

North

America

Central

and South

America



Figure 1.4: Natural gas price fluctuation ⁹²



Figure 1.5: Crude oil price fluctuation ⁹³



Figure 1.6: Typical flow-chart configuration of a pre-reformer ⁹⁹



Figure 1.7: Pre-reformer temperature profiles for different feeds ⁸⁷



Figure 1.8: Reforming section for production of ammonia synthesis gas ⁶⁵



Figure 1.9: Reforming for the production of methanol synthesis gas ⁶⁵



Figure 1.10: Relative rates of carbon formation on nickel catalysts ⁹⁴



Figure 1.11: Equilibrium methane conversion in steam reforming of methane as a function of temperature and pressure (steam-to-carbon ratio = 3) 122



Figure 1.12: Enhancement of methane conversion with in-situ hydrogen removal. Steam-tocarbon ratio = 3, reactor pressure = 1000 kPa^{66}



Temperature in K

Figure 1.13: Hydrogen permeabilities of selected metals ¹³²



Figure 1.14: Pressure-composition isotherms of Pd-H system ^{144, 145}



Figure 1.15: Equilibrium compositions for heptane steam reforming



Figure 1.16: Circulating fluidized bed membrane reformer configuration for steam reforming of heptane ^{49,164}

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CHAPTER 2. PILOT SCALE EXPERIMENTAL SETUP FOR HYDROGEN PRODUCTION FROM HIGHER HYDROCARBONS: SAFETY CONSIDERATIONS AND IMPLEMENTATION[†]

2.1 Introduction

Growing demand for hydrogen and synthesis gas in the process sector, and projected utilization of pure hydrogen for fuel cells make research on steam reforming very important, the main focus being overcoming the several drawbacks associated with traditional fixed bed steam reformers. When higher hydrocarbon feedstocks are used for hydrogen generation, the main reactions can be written¹ as:

$$C_n H_m + nH_2 O \to nCO + \left(n + \frac{m}{2}\right) H_2$$
 ($\Delta H^{o}_{298} = 1108 \text{ kJ/mol} \text{ for } n = 7$) (2.1)

The following reactions are also important:

$$CH_4 + H_2O \leftrightarrows CO + 3 H_2 \qquad \qquad \Delta H^{\circ}_{298} = 206 \text{ kJ/mol} \qquad (2.2)$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad \qquad \Delta H^{\circ}_{298} = -41 \text{ kJ/mol} \qquad (2.3)$$

$$CH_4 + 2H_2O \leftrightarrows CO_2 + 4H_2$$
 $\Delta H^{\circ}_{298} = 165 \text{ kJ/mol}$ (2.4)

Although methane is not present in the feed, it immediately starts to appear in the system due to the methanation reactions (reverse of reactions (2.2) and (2.4)), once H₂, CO and CO₂ appear in the system by reactions (2.1) and (2.3). Hence the process proceeds in an identical manner to steam reforming of methane^{2,3}. The methane yield decreases with increasing temperature due to the endothermicity of the steam reforming reaction of methane. As a result, H₂ yield continues to increase. If this H₂ can be selectively removed from the system as in steam methane reforming^{4,5}, the CH₄ yield will decrease further, due to forward equilibrium shift of reactions (2.2), (2.3) and (2.4). Thus,

[†] A version of this chapter has been submitted for publication: **Rakib, M.A.**, Grace, J.R., Lim, C.J., Elnashaie, S.S.E.H., Epp, M., Gulamhusein, A., Boyd, T., and Keelan, A., Pilot Scale Experimental Setup for Hydrogen Production from Higher Hydrocarbons: Safety Considerations and Implementation (2010).

(a) Hydrogen generation by steam reforming of higher hydrocarbon feedstock is constrained by the equilibrium of steam reforming of methane, once CO and H_2 are produced. Continual removal of hydrogen from the reaction stream by hydrogen permselective membranes can minimize this limitation, and maximize the production of hydrogen.

(b) To overcome very low catalyst effectiveness factors due to diffusional limitations in traditional fixed bed reformers, fine catalyst powders can be used in the fluidization mode.

Based on these two concepts, a fluidized bed membrane reactor was modeled⁶, built, commissioned and operated using model compounds for proof-of-concept. This paper briefly describes the process flow layout and the safety considerations that were implemented to ensure personnel safety and control leading to efficient experimentation.

2.2 Pilot Plant Layout

The fluidized bed membrane reactor (FBMR), which is at the heart of the process, is shown in Figure 2.1. Figures 2.2(a) through (d) show the P&ID for the pilot plant layout, segmented into nodes for a HAZOP study. Based on this, the pilot plant layout can be visualized to consist of:

(a) The feeding section covered in Nodes 1 through 6 in the P&ID in the HAZOP worksheet,

(b) The main reactor, the FBMR is covered as Node 7 in the P&ID,

(c) The pure hydrogen product section is covered as Node 10 in the P&ID,

(d) The reformer off-gas section is shown in Node 8, and

(e) Sample gas analysis is included in Node 9.

2.2.1 Feeding section

For outdoor gaseous hydrogen systems, the minimum clearance distance from installations of flammable and combustible liquids above ground (0 to 3785 liters) is 3.1 m^{7,8}. Alternatively, a minimum of one hour fire-rating capable barrier needs to be installed between these two storage sections to limit direct propagation of flames should a fire start in either of the sections. The heptane tank storage capacity is 28 liters, and the propane tank capacity (FX size) is 108.5 liters. In our case, a two-hour-fire-rating capable barrier was installed between the liquid hydrocarbons section (propane and heptane) and the hydrogen cylinders storage section.

Hydrocarbon storage and feeding section: The hydrogen storage facilities are shown as part of the P&ID in Figure 2.2(b). The reactor can be fed with three categories of hydrocarbons: C_1 represented by either natural gas or pure methane, C_3 represented by propane, or C_7 represented

by heptane. The liquid hydrocarbon feeding system is shown as Node 4, while the natural gas or methane feeding system appears as Node 3.

Sulphur compounds are removed from the natural gas by passing through a bed of desulfurizer sorbent Sulfusorb-8, a CuO-impregnated activated charcoal product from Calgon Carbon Corporation. When pure methane (Grade 2.0) is fed as a substitute for mains natural gas, the desulfurizer is bypassed.

A helium (Grade 4.5) size T cylinder with a delivery pressure set to 15 barg, is connected to the top of the propane (Grade 2.0) cylinder (FX size), so that it creates a helium "pad" over the liquid propane. A gas regulator regulates the helium pressures up to 17 barg. With this helium padding system, the head pressure in the propane tank is maintained at a constant value.

For heptane supply, a 203 mm ID x 864 mm deep vertically positioned cylindrical tank is used to store heptane. Under the NFPA 30 ⁹ classification, heptane is classified as a Class IB liquid, and has a fire rating of 3 as per NFPA 704 ¹⁰. When the FBMR is fed with heptane, the vapor headspace is pressurized with helium to provide a pressure head to push the heptane into the feed system. Proper care also needs to be taken to purge the vapor headspace in the heptane tank. Residual air in the headspace may create an explosive mixture with heptane vapor, and an explosion could be triggered by electrostatic charge buildup. The whole liquid hydrocarbon feeding system is therefore fully grounded.

Since the FBMR is fed with one hydrocarbon at a time, a common liquid mass flow controller is used to meter either propane or heptane into the feed system. A separate gas mass flow controller is used for natural gas or methane.

The propane tank as well as the heptane tank has its own pressure rating. To avoid injury by accidentally over pressurizing either tank, the pressurizing helium line is fitted with a pressure relief valve set at a maximum pressure of 15 barg. A 3-way selector valve is installed to select either a propane or heptane feed.

Steam feeding system: Water is accurately metered and pumped through a vaporizer, as shown in Figure 2.2(b). The liquid water pumping and metering system is indicated in Node 5, whereas the feed mixing and vaporizer section is included under Node 6. A low-level indicator switch is installed in the water tank to safeguard against dry-out of the tank as water shortage would lead to heavy deactivation of the catalyst so that the hydrocarbon feed would then need to be immediately stopped. Control logic described in detail below accomplishes this by closing the corresponding hydrocarbon solenoid valve. Metered natural gas or pure methane is pre-mixed with the pumped water before passing through the vaporizer. Metered propane or heptane is

introduced as a liquid feed into superheated steam after the vaporizer, with the feed line being completely heat-traced to the entrance into the FBMR.

The vaporizer needs to evaporate and superheat water at temperatures as high as 600°C, while satisfying the material of construction temperature constraints. This is achieved by creating control logic which turns off the vaporizer heaters if the vaporizer skin temperature should reach its limit.

Nitrogen supply system: The nitrogen supply system is indicated as Node 1 in the P&ID section in Figure 2.2(a). Nitrogen from the bank of cylinders at the storage rack is split into two streams: one is set at a maximum pressure of 10 barg for purging the reactor or leak testing of the reactor and other items at the pressure boundary, whereas the other is a low pressure one to purge the permeate line.

Hydrogen supply system: The Ni-based catalysts may experience oxidation of the active phase to NiO with time during storage. Hence hydrogen is used to reduce the catalysts to the active Ni phase, prior to introducing the hydrocarbon feeds. The hydrogen supply system is indicated as Node 2 in the P&ID section in Figure 2.2(a). Hydrogen can also be used to test the permeability of the installed membranes as a function of time and operating conditions.

The nitrogen and hydrogen manifolds are each fitted with relief valves. In addition, the pressure sensor upstream of the vaporizer inlet, as well as the one before the FBMR feed inlet, is coupled with control logic to shut off all the solenoid valves if the upper pressure limits should be breached. Hydrogen, methane, and nitrogen are procured from Praxair Inc. Storage, securing and handling of such compressed gases are governed by NFPA 55¹¹. Table 2.1 lists the consumable gases and liquids used, together with their purity specifications.

2.2.2 Fluidized Bed Membrane Reactor (FBMR)

The FBMR, the heart of the process, is shown in Figure 2.1, and depicted schematically as Node 7 in the P&ID. Based on preliminary modeling⁶, the FBMR was conceptualized as a vertically positioned cylindrical pressure shell, with vertical slits alternating in sides along the height of the shell, to accommodate six membrane panels. These panels are arranged vertically one above the other, each passing through the centerline of the reactor shell dividing the cross-section into two communicating sections. The mechanical design was executed by Jenmar Concepts Inc. to conform to the Pressure Vessel code (ASME Section VIII, Division 1). The design was certified by British Columbia Safety Authority (BCSA). Fabrication was executed by Axton Inc., which specializes in fabrication of industrial pressure vessels, tanks, and heat exchangers.

FBMR material of construction: SS304 has outstanding weldability, where all standard welding techniques can be used, although machinability of SS304 is lower than for most carbon steels. SS316 has virtually the same mechanical, physical and fabrication characteristics as 304 with better corrosion resistance, particularly to pitting corrosion in warm chloride environments, and has excellent corrosion resistance in a wide range of media.

Low carbon "L" grades are used where high temperature exposure occurs, including welding of medium or heavy sections. The low carbon assists in delaying or preventing grain boundary carbide precipitation (often referred to as sensitization) which can result in intergranular corrosion in corrosive service environments. Stainless steel with higher carbon content (>0.04% C) as in the "H" grades, increases the strength, particularly at temperatures above ~500 °C. Long-term creep strength is also higher. Among the materials compatible enough for the design conditions (621°C and 10.3 barg), SS316H and SS304H would be suitable choices. However, because SS316H was not available, SS304H was chosen as the material of construction, selected for its strength and corrosion resistance at high temperatures, operation at these high temperatures will cause precipitation of inter-granular carbides causing a reduction in the ability of the material to resist corrosion. However in applications where no liquids (condensation or steam) are present this is usually not an issue. During operation, the process stream contains superheated steam. On shutdown, the pressure vessel is purged to minimize water condensation.

Hydrogen can seriously affect the properties of materials by several mechanisms:

(a) Hydrogen embrittlement (HE) occurs by ingress of hydrogen into metallic materials, seriously affecting the ductility and load-bearing capacity, sometimes followed by catastrophic brittle fracture at stresses below the yield stress. Hydrogen embrittlement is seen with carbon and low alloy steels, ferritic and martenstitic stainless steels, and duplex stainless steels. Although it is normally not a problem with austenitic stainless steels¹²⁻¹⁴, metastable austenitic stainless steels (e.g. 304 or 316 type) may experience hydrogen embrittlement whereas stable austenitic stainless steels like 310S are not affected by hydrogen environment^{15,16}. However, embrittlement effects are generally confined to near-ambient temperatures, with a maximum effect at room temperatures¹³. In our case, hydrogen is not introduced into the FBMR below 400°C for catalyst reduction, and hydrocarbons are only fed to the FBMR for hydrogen generation above 475°C. Hence, under normal experimental conditions, hydrogen embrittlement is not expected to be important for the FBMR. This is also ensured by shutting off the hydrogen delivery solenoid

valve if the FBMR temperature drops below 300°C, the primary objective of which is to prevent swelling of the Pd-Ag membranes.

(b) Hydrogen attack, also known as high temperature hydrogen attack (HTHA), occurs above $\sim 220^{\circ}$ C as a consequence of hydrogen ingress into steel¹⁴. Dissolved hydrogen attacks iron carbide (Fe₃C), generating methane gas. Since the methane molecule is too large to diffuse within the solid alloy, the gas stays trapped along the grain boundaries. Gas build-up can tear the grain boundaries apart, ultimately leading to severe cracks^{17,18}. However, austenitic stainless steels are generally unaffected by hydrogen attack, and hence it is not a concern for the FBMR¹⁴.

Carbonyl corrosion is a concern is industrial systems encountering carbon monoxide, e.g. in manufacture of methanol. However for the FBMR operation, the probability of this is minimal, since:

i) At operating temperatures of interest (<600°C), CO production is normally very low (about 2% of dry gas composition).

ii) Carbonyl corrosion commences only at pressures above 100 bars, and is a serious issue only between temperatures of 150° C to 200° C¹⁹⁻²¹.

The operating temperatures of this vessel fall into the creep range for the materials used. For this reason, it is required that the entire pressure vessel assembly be uniformly insulated to minimize temperature gradients to avoid thermal stresses and thermal fatigue from temperature cycling. In addition, heating of the pressure vessel at start-up is to be strictly controlled, with a maximum heat up rate of 5°C/min. A similar gradual cool down rate on shutdown is also implemented.

From the allowable stress characteristics for SS304H as a function of temperature the reactor pressure rating would drop dramatically if its temperature were to exceed 600°C, as shown in Figure 2.3(a). This is reflected in the MAWP (Maximum Allowable Working Pressure) rating of the pressure vessel for different operating temperatures. As the pressure vessel design calculations are based on the yield and allowable stresses under a particular combination of temperature and pressure, the safest or ideal operating conditions would be to work within the maximum ranges of both the temperature and MAWP. However, if the test conditions demand otherwise, the MAWP can be flexible depending on the operating temperature, as depicted in Figure 2.3(b).

Being a non-standard flange, the six lateral rectangular flanges were the main challenge in the mechanical design of the pressure vessel. Forged bars of SA182 SS304H were used for the lateral flanges and SA240 SS304H for the blind flange covers. Forged bars are preferred over plates to overcome the tendency to delaminate under stress. Rectangular slots 241.3 mm x 22.2 mm are provided for insertion of the rectangular membrane panels. These panels are supported onto the blind rectangular cover flanges.

Reactor shell weld-on ports: Seven weld-on ports were provided on the reactor shell along the height, to allow future additional feed ports, or pressure/ sample gas taps. These holes could also allow withdrawal of catalyst samples at different heights during down periods. Near the bottom, and above the distributor, an additional port, angled downwards at 45° to the vertical, was provided which could function as a catalyst recirculation port if the reformer were to be operated in the future under fast fluidization conditions.

Lateral flange weld-on ports: Fittings are installed for one thermocouple to measure bed temperature, one pressure tap, two sample gas outlets, and one tap for removal of hydrogen permeated through the palladium surface into the membrane panels. This is shown in Figure 2.4(a).

Membrane panels: Pd membranes are infinitely selective to permeation of hydrogen due to the unique solution-diffusion mechanism of permeation^{22,23}. Diffusion depends on the difference of the square roots of partial pressures on the two sides according to Sieverts' law when hydrogen diffusion is the rate determining step²⁴. Pd membranes are susceptible to hydrogen embrittlement due to phase transition at temperatures around 300°C, resulting in expansion of the metal lattice^{5,25-27}. Pd is often alloyed with other metals like Ag, Cu and Ru to improve mechanical stability, resistance to hydrogen embrittlement and hydrogen permeation flux. A Pd₇₇Ag₂₃ alloy, for example, leads to a 70% gain in hydrogen flux compared with pure Pd^{5,28}. Packing too many vertical surfaces with small gaps between adjacent ones in a fluidized bed decreases the quality of fluidization, e.g., may cause defluidization due to solids bridging in the gaps between the surfaces²⁹. Thus, although a bundle of tubular membranes could provide the maximum membrane area per unit volume of reactor, in practice this cannot be utilized in fluidized beds. Moreover, in terms of fabrication, numerous small diameter tubes connected to a header or manifolding poses challenges of sealing. In addition, membrane panels produced by bonding membrane foils onto the porous support provides a more robust performance for operating temperatures about 500°C or higher in a fluidized bed environment, compared to membrane panels prepared by coating methods. Planar membrane panels also provide better and easier sealing compared to tubular panels. So, flat planar membrane panels were used for withdrawing hydrogen from the reaction environment. Double-sided Pd-Ag membrane panels are inserted through vertical slits on the wall of the FBMR reactor. These panels, shown in Figure 2.4(b)

were manufactured and supplied by Membrane Reactor Technologies³⁰. The overall dimensions of the panels are 231.8 mm x 73.0 mm x 6.35 mm thick. Accounting for weld space and bonding space, the active area of each membrane is 206.4 mm x 50.8 mm on each side of the membrane panel. The flux of hydrogen through the membranes can be increased by reducing the hydrogen partial pressure on the permeate side. This can be achieved either by using sweep gas or by evacuating the permeate side. In our experiments, a vacuum pump downstream of the hydrogen permeate manifold was employed.

FBMR bed cross-section: From reactor modeling prior to sizing, it was clear that the membrane permeation area per unit volume of reactor needs to be maximized in order to optimize the pure hydrogen yield. In practice, an upper limit to this is set by the tendency of the catalyst particles to form an immobile bridge in the gap between the membrane panel and the reactor wall if this gap is too small. To avoid defluidization in this gap and thereby avoid gas channeling, the width of this gap should be greater than about 30d_p (where d_p is the mean particle diameter)²⁹. Given this constraint, the need to maximize permeation area per unit volume indicates that for the rectangular flat membrane panels, the reactor cross-sectional area should be rectangular. The circular cross-section of a 73.6 mm ID SS304H pipe was converted to rectangular by using reinforced ceramic cement. The ceramic blockers were intermittently grooved laterally on the surface to accommodate rope gaskets which prevent vertical channeling of gas.

Distributor: The gas distributor is doughnut-shaped, with six equally-spaced holes drilled on the inner side. These holes point radially inwards and downwards at an angle of 45° to the vertical, to reduce back-sifting of catalyst particles into the windbox, located inside and at the bottom of the FBMR. The FBMR feed line is welded onto the bottom of the distributor housing, passing through the bottom head cover via sealed fittings. This design allows spent catalyst particles from the FBMR to be discharged by unfastening a cap through a simple catalyst drain in the bottom head cover, without requiring complete disassembly of the bottom head. A similar concept was used by Wang et al.³¹, involving a non-conventional manifold distributor with holes though the wall around the vessel.

End flanges and Rupture disk: ASME SA182F SS304H weld-neck flanges are welded onto the reactor shell ends, with blind covers fabricated from the same material. The inlet (bottom) cover is fitted with a catalyst drain, a feed gas inlet, and four heater tubes. Fittings at the outlet (top) allow catalyst filling and gas to leave the reactor through a sintered metal filter. The catalyst filling port is also connected to a rupture disc to protect the vessel from damage due to over-pressurization. A rupture disc from Fike Canada was installed to avoid over pressurization

of the reactor. This rupture disc, which also holds an ASME Code, Section VIII, Div 1, UD/CRN certification, is a 25.4 mm AXIUS style reverse bulged, non-fragmenting rupture disc, made from SS316 seal with a seat ring on the vent side. The stamped pressure rating for the FBMR pressure vessel is 10.3 barg at 621°C.

Reformer off-gas filter: A sintered metal filter from Mott Corporation, with the porous part consisting of a 152.4 mm long x 12.7 mm OD tube and a wall thickness 2 mm, captured the catalyst fines from the reformer off-gas. The porous sintered metal filter is SS316L, with a media grade of 40. This filter was inside the reactor, with the off-gas leaving through a 6.35 mm line.

Probe filters: The probe filters each contained a 6.35 mm sintered Hastelloy-C276 disc, 3.18 mm thick, spot-welded onto a 6.35 mm SS316 tube. Hastelloy-C276 is ideal up to temperatures of \sim 540°C under reducing conditions. These filter lines protect the gas sample analyzer, as well as the pressure sensor, against damage due to fine particles. The pressure sensor filter to be as thin as possible to minimize damping of pressure fluctuations.

Reformer heaters: 1524 mm long, 3.18 mm diameter narrow cable heaters, sealed by weld-on Conax fittings, provide the primary heat needed to bring the reactor up to \sim 600°C, and then to maintain the desired temperature. Depending on the space available, 88.9 mm ID band heaters, either 76.2 or 152.4 mm long, are installed in the semicircular spaces opposite each lateral flange. One strip heater per lateral flange is deployed on either of the vertical sides of these flanges. Due to their mounting mode, the cable heaters are termed internal heaters, whereas the band and strip heaters are called external heaters. When operated at maximum capacity, the total power supplied is 7.65 kW for the external heaters and 3.60 kW for the internal heaters. This power is drawn from a 220VAC supply. The location of the heaters, mounting mode and maximum power output of the heaters are listed in Table 2.2. During the operation, roughly 30 to 40% of the full power rating was required to maintain the FBMR at the operating temperature. To minimize thermal stresses, the output power of the heaters is adjusted such that the heating rate of all portions of the FBMR material does not exceed 5°C/min.

Catalysts: A proprietary RK-212 catalyst from Haldor Topsoe A/S is employed. It is available as 7-holed black tableted pellets, in the pre-reduced form, with the size and shape optimized for a fixed bed catalyst loading with the required material strength and low pressure drop. In order to use them in a fluidized bed mode, the pellets are carefully crushed and sieved to different size cuts. The FBMR catalyst load consisted of an equal weight mixture of +150 μ m -180 μ m and +180 μ m -212 μ m size cuts giving a Sauter mean particle diameter of 179 μ m. The catalyst
loading was just sufficient to immerse all the membrane panels, facilitating temperature uniformity and thereby preventing membrane failure and leakage.

FBMR insulation: Proper insulation is required to minimize heat losses. A ceramic thermal insulator jacket of minimum thickness of 50 mm is wrapped around the outside of the vessel. The entire pressure vessel assembly is uniformly insulated to minimize temperature gradients to avoid thermal stresses and thermal fatigue from temperature cycling.

2.2.3 Hydrogen permeation section

The hydrogen permeation section appears on the P&ID in Figure 2.2(d), referred to as Node 10. The flow of pure hydrogen permeating through each of the membranes is determined by hydrogen mass flowmeters, FMA1818 from Omega Instruments. To facilitate pure hydrogen permeation, thereby enhancing conversion of the hydrocarbons, the permeate streams are extracted by a powerful spark-proof hydrogen vacuum pump. Given the wide flammability range of hydrogen, the permeate section must be adequately purged with an inert gas like nitrogen before operating the vacuum pump, and the oxygen content is monitored during operation.

2.2.4 Reformer gas withdrawal section

The reformer off-gas is cooled using a condenser; the condensed water is caught in a condensate trap, and the off-gas throttled through a pressure control valve before being vented. The reactor pressure is controlled by this pressure control valve. This section is denoted Node 8 in Figure 2.2(c).

2.2.5 Gas sampling

To monitor reactor performance, gas samples were vented from specific locations in the reactor through a sample selection valve to a Varian CP-4900 micro-GC. The gas composition for steam reforming products from methane, propane and heptane is analyzed by a combination of GC columns as listed in Table 2.3, using micro-machined thermal conductivity detectors (TCD).

2.3 Objectives of Experimental Setup

The experimental setup was designed and installed for a Proof-of-Concept study to investigate whether higher hydrocarbon feedstocks can be steam reformed at temperatures lower than 600°C, while minimizing catalyst deactivation and achieving high yield of pure hydrogen by means of hydrogen permselective Pd-alloy membranes. Variables include reformer temperature,

reformer pressure, pressure of the pure hydrogen permeate stream, steam-to-carbon molar ratio of the feed, and superficial gas velocity. Hydrocarbons studied are n-heptane (a model component for naphtha), propane (a key constituent of LPG), and methane (the major component of natural gas). Other subjects of special interest include membrane fouling, and catalyst deactivation. Table 2.4 lists the parameters which are varied, their ranges and how this is accomplished. Table 2.5 indicates the quantities which are directly monitored or calculated to evaluate the FBMR performance.

2.4 Toxicological and Safety Information of Materials Encountered

Table 2.6 shows that special care has to be taken in handling pressurized systems containing substances like hydrogen, carbon monoxide, methane, propane or heptane. The laboratory is equipped with mono-ammonium phosphate based dry powder fire extinguishers, one at each of the three laboratory entry points, and two adjacent to the experimental setup. A strong exhaust ventilation system at the roof of the laboratory prevents accumulation of gases such as hydrogen. <u>Toxic substances:</u>

(a) Carbon monoxide: Carbon monoxide is an asphyxiant and a highly toxic gas that combines with the hemoglobin of the blood, forming carboxyhaemoglobin, decreasing the delivery of oxygen to the tissues.

(b) Nickel dust: Occupational exposure to nickel aerosols due to inhalation can result in development of asthma specific to nickel. Inhalation of nickel dust can cause chronic ailments as well as carcinogenic effects to the respiratory system. "Evidence for the carcinogenicity of nickel metal and other compounds is relatively weak or inconclusive, but insoluble dusts of nickel oxides, and soluble aerosols of nickel sulfate, nitrate, and chloride, have been implicated as potential carcinogens."³².

Nickel carbonyl formation due to the interaction of nickel and CO

$$Ni + 4CO \rightarrow Ni(CO)_4$$

(2.5)

is unlikely to occur at the operating conditions of the reformer, but must be considered, given the toxicity of the material, not only due to its CO content which itself is toxic, but also due to nickel which can be released into the body^{33,34}.

Flammable substances:

The flammability characteristics of species encountered in the operation of the system is given in Table 2.6. Although the auto-ignition temperature for hydrogen is much higher than for propane

or heptane, the minimum energy for ignition is much less, and it is hence more readily ignitable³⁵.

(a) Hydrogen burns with an invisible flame and may also form a fireball. It has a wide flammability range.

(b) Carbon monoxide also has a wide flammability range, but fire hazard caused by CO is less probable for this installation, since the dry gas composition of the synthesis gas mixture produced is expected to be about 1%. However, as mentioned above, CO build-up must be monitored due to its highly toxic nature.

(c) Hydrocarbons: Methane, propane and heptane have narrower flammability ranges than hydrogen, but a number of other factors are also important:

- (i) The LEL of propane and heptane are considerably lower than for hydrogen and methane;
- (ii) The diffusivity of hydrogen is much greater than for propane, methane or heptane; and
- (iii) Propane and heptane vapor are significantly denser than air..

However, for a confined space with inadequate ventilation, hydrogen and methane would form combustible mixtures more rapidly than propane and heptane. In such a case, hydrogen is expected to form combustible mixtures more rapidly than methane since hydrogen has higher buoyant velocity and slightly lower flammable limit³⁵. Thus, a fire hazard is likely to be in the orders of hydrogen, methane, propane and heptane, and to persist in the reverse order³⁵.

2.5 Safety Considerations during FBMR Operation

The laboratory setup comes under the scope of NFPA 45 ³⁶. It is adequately equipped with portable fire extinguishers. There are three exit doors installed to swing in the direction of exit.

2.5.1 Temperature control

Proper temperature control is needed to:

- (a) Safeguard the pressurized FBMR and the feed and product lines against mechanical failure.
- (b) Minimize catalyst deactivation by enhanced carbon formation or sintering at temperatures exceeding the recommended range.
- (c) Prevent membrane failure causing leakage at higher temperatures.
- (d) Avoid the presence of hydrogen in the vicinity of the Pd-Ag membranes below the recommended temperature of 300°C to prevent membrane swelling^{5,25,27}.

- (e) Avoid feeding steam to the FBMR at temperatures below 350°C.
- (f) Avoid use of the hydrogen vacuum pump above recommended temperatures.

A cause and effect matrix of the control logic is used to specify suitable upper and lower temperatures for important locations in the process layout, thereby cutting electrical power to relevant heaters or pumps.

Thermocouples were inserted close to the center of the membrane panels, through the lateral rectangular flange covers, and also at the level of the ROG filter. In addition, thermocouples were added below each external heater to limit the skin temperatures, which are likely to be at local maxima directly beneath the heaters, by cutting off the electrical power if the limit is breached.

2.5.2 Pressure control

Reliable pressure control is required to safeguard the FBMR vessel and its components against mechanical failure. For example, excessive pressure in the permeate line could cause the membrane foils to detach from their supports. A rupture disc on the FBMR vessel and pressure relief valves in each of the feed lines (hydrogen, nitrogen, individual hydrocarbons, water pump discharge outlet and permeate line) were installed. Indirect mechanisms were also incorporated in the form of pressure sensors with input to the PLC logic capable to shut solenoid valves on the feed lines or open the pneumatically-controlled FBMR pressure control valve. Under normal operating conditions, the pressure control valve is designed to ensure proper pressure regulation.

The absolute pressure sensor in the freeboard, and differential pressure transducers on the lateral rectangular flanges indicate the quality of fluidization inside the bed³⁷. The differential pressure transducer outputs were recorded only, in addition to online graphical visualization so that corrective measures could be taken. The absolute pressure transducers data were input to the PLC so that the FBMR pressure can be regulated. This is necessary, for example, to avoid channeling, where the bed would operate as a packed bed, with poor gas-solid contacting. The arrangement of pressure transducers connected directly to the FBMR is shown in Figure 2.5.

2.5.3 **Prevention of backflow**

Flow reversals could conceivably occur due to unexpected process parameters deviation, or when there is a sudden blockage of the FBMR off-gas filter due to catalyst cake formation. Such flow reversals are prevented by check valves at appropriate locations, as outlined in the HAZOP worksheet.

2.5.4 Hazardous gas leakage

Leakage of dangerous gas such as carbon monoxide, hydrogen, methane, propane or heptane into the workspace and/or around the high temperature equipments must be prevented. Flammable mixtures of air and hydrogen can auto-ignite if in contact with hot surfaces above 500°C⁷, and may be accompanied by explosion or toxic gas poisoning. The interfaces between the flanges and covers for the lateral, top and bottom flanges were sealed using SS316-reinforced graphoil gaskets. The flange nut and bolts were tightened using a torque-wrench, taking care not to exceed the specified design torques.

A CO gas detector, TS400 and a combustible gas detector, S4000C, both from General Monitors, were installed close to the reactor. Output signals from these detectors are continuously logged during operation. If the specified safe limits should be exceeded at any moment, an emergency shutdown would be triggered. A hydrogen sensor (MSA Orion multigas detector) was also deployed periodically to identify any leaks. In addition, a CO monitor was located near the top of the FBMR near the reactor exit, and another adjacent to the sampling system to the micro-GC.

2.5.5 Air ingress into hydrogen permeate section

Hydrogen has a wide explosive range in mixtures with air or pure oxygen. It is essential that the hydrogen suction system be leak-proof. Leak testing by pressurization was performed for each of the six permeate lines individually and for the entire permeate manifold system by determining the pressure holding capability. The permeate lines, manifold system, and vacuum pump were also subjected to vacuum, and left overnight to check the vacuum loss rate due to air ingress. As per the Canadian Hydrogen Installation Code⁷ under Article 7.7 for compressor requirement, if hydrogen comes from a sub-atmospheric pressure source, the oxygen content of the hydrogen needs to be continuously monitored, and the compressor needs to be shut down should the oxygen content exceed 1% by volume. This will ensure that the oxygen concentration is too low to sustain combustion should the concentration of hydrogen be in the flammable range. In our case, since the feed to the hydrogen vacuum pump comes from membrane panels under vacuum, an oxygen sensor from Teledyne Analytical Instruments was used to monitor the oxygen pump to remove any oxygen buildup.

2.5.6 Gas sampling

Gas samples could contain high moisture content (e.g. 30-50%), depending on the operating conditions and hydrocarbon conversion. High moisture content could damage some of the columns in the micro-GC. Hence precautions were implemented to avoid this:

(a) Installation of a condenser which could be emptied periodically.

(b) Installation of a genie filter which does not allow liquid water to pass through it, but allows passage of every other component, including uncondensed steam and condensed heptane.

(c) Installation of a micro-gasifier before sample injection, which allows controlled heated pressure reduction of sample gases originating in the high pressure FBMR.

(c) Maintaining the sample injection and column temperatures $\geq 110^{\circ}$ C to prevent condensation after sample injection.

(d) Adequate back flushing time settings for each of the GC columns to limit steam flow.

(e) The sample gas bypass line is connected to the venting line to prevent hazardous gas from reaching the workspace.

2.5.7 Trips and emergency shutdown

Some operating conditions deviations could have hazardous consequences. For example, excessive temperatures or pressure limitations of the FBMR pressure vessel could cause the vessel to fail mechanically, leading to explosion and toxic gas release. The system was designed so that pressures exceeding specified values trigger shut-off of all feed streams and opening of the pressure control valve completely. Excessive temperatures cause shutdown of the corresponding heater. In both cases, user input is required to restore the system to regular operation.

Some situations lead to immediate emergency shutdown. Toxic or combustible gas release in the surrounding atmosphere indicates a leak which could endanger safety. Similarly low instrument air means that proper regulation of the FBMR pressure could be disrupted. In such situations, the priority is to check the system integrity, and an emergency shutdown is thus actuated by the Cause & Effect matrix of the PLC. As an additional safeguard, an Emergency Shutdown button is within reach of the operators. Pressing this button immediately cuts electrical power to the instruments and opens the reactor pressure control valve.

2.5.8 Catalyst handling

The commercial RK-212 catalyst pellets (pre-reduced nickel supported on alumina) were crushed and sieved to obtain a narrow size distribution of Sauter mean diameter 179 μ m. When stored under atmospheric conditions, the catalyst particles contain roughly 15 to 20% by weight Ni or NiO. NiO is toxicologically classified as a potential carcinogen. Thus all the relevant catalyst handling steps of crushing, sieving, and loading into the FBMR require special care to avoid exposure to personnel.

2.5.9 Insulation

Proper insulation is required to minimize heat losses, and to ensure personnel safety by avoiding exposure to hot surfaces. A refractory ceramic fiber product, Cerablanket, supplied by Thermal Ceramics Inc., insulates the reactor. The MSDS for this material does not indicate any respiratory disease attributed to exposure to this material, while many health agencies like International Agency for Research on Cancer (IARC), Canadian Environmental Protection Agency (CEPA), and American Conference of Governmental Industrial Hygienists (ACGIH) classify it as possible human carcinogen³⁸. A particulate face mask was therefore used while handling and installing the insulation. While heating up the system for the first time with new insulation, significant amounts of volatiles are emitted which could be harmful to health, and also is a potential fire hazard. Hence, powerful ventilation and gradual temperature increase were implemented during initial reactor operation.

2.5.10 Electrical safety

All power distribution systems, heaters and other electrical appliances were properly grounded and checked for ground faults. Similar precautions were taken to eliminate electrostatic charge buildup in the combustible substances storage area.

2.5.11 Safety apparel

Safety apparel required for regular operation of the reactor system include:

- (a) Regular lab coats
- (b) Latex gloves
- (c) Goggles
- (d) Full-toed shoes

Additional precautions are required while working with particulates, e.g. while handling the catalyst and insulation:

- (e) Full head-to-toe clothing.
- (f) Particulate masks.

In addition, appropriate gloves were required to prevent frostbite when dealing with propane line commissioning.

2.5.12 Safe working habits

The following additional measures promote safety:

- (a) Clearly written and distinctly visible "Emergency Shutdown Procedure" (ESD) instructions.
- (b) No food or drinks in the laboratory work area.
- (c) Clear visible locations of emergency showers, eyewash stations, first aid and firefighting equipment.
- (d) Material safety data sheets (MSDS) are conspicuously located, and referred to before working with any new substance.
- (e) Written working plans, not only to ensure well-organized and efficient experimentation, but also to think through all procedures and steps which could affect safety.
- (f) Prohibition of working alone when the FBMR is operating.

2.5.13 Process control for FBMR operation

The FBMR process control system was configured by Membrane Reactor Technologies in their control (Delta V) system. Safety issues discussed in previous sections were taken into account during the Hazard and Operability studies as shown in Tables 2.7 and 2.8, leading to the Cause and Effect matrix shown in Table 2.9. To ensure safe operation, a high level HMI ladder logic is used to specify PLC actions based on the matrix.

2.6 Conclusions

A novel fluidized bed membrane reactor system has been designed, built and commissioned at the University of British Columbia for a Proof-of-Concept study for steam reforming of higher hydrocarbons to produce pure hydrogen. Operation at high temperature and pressure, combined with toxic and combustible substances, required close attention to safety issues. Detail of the experimental setup and safety measures are summarized. A process control plan was developed based on a cause and effect matrix with respect to the PLC.

Substance	Chemical formula	Molecular weight	Supplier	Purity/ Grade
Methane	CH ₄	16	Praxair	2.0
Propane	C ₃ H ₈	44	Praxair	2.5
Heptane	C_7H_{16}	100	Sigma-Aldrich	99.5%
Nitrogen	N ₂	28	Praxair	Industrial
Hydrogen	H ₂	2	Praxair	Industrial
Water / Steam	H ₂ O	18	UBC	Distilled water

Table 2.1: Gases and liquids in FBMR steam reforming process

Table 2.2:Heaters distribution for the FBMR

Heater ID	Description	Height (mm)	Maximum power output (W)
HT-CA-901	4 cable heaters, one at	0 - 1524	900
HT-CA-902	each corner of the	0-1524	900
HT-CA-903	rectangular channel of	0-1524	900
HT-CA-904	the FBMR	0-1524	900
HT-BA-901	The band heaters are	143 - 448	900
HT-BA-902	mounted on the semi-	473 - 625	450
HT-BA-903	circular spaces	651 – 956	900
HT-BA-904	opposite to each lateral	981 - 1133	450
HT-BA-905	flange.	1159 - 1464	900
HT-BA-906		1413 - 1718	900
HT-BA-907		1800 - 1952	450
HT-BA-908		1800 - 1952	450
HT-BA-909		2000 - 2152	450
HT-BA-910		2050 - 2202	450
HT-ST-901	The strip heaters are	143 - 448	225
HT-ST-902	vertically mounted on	397 - 702	225
HT-ST-903	the lateral flanges.	651 - 956	225
HT-ST-904		905 - 1210	225
HT-ST-905		1159 - 1464	225
HT-ST-906		1413 - 1718	225

*Height is measured from distributor level

Table 2.3:
 Micro-GC column information for product gas analysis

Channel	Column Description	Carrier Gas	Gases Analyzed	Detection limits		
1	10 m molsieve 5A	Argon	He, H_2 , O_2 , N_2 , CH_4 and	10 – 100 ppm		
	with pre-column backflush		CO			
2	10 m PPU	Helium	CO ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₂ H ₂ ,	10 – 100 ppm		
	with pre-column backflush		H ₂ S and COS			
3	8 m Silica PLOT	Helium	C3 and C4 isomers	10 – 100 ppm		
	with pre-column backflush					
4	8 m CP-Sil 5	Helium	C5 to C12 components	1 – 10 ppm		
	with no pre-column					

Table 2.4:Controlled parameters for FBMR steam reforming process

Parameter	Range of	f Monitoring instrument and variation mechanism					
	parameters						
Bed temperature	475 – 550°C	Feed temperature, bed temperatures, and reformer off-gas temperature close to gas filter located in the freeboard are measured by K-type thermocouples. Temperatures are varied by changing the power supplied to the internal and external heaters.					
Reactor pressure	300 – 900 kPa	Figure 5 includes a schematic of the differential and absolute pressure probe arrangements. This could be varied by a pneumatically-controlled Pressure Control Valve downstream of the FBMR in the off-gas vent line.					
Permeate pressure	25 – 101 kPa	An absolute pressure transducer was located downstream of the hydrogen flow meters, and upstream of the hydrogen vacuum pump. This could be varied by changing the speed of the hydrogen vacuum pump.					
Steam-to-carbon molar feed ratio	4-6	Monitored based on flow rates of the steam and hydrocarbon feeds. This could be varied by changing the mass flow controller set points.					
Feed superficial velocity	6 – 9 cm/s	Feed superficial velocity is calculated based on feed conditions and flow rates.					

Parameter	Monitoring Instrument or Basis
Bed gas composition	Online injection to MicroGC model no. CP-4900 from Varian Inc.
Exit gas composition	Online injection to MicroGC model no. CP-4900 from Varian Inc.
Permeate product flow rate	Hydrogen flowmeters from Omega Instruments, model no. FMA-1818
Permeate product purity	Syringe injection to MicroGC model no. CP-4900 from Varian Inc.
Hydrocarbon conversion	Carbon balance based on known feed flow rates, and measured sample gas compositions.
Hydrogen yield	Moles of pure hydrogen produced per mole of hydrocarbon fed. *
Methane yield	Moles of methane produced per mole of higher hydrocarbon fed. *

Table 2.5: Performance parameters for FBMR steam reforming process

* Normally product yields would be defined based on the amount of a feed species consumed. However, for the higher hydrocarbons, the conversion is virtually 100%, so yields are defined based on the hydrocarbon fed.

	Hydrogen	Carbon Monoxide	Methane	Propane	Heptane		
Auto-ignition temperature (°C)	560	620	595	470	222		
Flame temperature in air (°C)	2210	2468	1950	1980	2000		
Flash point	Flammable Gas	Flammable Gas	Flammable Gas	-104°C	-1°C		
Flammability limits (vol% in air)	mability limits 4 - 75 12.5 - 74.2		5 - 15	2.1 - 9.5	1.1 - 7		
Minimum energy for ignition in air (MJ)	imum energy 0.02 < 0.3 gnition in air		0.29	0.305	0.24		
NFPA fire rating	4	4	4	4	3		
Diffusion coefficient in air (cm ² /s), 25°C	0.61		0.16	0.10	0.05		
Gas/vapor density (Air = 1)	Gas/vapor density 0.0696 0.968 Air = 1) 0.0696 0.968		0.55	1.55	3.5		
TLV	Simple 25 ppm TWA Asphyxiant		Simple Asphyxiant	2500 ppm TWA	500 ppm TWA		

Table 2.6:
 Flammability and safety information of some species encountered ^{35,36}

Nodes	Description
1 - 6	Deals with feed delivery section. Consequences focus on causes that restrict the delivery, i.e. leaks, empty cylinders etc
7 - 8	Directly to the FBMR; mainly consequences of temperature and pressure deviation
9 - 10	Relate to the products sampling and analysis. Consequences focus on causes resulting from the unit operation itself.

Table 2.8:Hazards and Operability Study Worksheet

Hazards and Operability Study									
Proc	ess: Fluidized Bed Me	embrane Reactor for Ste	am Reforming of Hig	her Hydrocarbons					
No	ode and Description	Parameter/Deviation	Cause(s)	Consequences	Safeguards				
	Nitrogen feed line	Pressure / Less	Empty cylinder	Purging unavailable	Low pressure alarm for PT-101				
1	from facility. Considers effects on FBMR purging and	Pressure / More	Pressure regulator failure	Exceed system design pressure	Relief valve PSV-010. High pressure trips PAHH-1001 and PAHH-1200				
	startup.	Flow / Reverse	Higher downstream pressure	Mixing of streams: Poor reactor performance	Check valves VCK-101, VCK- 107, VCK-1101				
2	Hydrogen feed line	Pressure / Less	Empty cylinder	No safety issue but no catalyst reduction: Poor reactor performance	Periodically check cylinder pressure				
	from facility. Considers effect on start-up	Pressure / More	Pressure regulator failure	Exceed system design pressure	Relief valve PSV-301. High pressure trips PAHH-1001 and PAHH-1200				
		Flow / Reverse	Higher downstream pressure	Mixing of streams: Poor reactor performance	Check valves VCK-301, VCK-107				
		Pressure / Less	Empty cylinder	No safety issue but no reaction. Catalyst re-oxidation: Poor reactor performance	Check valves VCK-101, VCK- 107, VCK-1101				
		Pressure / More	Pressure regulator failure	Exceed system design pressure	Relief valve PSV-403. High pressure trips PAHH-1001 and PAHH-1200				
3	Natural gas feed lines from facility.	Flow / Less	System fluctuation	Catalyst re-oxidation; Poor reactor performance	Low steam to carbon mole ratio alarm FFDALL-401				
	desulfurizer.	Flow / More	System fluctuation	Catalyst deactivation	High steam to carbon mole ratio alarm FFDAHH-401				
		Flow / Reverse	Higher downstream pressure	Mixing of streams: Poor reactor performance	Check valves: VCK-405				
		Composition/ Fluctuation	Spent desulfurization sorbent	Reforming catalyst poisoning	Sample port V-413 for NG sulfur content analysis. Replace sorbent when saturated				

Node and Description		Parameter/Deviation	Cause(s)	Consequences	Safeguards	
		Pressure / Less	Empty helium cylinder	Poor reactor performance (no reactor feed); Catalyst re-oxidation	Check valves VCK-101, VCK- 107, VCK-1101	
		Pressure / More	Helium pressure regulator (V-1201) failure	Exceed propane tank/ helium tank design pressure	Relief valve PSV-403	
	Liquid hydrogarbon	Level / More	Over-filling of tanks		MI-001 scale for net propane in	
4	feed line. Includes liquid propane and heptane and helium pressurization lines.	Level / Less	Empty tanks	No safety issue but no reaction. Catalyst re-oxidation: Poor reactor performance	tank; LS-1203 and LS-1204 high / low heptane tank level alarms	
		Flow / Less		Poor reactor performance	Low steam-carbon ratio alarms FFDALL-1204 for propane, FFDALL-1205 for heptane	
		Flow / More	System fluctuation	Catalyst deactivation	High steam-carbon ratio alarms FFDAHH-1204 for propane FFDAHH-1205 for heptane	
		Flow / Reverse	Higher downstream pressure	Mixing of streams: Poor reactor performance	Check valve VCK-1202	
		Pressure / Less	Pump malfunction	Low water flow/ catalyst deactivation	Alarms for low steam-carbon ratios for each hydrocarbon	
		Pressure / More		Exceed system design pressure	Relief valve PSV-501. High pressure trips PAHH-1001 and PAHH-1200	
5	Water feed line.	Level / Less	Empty tank	No steam in feed. Coking in preheater Catalyst deactivation. Pump damage.	Water tank low level alarm LS- 1202	
		Flow / Less	MFC malfunction	Catalyst deactivation	Alarms for low steam-carbon ratios for each hydrocarbon	
		Flow / More	MFC malfunction	Poor reactor performance	Alarms for high steam-carbon ratios for each hydrocarbon	
		Flow / Reverse	Higher downstream pressure	Hydrocarbons enter water line	Check valve VCK-501	

 Table 2.8: Hazards and Operability Study Worksheet (....continued)

Node and Description		Parameter/Deviation	Cause(s)	Consequences	Safeguards
	Preheater System	Temperature / More	Heaters controller malfunction	High feed temperature, high preheater tube skin temperature	High level alarms TAHH-1000 and TAHH-1001
6	(HX-1001 to HX- 1051)	Temperature / Less	Heaters failure/ high water flow rate	Poor reactor performance	Low level alarm TALL-1001. Shuts off water pump to prevent liquid water from entering FBMR
		FBMR Pressure / More	ore Clogged ROG filter, or feed flow fluctuations Exceeds design pressure at operating temperature. Physical injury		High pressure alarms PAHH-1001 and PAHH-600 will shut off all feeds and open PCV-600 fully. Rupture disc E-RD-001 also protects against overpressurization.
7	FBMR: Includes FBMR vessel, rupture disc, catalyst filling line	BMR: Includes FBMR vessel, rupture disc, talyst filling line FBMR Temperature / More		Exceeds design temperature at operating pressure. Physical injury	High temperature alarms for skin temperatures below any band and strip heater will turn off all external heaters
		FBMR Temperature / Less	Heaters failure/ high water flow rate	Poor reactor performance	Low level alarms TALL-601 to TALL-608. Shuts off water pump to prevent liquid water from entering FBMR
8	ROG line to vent	Temperature / More	High ROG temperature	Damage to pressure control valve (PR-600)	High temperature alarm TAHH- 640
0		Pressure / Less	Blockage of sample line filtersInability to sample gases.No safety issues		Clean filters on next reactor shutdown.
9	Sample lines.	Pressure / More	No safety issues;	Pressure won't be higher than FBMR	
		Pressure / Less	High suction from hydrogen pump	No safety issues	
		Pressure / More	Membrane leak	Poor reactor performance.	High pressure alarm PAHH-703
	Permeate lines.	Temperature / More	Membrane leak	Damage to vacuum pump, Poor reactor performance	High temperature alarm TAHH- 702
10	permeate lines	Temperature / Less		No safety issues	Low temperature alarm TALL-702
	and venting operation	Flow / More	Membrane leak	Poor reactor performance.	Taken care of by high pressure alarm PAHH-703
		Flow / Less		No safety issues	
		Composition/Fluctuation	Membrane leak	Poor reactor performance.	Occasional sampling of permeates

Table 2.8: Hazards and Operability Study Worksheet (....continued)

					1	2	б	5	9	7	8	6	11	12	13	14	
Legends:		-	TAG#	HS-501	PCV-601	HS-701	XV-119	XV-419	XV-315	XV-1204	XV-205	009-XH	006-XH	HX-1001	HX-1050		
O = O FO = SP =	Dpen Fully Open Stop		(STUTT)	P&ID													
Notes (1) F trigge initia 1204	Ar 500p ST= Start FOOLD Notes: 1) 1) FALL-401 / 1204 effects not riggered until FI-401 / 1204 has nitially surpassed FALL-401 / 1204 value		EFFECT (OU	SERVICE DESCRIPTION	Water Pump	Reactor Pressure Control Valve	Hydrogen Vacuum Pump	Process N2 Solenoid	Process NG Solenoid	Startup Hydrogen Solenoid	Propane / Heptane Solenoid	Water Solenoid	Reactor Internal Heaters	Reactor External Heaters	Process Feed Super Heater	FBMR Feed Heat Rope	
	CAUSE (INPU)	ΓS)															
	TAG #	P&ID Sheet	SERVICE DE	SCRIPTION													COMMENTS
1	ESD BUTTON				SP	FO	SP	0	С	С	С	С	SP	SP	SP	SP	ESD
2	AAHH-603	3	Toxic Gas	Monitor	SP	FO	SP	0	С	С	С	С	SP	SP	SP	SP	Triggers ESD
3	AAHH-605	3	Combustible Gas Monitor		SP	FO	SP	0	С	С	С	С	SP	SP	SP	SP	Triggers ESD
4	FALL-1204	2	Low Propane / Heptane Flow					0			С						Note 1 below
5	FALL-401	2	Low Process NG Flow					0	С								Note 1 below
6	FFDAHH-500	2	Steam to Carbon Mole Ratio		SP							С					
7	FFDALL-500	2	Steam to Carbo	on Mole Ratio				0	С		С						
8	HS-703 - off	4	Scroll Pump co	ooling fan off			SP										

Table 2.9:Cause & Effect matrix for actions by the PLC

				1					(1
				HS-501	PCV-601	HS-701	XV-119	XV-419	XV-315	XV-1204	XV-205	009-XH	006-XH	HX-1001	HX-1050	
9	PAHH-1001	2	Feed line pressure	SP	FO	SP	С	С	С	С	С	SP	SP	SP	SP	High P Trip
10	PAHH-1200	2	Vaporizer upstream Pressure	SP	FO	SP	С	С	С	С	С	SP	SP	SP	SP	High P Trip
11	PAHH-501	2	High Water Pump Discharge	SP							С					
12	PAHH-600	3	Freeboard Absolute Pressure	SP	FO	SP	С	С	С	С	С	SP	SP	SP	SP	High P Trip
13	PAHH-701	4	Permeate Header Pressure			SP										
14	PAHH-703	4	H ₂ Vacuum Pump Dishcarge			SP										
15	PALL-005	1	Low Instrument Air	SP	FO	SP	0	С	С	С	С	SP	SP	SP	SP	Triggers ESD
16	PALL-701	4	Permeate Header Pressure			SP										
17	PAHH-912	3	FBMR pressure above distribuor	SP	FO	SP	С	С	С	С	С	SP	SP	SP	SP	High P Trip
18	TAHH-1000	2	High Vaporizer Skin Temperature											SP		
19	TAHH-1001	2	High Vaporizer Product											SP	SP	
			Temperature													
20	TAHH-601	3	FBMR Temperature (Flange 1)									SP	SP	SP	SP	
21	ТАНН-602	3	FBMR Temperature (Flange 2)									SP	SP	SP	SP	
22	TAHH-603	3	FBMR Temperature (Flange 3)									SP	SP	SP	SP	
23	TAHH-604	3	FBMR Temperature (Flange 4)									SP	SP	SP	SP	Grouped as
24	TAHH-605	3	FBMR Temperature (Flange 5)									SP	SP	SP	SP	common high
25	TAHH-606	3	FBMR Temperature (Flange 6)									SP	SP	SP	SP	FBMR temp
26	TAHH607	3	FBMR Temperature (Freeboard)									SP	SP	SP	SP	
27	TAHH-608	3	FBMR Temperature (Above									SP	SP	SP	SP	
			Distributor)													
28	TAHH-640	3	High ROG Temperature									SP	SP	SP	SP	
29	ТАНН-702	4	H ₂ Vacuum Pump Discharge			SP										

Table 2.9: Cause & Effect Matrix for actions by the PLC (.... Continued)

				HS-501	PCV-601	HS-701	XV-119	XV-419	XV-315	XV-1204	XV-205	009-XH	006-XH	HX-1001	HX-1050				
34	ТАНН-915	3	HT-BA901 Temperature										SP						
35	TAHH-916	3	HT-BA902 Temperature										SP						
36	TAHH-917	3	HT-BA903 Temperature										SP						
37	TAHH-918	3	HT-BA904 Temperature										SP						
38	TAHH-919	3	HT-BA905 Temperature										SP						
39	ТАНН-920	3	HT-BA906 Temperature										SP						
40	ТАНН-921	3	HT-BA907 Temperature										SP			Grouped as common high			
41	ТАНН-922	3	HT-BA908 Temperature										SP						
42	ТАНН-923	3	HT-BA-909 Temperature										SP			external heaters temperature			
43	ТАНН-924	3	HT-BA-910 Temperature										SP						
44	ТАНН-925	3	HT-ST901 Temperature										SP						
45	ТАНН-926	3	HT-ST902 Temperature										SP						
46	ТАНН-927	3	HT-ST903 Temperature										SP						
47	ТАНН-928	3	HT-ST904 Temperature										SP						
48	ТАНН-929	3	HT-ST905 Temperature										SP						
49	ТАНН-930	3	HT-ST906 Temperature										SP						
50	ТАНН-939	3	High Rupture Disc Temperature	SP	FO	SP	0	С	С	С	С	SP	SP	SP	SP	ESD			
51	TALL-1001	2	Low Vaporizer Product	SP							С								
			Temperature																
52	TALL-601	3	FBMR Temperature (Flange 1)	SP							С								
53	TALL-602	3	FBMR Temperature (Flange 2)	SP							С								
54	TALL-603	3	FBMR Temperature (Flange 3)	SP							С								
55	TALL-604	3	FBMR Temperature (Flange 4)	SP							С					Grouped as			
56	TALL-605	3	FBMR Temperature (Flange 5)	SP							С					common low			
57	TALL-606	3	FBMR Temperature (Flange 6)	SP							С					FBMR Temp			
58	TALL-607	3	FBMR Temperature (Freeboard)	SP							С								
59	TALL-608	3	FBMR Temperature (Above Distributor)	SP							С								

Table 2.9: Cause & Effect Matrix for actions by the PLC (.... Continued)



Figure 2.1: FBMR pressure vessel supported on a mobile stand



Figure 2.2 (a):P&ID of pilot plant layout (Supplementary gas feeding section)



Figure 2.2 (b): P&ID of pilot plant layout (Steam and hydrocarbon feeding section)



Figure 2.2 (c): P&ID of pilot plant layout (FBMR)



Figure 2.2 (d): P&ID of pilot plant layout (Gas sampling and Permeate sections)



Figure 2.3 (a): Strength of SA-240 grade 304H plate material as a function of temperature (*Ref: ASME - International Boiler and Pressure Vessel Code – 2007 Edition*)



Figure 2.3 (b): MAWP rating of the FBMR pressure vessel (provided by Jenmar Concepts Inc.)



Figure 2.4 (a): Instrumentation ports on a lateral flange cover, also showing a membrane panel installed



Figure 2.4 (b): Membrane panel dimensions



Figure 2.5: Pressure transducers arrangement

2.7 References

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CHAPTER 3. STEAM REFORMING OF PROPANE IN A FLUIDIZED BED MEMBRANE REACTOR FOR HYDROGEN PRODUCTION*

3.1 Introduction

3.1.1 Background

Hydrogen is an important feedstock in several industries, especially for making ammonia and in petrochemical and petroleum refining processes¹⁻³. Stringent environmental regulations require increasing quantities of hydrogen for hydro-treating processes in oil refineries, especially as available crudes become heavier. The demand is likely to increase sharply in the future due to projected hydrogen demand by the automobile sector^{4,5}. Many uses of hydrogen like fuel cell processes also put special demand on the purity of the hydrogen.

Table 3.1 shows hydrogen content in liquid methane (for conditions similar to LNG storage), liquid propane (conditions similar to commercial LPG tanks) and n-heptane, a liquid under normal ambient conditions. While the hydrogen content is highest for methane, the volumetric hydrogen density is most favorable for higher hydrocarbons which are liquids at or near ambient conditions.

Currently, the most favored feedstock for hydrogen production is natural gas due to its availability and advantageous price. In addition, compared with higher hydrocarbon feedstocks like LPG or naphtha, the challenges from the feedstock sweetening process and catalyst deactivation are much easier to handle with natural gas as feedstock. However, higher hydrocarbons are preferred in many places, depending on local availability and local prices relative to natural gas. This is especially important in oil refineries where demand for hydrocarbon feedstock and products vary over time, so that the industry gains from flexibility of feedstock choice. Fuel cell applications for on-board hydrogen generation or distributed

^{*} A version of this chapter has been accepted for publication: **Rakib**, **M.A.**, Grace, J.R., Lim, C.J., Elnashaie, S.S.E.H., and Ghiasi, B, Steam Reforming of Propane in a Fluidized Bed Membrane Reactor for Hydrogen Production, *International Journal of Hydrogen Energy* (2010)

hydrogen filling stations also demand that the feedstock have a high volumetric hydrogen density, preferably at atmospheric or near-ambient pressures.

LPG or Liquefied Petroleum Gas can be liquefied under relatively low pressures and is an abundant feedstock from refinery operations. The advantage of LPG relative to heavier hydrocarbon feedstocks like naphtha or diesel as a source of hydrogen is that it is cleaner and contains a higher weight percent of hydrogen. Also, depending on seasonal demand, refinery operations often result in a surplus of different feedstocks. For example, LPG demand soars in winter due to increased heating requirements, whereas it is usually in surplus throughout the summer.

LPG is a mixture of hydrocarbons, predominantly propane and n-butane, with its composition depending on the source, recovery processes, and season. It can be a mixture of either predominantly butane, or predominantly propane, with propylene and butylenes also present in small amounts. The most common LPG is predominantly propane. In the US and Canada, LPG is at least 95% propane. This paper deals with an experimental study of a novel steam reformer and its operation with propane as the feedstock.

There are various methods for generating hydrogen from propane:

Propane steam reforming

$$C_{3}H_{8} + 3H_{2}O \rightarrow 3CO + 7H_{2}$$
 $\Delta H^{\circ}_{298} = 499 \text{ kJ/mol}$ (3.1)

Propane CO₂ reforming

$$C_{3}H_{8} + 3CO_{2} \rightleftharpoons 6CO + 4H_{2} \qquad \qquad \Delta H^{\circ}_{298} = 622 \text{ kJ/mol} \qquad (3.2)$$

Propane partial oxidation

$$C_{3}H_{8} + 3/2 O_{2} \rightarrow 3CO + 4H_{2}$$
 $\Delta H^{\circ}_{298} = -227 \text{ kJ/mol}$ (3.3)

Propane decomposition

$$C_{3}H_{8} \rightarrow 3C + 4H_{2}$$
 $\Delta H^{\circ}_{298} = 105 \text{ kJ/mol}$ (3.4)

Among these, CO₂ reforming of propane^{6,7} is relatively slow, and hence un-economical compared to steam reforming⁸. The decomposition pathway⁹⁻¹¹ is attractive since the hydrogen produced is free of CO, while also ensuring that no additional greenhouse gases like CO₂ or CH₄ are produced. However, this reaction is challenging from a catalyst stability point of view. Partial oxidation¹² is preferred when a carbon-monoxide-rich syngas is desired or if inexpensive oxygen is available. Steam reforming is the most economical pathway in terms of hydrogen yield¹³⁻¹⁶, since hydrogen is produced from steam as well as propane. Autothermal reforming has also been employed as a combination of partial oxidation and steam reforming¹⁷⁻²¹. Steam

reforming has been studied in our research. Several other reactions take place following the main steam reforming process:

Methanation and Methane steam reforming

$$CO + 3 H_2 \rightleftharpoons CH_4 + H_2O \qquad \qquad \Delta H^{\circ}_{298} = -206 \text{ kJ/mol} \qquad (3.5)$$

Water gas shift

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \qquad \Delta H^{\circ}_{298} = -41 \text{ kJ/mol} \qquad (3.6)$$

Methane overall steam reforming

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad \qquad \Delta H^{\circ}_{298} = 165 \text{ kJ/mol} \qquad (3.7)$$

Summing equation (3.1) and 3 times equation (3.6) leads to

Propane overall steam reforming

$$C_{3}H_{8} + 6H_{2}O = 3CO_{2} + 10H_{2}$$
 $\Delta H^{\circ}_{298} = 499 \text{ kJ/mol}$ (3.8)

Since industrial operations always use excess steam to minimize catalyst deactivation, the maximum yield of hydrogen per mole of propane fed can be 10. The following carbon formation processes can also take place as unwanted side reactions.

$C_3H_8 \rightarrow 3C + 4H_2$	(3.4)	1)	
	· ·	- /	

$$CH_4 \rightleftharpoons C + 2H_2$$
 (3.9)

$$2CO \rightleftharpoons C + CO_2$$
 (3.10)

$$CO + H_2 \rightleftharpoons H_2O + C$$
 (3.11)

$$CO_2 + 2H_2 \rightleftharpoons 2H_2O + C$$
 (3.12)

3.1.2 Equilibrium compositions in steam reforming of propane

Figure 3.1 shows the dry gas equilibrium compositions from HYSYS process simulation software, version Aspen HYSYS 7.1, for temperatures from 450 to 800°C and two pressures. Propane is seen to be fully converted at all temperatures in the range considered, indicating that steam reforming of propane is almost irreversible. No intermediate hydrocarbons were formed, except traces of ethane (~0.01%). Methane appears as an intermediate component by reverse steam reforming, and the overall conversion of hydrocarbons is limited by the steam reforming of methane. Since steam reforming of methane is highly endothermic, the methane yield decreases while the hydrogen yield increases, as temperature is increased. Since the overall reactions result in a net increase in the number of moles, increasing pressure causes a drop in the hydrogen yield, while increasing methane yield.

3.1.3 Steam reforming of propane: Industrial practice

Refineries are turning from net producers of hydrogen to be net consumers due to increasing demand of hydrotreating operations^{3,22}. With stricter governmental regulations of industrial emissions and growing need for additional hydrogen, refiners are sending off-gases, instead of flaring, and natural gases with varying contents of propane, in addition to LPG, to reformers for hydrogen production. If used in distributed production facilities for hydrogen, e.g. for hydrogen filling stations, propane or LPG may be fed to hydrogen production units. In refineries, the feedstock is fed first to a pre-reformer, operated at relatively low temperatures of 450 to $550^{\circ}C^{23}$. All hydrocarbons heavier than methane are completely converted to C₁ components (methane or carbon oxides), producing a methane-rich gas which is introduced to the steam reformer, which operates at higher temperatures of ~850 to 950°C. Using a pre-reformer means that the higher temperature steam reformer does not see variations in feedstock composition, and catalyst deactivation is minimized. The steam reformer is followed by a shift reactor section, followed by a pressure swing adsorption to produce hydrogen of 98 to 99.999% purity²⁴.

3.1.4 Fluidized bed membrane reactor (FBMR)

Fixed bed membrane reactors have been extensively studied for steam reforming of natural gas or methane²⁵⁻³⁰, and to a limited extent for LPG³¹ and liquid hydrocarbons^{32,33}. Achieving very high hydrogen yield in reforming propane is prevented by the equilibrium of the steam reforming of methane and water-gas-shift reaction. From Le Chatelier's principle, hydrogen yield can be maximized by selectively removing product hydrogen by perm-selective membrane panels. Another major drawback of traditional steam reformers arises from large intra-particle diffusional resistances. The effectiveness factors of the catalysts can be improved greatly from ~ 0.01 to 0.001 for industrial steam reforming catalyst pellets³⁴ to almost unity by reducing the catalyst particle size. Pressure drop limitations then dictate that the bed be operated in a fluidized mode for fine catalyst powders. Combining these concepts, a fluidized bed membrane reactor (FBMR) was developed at the University of British Columbia³⁵ for steam reforming of natural gas. The FBMR concept for hydrogen production from natural gas has been studied extensively³⁵⁻³⁸. This concept is extended to steam reforming of propane in this study. Rakib et al.³⁹ utilized a two-phase model for sizing an FBMR for our proof-of-concept experiments. Details of the layout planning, safety considerations and installation are described elsewhere⁴⁰. The same reactor was also used to reform $heptane^{41}$.

3.2 Catalysts for Steam Reforming of Propane

3.2.1 Catalyst selection

Steam reforming of hydrocarbons can be catalyzed by several transition metals. The specific activities of metals supported on alumina or magnesia have been found to be^{42,43} in rank order Rh, Ru > Ni, Pd, Pt > Re > Co. Catalyst selection from this list is predominantly an economic consideration. However, catalyst activity and stability are also important considerations. In terms of activity as well as stability, both ruthenium and rhodium are more effective catalysts than nickel⁴⁴, on which carbon formation appears to occur via a different mechanism. In addition to its lower activity, more coking arises with nickel because of formation, diffusion and dissolution of carbon in the metal, whereas dissolution of carbon in ruthenium and rhodium is considerably less. Despite their advantages, the cost and availability of Rh and Ru are such that these catalysts are not used widely in industrial applications.

The most widely used catalysts for large scale industrial reformers are Al_2O_3 -supported nickel. Especially for higher hydrocarbon feedstocks, these catalysts are frequently modified by promoters such as earth alkaline metals like Mg and Ca to improve their stability and selectivity, by reducing the acidity of the support, thereby suppressing cracking and polymerization reactions. Resistance to coke formation on Ni-based steam reforming catalysts can be significantly increased by adding K₂O, MgO or CaO⁴⁵⁻⁴⁸.

Commercial steam reforming catalysts are usually designed for operation at 850-900°C and above. However, FBMR operation typically does not exceed 600°C, so the catalyst must be active at this lower temperature. RK-212 naphtha steam reforming catalyst from Haldor Topsoe A/S was chosen based on the fact that it is used industrially for steam reforming of naphtha or lighter hydrocarbons at temperatures of 650°C or higher. The composition of the RK-212 catalyst is summarized in Table 3.2. It is available as 7-holed black pellets in pre-reduced form, with pellet size and shape optimized for fixed bed operation, adequate crushing strength and low pressure drop. In order to use the catalyst in a fluidized mode, the pellets were carefully crushed and sieved to narrow size cuts. The catalyst loaded to the FBMR was an equal weight mixture of +150 μ m -180 μ m and +180 μ m -212 μ m, size cuts, giving a mean particle diameter of 179 μ m. This particle size provided good hydrodynamics (as observed in a Plexiglas cold model replica of the reactor), and was small enough to give favorable effectiveness factors, but large enough to minimize entrainment. The minimum fluidization velocity estimated at ambient conditions was 0.026 m/s. For shapes of the particles, see Appendix E.
3.2.2 Micro-reactor testing of RK-212 catalyst particles

Compared to methane, steam reforming of higher hydrocarbon feedstocks, including propane, has a higher carbon formation propensity. Even though the minimum steam-carbon ratio is 2.2, ratios of 4 to 6 are common industrially^{23,49-51}.

A catalyst evaluation unit (CEU), shown schematically in Figure 3.2, was installed to identify the favorable operating conditions for the FBMR. The feed materials were water, hydrogen, and propane, accurately metered using mass flow controllers from Brooks Inc. Water is vaporized by passing through a steam generator, and mixes downstream with propane and hydrogen, before being fed to the vertical stainless steel microreactor of internal diameter 6.9 mm and length 457 mm. The actual catalyst bed height was about 50 mm, and the screen size cut +106 μ m –125 μ m. The product gases from the micro-reactor passed through a condenser to remove liquid water before venting or analysis. A pressure regulator was installed downstream of the condenser to maintain the required reactor pressure. Part of the product gas was sent to a Shimadzu GC-14B gas chromatograph for analysis.

Catalyst activity was monitored by following the propane conversion, based on a carbon mass balance. The total catalyst mass was fixed at 1 g. Figure 3.3 shows stability plots of the catalyst for an operating temperature of 525°C, steam-to-carbon ratios of 4 to 6, and a hydrogen-to-carbon feed molar ratio 1, with the feed rate of steam fixed at 30 g/h, and the propane flow rates adjusted accordingly. Thus one of the factors to be borne in mind while interpreting the results for the conversion of propane is that the feed gas superficial velocities differed from case to case. As expected, the conversion improved with higher steam-to-carbon ratio and higher temperature. For the time spans of operation, it is seen that the propane conversions were quite stable. Although no drop in conversion can be observed from these plots, TEM analysis showed growth of filamentous carbon, with a nickel crystallite at the tip, whereas no encapsulating carbon formation could be seen from EDX analysis. TEM pictures for spent catalysts subjected to different operating conditions indicate that higher steam-carbon ratios decrease the rate of filamentous carbon formation. A lower steam-to-carbon ratio of 3.5 led to heavy blockage of the catalyst bed due to large amounts of filamentous carbon.

The micro-reactor data were used to identify operating conditions where the FBMR could be operated for long durations without significant catalyst deactivation. A base steam-to-carbon ratio of 5.0, with 4.0 as the minimum, was used for the FBMR.

3.3 Experimental Set-up and Procedure

Figure 3.4(a) shows a schematic of the FBMR vessel, of height 2.33 m. The main section above the distributor is 1.87 m in height, with rectangular cross-sections of 1.82 x 10^{-3} m² and 2.30 x 10^{-3} m², with and without membrane panels installed respectively. Above is an expanded circular cross section of 73.7 mm diameter.

3.3.1 Selective hydrogen removal

Palladium membranes are infinitely selective to permeation of hydrogen due to the unique solution-diffusion mechanism of permeation ^{52,53}. Diffusion depends on the difference of square roots of partial pressures on the two sides according to Sieverts' law when hydrogen diffusion is the rate determining step⁵⁴.

$$Q_{H_2} = A_P \frac{P_{M0}}{\delta_{H_2}} \exp\left(\frac{-E_{H_2}}{RT}\right) (\sqrt{P_{H_2,R}} - \sqrt{P_{H_2,M}})$$
(3.13)

Pd membranes are susceptible to hydrogen embrittlement due to phase transition at temperatures around 300°C, resulting in expansion of the metal lattice^{28,55-57}. Pd is often alloyed with other metals like Ag, Cu and Ru to improve their mechanical stability, resistance to hydrogen embrittlement and H₂ permeation. A Pd₇₇Ag₂₃ alloy, for example, leads to a 70% gain in hydrogen flux compared with pure Pd^{28,58}.

Six double-sided Pd-Ag membrane panels were inserted through vertical slits on the wall of the FBMR from alternating sides along the reactor height. These panels were arranged vertically one above the other, passing through the centerline of the reactor shell, resulting in two communicating sections at all levels. They were manufactured and supplied by Membrane Reactor Technologies⁵⁹, and are shown in Figure 3.4(b). The overall dimensions of the membrane panels were 231.8 x 73.0 mm x 6.35 mm. Accounting for the weld space for the stainless steel frame and bonding space for the Pd membrane on the substrate, the active membrane foil cross-sections were 206.4 x 50.8 mm with a thickness of 0.025 mm, the thinnest membranes where pinhole-free surface could be guaranteed at the time of purchase. These foils were bonded onto each side of the membrane panel. Each side opening supporting a membrane panel also corresponds to several ports: (i) one centrally-located for pure permeate hydrogen withdrawal, (ii) one for a thermocouple close to the permeate port, and (iii) two reactor gas sampling ports vertically equidistant from each end on either side of the permeate port. The arrangement of these ports and a schematic of a membrane assembly are shown in Figure 3.4(c).

Decreasing the hydrogen partial pressure on the permeate side, e.g. by providing a suitable sweep gas, can improve the hydrogen flux according to Sieverts' law (Equation 3.13). Alternatively, suction can be provided. In our experiments, a vacuum pump downstream of the permeate hydrogen manifold was employed to increase the driving force for permeation.

3.3.2 Heat supply to the reactor

Electrical band heaters were installed on the semi-circular areas opposite the side-opening flanges holding the membrane panels (henceforth referred to as lateral flanges), and on the reactor shell in the freeboard region. Electrically heated tubular heaters were inserted through the bottom flange cover, extending from just above the distributor to the top of the highest membrane panel. Heat losses occur most notably from the various flanges. The band heaters, strapped onto the reactor wall, provided additional localized heating. This array of heaters led to irregular temperature distributions in the bed, as detailed below.

3.3.3 Experiments

3.3.3.1 Operation

Figure 3.5 shows a schematic of the experimental setup. Propane was pressurized above its vapor pressure using compressed helium, and its flow was metered by a Bronkhorst mass flow controller. Distilled water was pumped and metered by a Brooks mass flow controller, and fed to the vaporizer. Propane was mixed with the superheated steam downstream of the vaporizer. This superheated stream then fluidized the catalyst particles in the reactor where the generated hydrogen was separated from the reaction gas mixture by the membrane surfaces.

Sufficient RK-212 catalyst particles were loaded into the reactor to completely immerse all six membrane (or dummy) panels, leaving 30 mm of catalyst above the upper edge of the topmost panel. The catalyst was reduced by introducing a nitrogen flow diluted with 1/3 parts (by volume) of hydrogen overnight at a temperature of 525°C, taking special care that hydrogen was only introduced when the bed temperatures exceeded 350°C. To initiate the experiments, superheated steam at temperatures above 500°C was introduced with the hydrogen, gradually decreasing the nitrogen flow. To avoid catalyst oxidation, the steam-to-hydrogen molar ratio was maintained below 6. Propane was introduced after ensuring a steady flow of steam, and the hydrogen feed rate was then gradually decreased to 0. The hydrogen vacuum pump was then adjusted to maintain the required partial pressure of hydrogen on the permeate side. When the desired operating conditions of temperature, flow rates, reactor pressure and permeate pressure were achieved, sample gas compositions were continuously monitored from one of the gas sampling ports. Steady state was deemed to have been achieved when the dry gas hydrogen composition oscillated by less than $\pm 1\%$ about its mean value.

3.3.3.2 Sample gas analysis

Once steady state was reached, sample gases were analyzed using a Varian CP-4900 micro-GC from different sampling points along the reactor height, repeating the first sampling after all other samples had been analyzed. The GC columns were able to quantify the gas concentrations as follows:

<u>Channel 1</u>: 10 m Molsieve 5A with pre-column back-flush. With Argon carrier gas, the Molsieve is capable of analyzing He, H₂, O₂, N₂, CH₄ and CO. The argon allows for increased sensitivity and a linear range of He and H₂. The detection limits range was from 10 to 100 ppm with the Molsieve.

<u>Channel 2</u>: 10 m PPU with pre-column back-flush. To optimize sensitivity and analysis time, helium was the carrier gas. With the back-flush enabled, the PPU was able to analyze CO_2 , C_2H_4 , C_2H_6 , C_2H_2 , H_2S and COS. Detection limits were in the 10 to 100 ppm range with the PPU.

<u>Channel 3</u>: 8 m Silica PLOT with pre-column back-flush. The carrier was again helium. With the back-flush enabled, the Silica PLOT was capable of analyzing C_3 and C_4 isomers. The Silica PLOT was chosen because it allows separation of alkenes in the presence of water vapour. Detection limits were again in the 10 to 100 ppm range.

3.3.3.3 Experimental plan

The FBMR was operated in three combinations of active or dummy membrane panels.

(a) <u>Six stainless steel dummies</u>: These experiments was carried out to assess the catalyst stability under the planned operating conditions and to determine the baseline performance without any membranes, similar to the performance of a pre-reformer in traditional steam reforming process, where all the higher hydrocarbons would be fully converted to a gas mixture, limited by equilibrium of the methane steam reforming reactions. The dummy panels were stainless steel plates of dimensions 231.8 x 73.0 mm x 6.35 mm, i.e. the same dimensions as for the active membrane panels, so that the reactor internal geometry was identical for all experimental runs.

(b) <u>One active membrane panel</u>: Initially, only one membrane was installed before conducting experiments with the full set of membranes. This single membrane panel was installed at the fifth opening from the bottom.

(c) <u>Six active membrane panels</u>: The final and major set of experiments was conducted to utilize the full hydrogen extraction capacity of the FBMR.

In the current study, average bed temperatures ranged from 475 to 525°C at a steam-tocarbon ratio of 5.0. For most runs, the feed rates were adjusted to give similar gas superficial velocities based on the average bed temperature and the feed molar flow. Due to heat losses and the inability to locate a heater too near the bottom of the reactor, and the low superficial gas velocities (resulting in limited axial dispersion of solids and hence of heat), the temperatures there were much lower than the average bed temperature so that the superficial velocities were also lower there. Due to the increase in molar flow due to reaction, the gas superficial velocity increased along the reactor when no hydrogen was withdrawn via the membrane panels. In all cases examined, the bed operated in the bubbling fluidization flow regime.

In most experiments, two or three samples were analyzed at each position. The error bars plotted here correspond to the standard deviations $(\pm 1 \sigma)$ for each gas sampling position. In many cases these error bars are not visible due to the scale of plotting and to stable conditions for these runs.

Table 3.3 shows the steady state reactor measurements. The locations of the probes are listed in Table 3.4. Table 3.4 also gives the spans and heights of the active membrane areas. The temperatures, pressures and flow rates are time-average values over the duration of experiment for each set of steady state operating conditions, and are provided in Table 3.5. To compare the experimental values with the equilibrium values corresponding to local conditions, local temperatures at sample withdrawal locations were determined by interpolation of the recorded bed temperatures.

Hydrogen permeate purities were also measured for each membrane panel from time to time. Product hydrogen purity was > 99.99% at the beginning of the experiments, while for two membranes, this purity decreased to > 99.96% towards the end of the experiments.

3.4 Experimental Results

The FBMR performance is analyzed by the extent of pure hydrogen production and the degree of approach towards complete conversion of the hydrocarbons:

Pure hydrogen yield =
$$\frac{\text{molar flow of pure hydrogen extracted via membranes}}{\text{molar flow of propane in feed stream}}$$
 (3.14)
Retentate hydrogen yield = $\frac{\text{molar flow of hydrogen in retentate stream}}{\text{molar flow of propane in feed stream}}$ (3.15)
Total hydrogen yield = Pure hydrogen yield + Retentate hydrogen yield (3.16)

The amount of carbon oxides generated is indicative of the conversion of propane and intermediate methane; hence we also calculated:

Carbon oxides yield =
$$\frac{(\text{molar flow of CO} + \text{molar flow of CO}_2)\text{ in retentate stream}}{3 \text{ x molar flow of propane in feed stream}}$$
 (3.17)

Methane yield =
$$\frac{\text{molar flow of methane in retentate stream}}{3 \text{ x molar flow of propane in feed stream}}$$
 (3.18)

In all of our propane steam reforming experiments, the propane conversion exceeded 99% from the lowermost sampling point, and hence it is not plotted here. Intermediate hydrocarbons like propylene and ethylene were not detected, whereas traces of ethane (less than 0.01% by volume in all cases) were detected, but are not considered in the performance calculations given their low levels.

Figure 3.6 depicts the performance of propane steam reforming with no in-situ hydrogen removal, i.e. with dummy stainless plates inserted through the six lateral openings, corresponding to experiments 1.a, 1.b and 1.c in Table 3.5. There is considerable axial temperature variation due to the low superficial gas velocity and limited coverage of the heater sections. As expected from thermodynamics, the carbon oxides and hydrogen yields decrease and methane yield increases with increasing reactor pressure. This could also have been affected somewhat by the fact that for these runs, the total molar feed rate was unchanged, meaning that higher pressure led to higher residence time.

The parity plot in Figure 3.7 shows that most experimental hydrogen yields were very close to the local equilibrium values. The hydrogen yields follow the same trend as the local bed temperatures, clearly indicating that the reactor behavior was controlled by local equilibrium conditions when no hydrogen was withdrawn from the reactor.

Figure 3.8 corresponds to experiments 2.a to 2.d where only one active membrane panel was installed at the 5th level from the bottom (corresponding to the shaded region), with dummy panels in the other five lateral openings. Pure hydrogen was drawn from the middle location of this opening (1.31 m above the distributor), whereas reactor gas samples were drawn from two different locations (1.235 m and 1.387 m respectively above the distributor) just below and above a permeate hydrogen port. For calculation purposes, the pure hydrogen drawn from this was allocated in equal proportions to the levels of the gas sample ports. All four sets of experiments reported in Figure 3.8 had identical feed molar flow rates, so that the feed superficial velocities decreased with increasing pressure. Thus experiments 2.a and 2.b had lower residence times than 2.c and 2.d. Temperature again varied significantly in the axial

direction. Two levels of permeate pressure were studied for each reactor pressure. Experiments 2.a and 2.c had similar performances. This can be attributed to a higher driving force for hydrogen permeation, as well as a higher residence time for permeation for 2.c compared to 2.a, counteracted by a negative impact on thermodynamic equilibrium. Similarly, experiments 2.b and 2.d showed similar performance for the same permeate pressures of 30 kPa, but this pair gave better performance than 2.a and 2.c where no vacuum was applied downstream of the membranes (permeate pressure = 101 kPa). Note also that the difference for these two pairs only became prominent after reaching the 5th lateral flange where the single membrane panel was installed. Higher pressure also increases the gas species concentrations, accelerating the reaction rates, an effect which cannot be confirmed here due to the already-fast kinetics of the steam reforming reactions.

From Figure 3.9 onwards, all plots depict results for experiments conducted with active membrane panels installed at all six lateral flanges. Compared to Figure 3.8, the performance is affected by membrane permeation starting from the lowest lateral flange, instead of the 5th flange. The shaded regions again correspond to height intervals where there were membrane surfaces.

Figure 3.9 corresponds to experiments 3.a, 3.b and 3.c, in which only the permeate side pressure was varied, other parameters remaining the same. It shows significant improvements in hydrogen yield and a drop in methane yield as the permeate pressure was reduced. This confirms the effect of the driving force as a key parameter for higher pure hydrogen yield and a significant equilibrium shift.

Figure 3.10 depicts the influence of reactor pressure with the average reactor temperature maintained at 500°C for reactor pressures of 400, 600 and 800 kPa, the permeate side pressures being 25 kPa for all three cases. The flow rates were adjusted to give similar superficial gas velocities. Higher reactor pressure led to poorer hydrogen yield. This can be understood in the light of a higher pressure increasing the hydrogen permeation driving force, but the performance being negatively affected by thermodynamics which means that higher pressures may or may not always translate into higher FBMR performance.

Figure 3.11 shows the effect of varying the steam-to-carbon ratio for an average bed temperature of 500°C and a reactor pressure of 600 kPa. Total feed molar flow rates were identical in these three runs. From a thermodynamics point of view, higher steam partial pressure positively affects the reactor performance, leading to a higher yield of hydrogen. A higher hydrogen partial pressure in the reactor results in more pure hydrogen production as seen in

Figure 3.11, followed by higher yields of carbon oxides and total hydrogen, and lower yields of methane as the steam-to-carbon ratio increases. Excessive steam could actually decrease the performance by diluting the hydrogen, leading to less permeation.

Higher reactor temperature greatly enhances the reaction rates. For equilibrium-limited endothermic reactions, higher temperatures also shift the reaction in the forward direction. Higher temperature also improves the permeability of hydrogen through the membranes. To show the influence of temperature, Figure 3.12 compares results from experiments 6.a and 6.b, with average bed temperatures of 475 and 525°C respectively, to those from experiment 3.c, where the average bed temperature was 500°C, all other operating conditions being the same, with the reactor feed rates adjusted to give the same superficial velocities. Higher average temperatures were not investigated to protect the membranes. One data point corresponding to 525°C is missing for the off-gas sample because the reservoir ran out of propane at that point of time. However, the more important data for samples from the dense catalyst bed for this temperature could be collected adequately as reported. Note from Figure 3.12 that the total hydrogen yield was as high as 9.26, close to the maximum possible value of 10. Consistently higher carbon oxides yield and dwindling methane yield are found as temperature increased.

The effect of total molar feed rate, and hence superficial gas velocity inside the reactor was also investigated. Experiment 7 had a 33% higher molar feed rate than experiment 3.c, all other conditions being essentially the same. Results are shown in Figure 3.13. One of the important effects of higher gas velocity was an improvement in temperature uniformity, probably due to more axial solids mixing. A slight increase in pure hydrogen yield with decreasing total molar feed rate is evident, but there was little effect on any of the yields.

In Figure 3.14, the effects of hydrogen removal on the methane and total hydrogen yields are compared in a parity plot of the experimental yields versus the equilibrium values if no hydrogen was removed. The experimental data correspond to values at 1.64 m above the distributor, i.e. the top of the sixth (uppermost) membrane panel, with the equilibrium values based on the local temperatures. Without hydrogen removal, the experimental hydrogen yield is somewhat lower than the equilibrium values. With six membrane panels, evacuating the permeate side to 50 kPa boosted the hydrogen yield above the equilibrium value, while evacuating it further to 25 kPa gave further improvement. The methane slip also decreased with membranes present and increased vacuum on the permeate side. Decreasing the partial pressure of hydrogen on the permeate side, and increasing the active membrane surface area

(corresponding to the number of membrane panels here) are clearly the most important means of improving the hydrogen and methane yields from the FBMR.

3.5 Discussion

Steam reforming of propane can be viewed as producing CO and H_2 by Equation 3.1, followed by production of methane by Equation 3.5, with the propane completely consumed within a very short distance above the distributor, and the water gas shift (Equation 3.6), and methane steam reforming (Equations 3.5 and 3.7) reactions taking place in the bulk of the FBMR. The latter equilibrium-limited reactions are driven towards producing more hydrogen, as hydrogen is progressively and selectively removed from the system.

The results demonstrate that by steam reforming propane in an FBMR, a pre-reformer is not needed since high hydrogen yields can be attained in the reformer itself due to shifting the performance well beyond the normal equilibrium, even at the relatively low temperatures typical of pre-reformer operations. A moderate operating temperature of ~500°C can reach conversions otherwise only achievable at >750°C, and minimize catalyst deactivation problems for higher hydrocarbons. Operation at such moderate temperatures also assists in saving energy and in avoiding the expensive containment alloys for high-temperature operation required in conventional steam reformers. A separate downstream purifier for extracting pure hydrogen is also not required.

Flexibility in feedstock is possible, since the FBMR was demonstrated here to work well with propane as feedstock, while it has also been shown to work with natural gas³⁵ and heptane⁴¹. However, heavier feedstocks require higher steam-to-carbon ratios. The hydrodynamic implications resulting from this may need to be investigated.

Membrane separation of pure hydrogen from the reactor gas mixture improves the reactor performance significantly, resulting in higher hydrogen yield. Performance can be improved either by increasing the reactor pressure or by decreasing the permeate side hydrogen partial pressure. However, increasing the reactor pressure causes a decrease in equilibrium hydrogen yield in the FBMR, and hence does not necessarily translate into higher hydrogen partial pressure. Decreasing the hydrogen partial pressure on the permeate side, on the other hand, is effective and relatively straightforward, achievable either by a vacuum pump or by using a sweep gas like steam. At the relatively lower steam reforming temperatures (450 to 550°C) of this study, the CO content of the reformer outlet is very low, since the water gas shift reaction is favoured at low temperatures. This was observed with the dry gas content of CO mostly less than 1.5%, much lower than in traditional steam reformers. So, in addition to high hydrogen yield, the product gas very-low CO content is an additional advantage of FBMR, where the retentate dry gas composition was typically 45-50% CO₂, 30-40% H₂, 7-15% CH₄, and 0-2% CO, depending on the operating conditions.

Parametric studies were carried out to characterize the reactor performance. For an average bed temperature of 500°C, reactor pressure of 800 kPa, permeate pressure of 25 kPa, steam-to-carbon molar ratio of 5.0, a total feed rate of 0.819 mols/min, and a total membrane permeation area of 0.126 m², the FBMR produced 0.435 Nm³/h of pure hydrogen. The maximum hydrogen yield in the experiments, for a low feed rate (0.595 mols/min) and a higher average bed temperature (525°C), was 7.71 moles of pure hydrogen (and 9.26 moles of total hydrogen) per mole of propane fed, the theoretically possible maximum being 10.

High-purity hydrogen (~99.99% hydrogen) was produced from each of the membrane panels. Theoretically, Pd-based membranes have infinite selectivity for hydrogen. However, in these experiments, the hydrogen permeate was not 100% pure, probably due to structural defects or faults, commonly called pinholes, in the membranes.

3.6 Conclusions

Steam reforming of propane was studied in a fluidized bed membrane reactor for production of pure hydrogen. Experiments with membrane dummies, instead of active membranes, indicate that for the operating conditions studied, the local gas compositions in the reactor closely approach equilibrium corresponding to the local temperatures and pressures. Continuous removal of pure hydrogen selectively through Pd-Ag membrane shifts the equilibrium towards production of more hydrogen. Experiments with one membrane panel and with six membrane panels show that the performance of an FBMR improves relative to the no-membrane case, but the extent of improvement is limited by the membrane permeation capacity. Higher reactor side pressure do not always improve the hydrogen yield, because higher driving forces of permeation are offset by lower equilibrium conversions. Since there is a continuous shift in the equilibrium towards more hydrogen production when there is continuous pure hydrogen removal, an FBMR for steam reforming of propane can combine the functions of a pre-reformer, reformer, shift

converter and purification section, into a single unit. High-purity hydrogen (~99.99% hydrogen) was produced from each membrane panel. Since high hydrogen yields can be obtained at relatively low temperatures like 475 to 550°C, catalyst deactivation by sintering and high temperature carbon formation can be minimized. Propane was fully consumed at the beginning of the FBMR, which predominantly acts as a methane steam reformer. Since the bulk of the FBMR does not see the higher hydrocarbon, the FBMR can be operated flexibly with a variety of feedstocks.

Hydrocarbon	Conditions	Liquid density	Molar density	Hydrogen content	Hydrogen proportion	
u		(kg/m ³)	(kmol/m ³)	(kg H ₂ / m ³ hydrocarbon)	(kg H ₂ / kg hydrocarbon)	
Methane	Ambient pressure, -162.5°C	424.9	26.48	106.7	0.25	
Methane	11.86 bar, -120.5°C	352.9	21.99	88.66	0.25	
Propane	8.62 bar, 20°C	500.3	11.35	91.53	0.18	
n-Butane	2.07 bar, 20°C	578.8	9.96	100.4	0.17	
n-Heptane	Ambient pressure, 20°C	682.4	6.81	109.8	0.16	

Table 3.1: Density of liquid/ liquefied hydrocarbons at ambient pressure

Table 3.2: Composition of RK-212 (catalyst provided by Haldor Topsoe A/S)

% (w/w)	Component			
12-15	Nickel	Ni		
0-3	Nickel monoxide	NiO		
25-30	Magnesium oxide	MgO		
60-65	Aluminium oxide	Al_2O_3		
1-2	Potassium oxide	K ₂ O		
1-4	Calcium oxide	CaO		
MgO bound as magnes	ium aluminate spinel (MgAl ₂ O ₄)			
CaO bound as calcium aluminate spinel (CaAl ₄ O ₇)				

Table 3.3:	Steady-state reactor measurements
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Performance	Device and Location			
variables				
Bed temperatures	One thermocouple just above distributor, one thermocouple			
	close to the center of each membrane panel, one for the			
	freeboard, and one just before reformer exit.			
Gas compositions	Two sampling ports for each of the lateral flanges			
	supporting a membrane panel, one for the ROG. These			
	thirteen sample gases are analyzed online by a Varian			
	micro-GC CP-4900 using sample selection valves.			
Permeate hydrogen	Flow rate of permeate hydrogen from each membrane panel			
	using mass flow meters.			
Purity of permeate	Checking hydrogen purity in permeate product from each			
hydrogen	membrane panel by the micro-GC.			
Pressures	Absolute pressures in the feed line, freeboard, and at the			
	distributor level in bed. Differential pressure between			
	alternate levels of side flanges (i.e. the pairs 1-3, 3-5, 2-			
	4, and 4-6) and between the distributor and freeboard.			

Table 3.4: Location of sampling ports, thermocouples and pure hydrogen withdrawal, and height intervals of active membrane surface

Description (Side opening	Location above	Height interval covered by		
counted from bottom)	distributor holes (m)	active membrane		
Thermocouple (Bottom)	0.01	-		
Thermocouple (Side opening 1)	0.32	-		
Thermocouple (Side opening 2)	0.52	-		
Thermocouple (Side opening 3)	0.78	-		
Thermocouple (Side opening 4)	1.08	-		
Thermocouple (Side opening 5)	1.29	-		
Thermocouple (Side opening 6)	1.59	-		
Thermocouple (Freeboard)	2.33	-		
Gas samples (Side opening 1)	0.22, 0.37	-		
Gas samples (Side opening 2)	0.47, 0.63	-		
Gas samples (Side opening 3)	0.73, 0.88	-		
Gas samples (Side opening 4)	0.98, 1.13	-		
Gas samples (Side opening 5)	1.24, 1.39	-		
Gas samples (Side opening 6)	1.49, 1.64	-		
Pure hydrogen (Side opening 1)	0.30	0.19 - 0.40		
Pure hydrogen (Side opening 2)	0.55	0.45 - 0.65		
Pure hydrogen (Side opening 3)	0.80	0.70 - 0.91		
Pure hydrogen (Side opening 4)	1.06	0.95 – 1.16		
Pure hydrogen (Side opening 5)	1.31	1.21 – 1.41		
Pure hydrogen (Side opening 6)	1.57	1.46 - 1.67		

Expt	Active Membranes	Total feed	T _{av}	Р	P_m	SCR
No.	(Location)	rate				
		(mols/min)	(°C)	(kPa)	(kPa)	
1.a		0.673	500	400	NA	6.0
1.b	None	0.673	500	600	NA	6.0
1.c		0.673	500	700	NA	6.0
2.a		0.717	485	515	101	5.0
2.b	1	0.717	485	515	30	5.0
2.c	(#5)	0.717	485	700	101	5.0
2.d		0.717	485	700	30	5.0
3.a	6	0.614	500	600	101	5.0
3.b	(#1 to #6)	0.614	500	600	50	5.0
3.c		0.614	500	600	25	5.0
4.a	6	0.410	500	400	25	5.0
4.b	(#1 to #6)	0.819	500	800	25	5.0
5.a	6	0.614	500	600	25	4.0
5.b	(#1 to #6)	0.614	500	600	25	6.0
6.a	6	0.635	475	600	25	5.0
6.b	(#1 to #6)	0.595	525	600	25	5.0
7	6	0.819	500	600	25	5.0
	(#1 to #6)					

Table 3.5:Experimental runs for steam reforming of propane



Figure 3.1: Equilibrium compositions (dry gas) in propane steam reforming for steam-tocarbon molar ratio = 5.0: (a) P = 400 kPa; (b) P = 1000 kPa



Figure 3.2: Schematic of micro-reactor set-up to study steam reforming of propane



Figure 3.3: Propane conversion for steam reforming in micro-reactor, T = 525 °C, $H_2O = 30$ g/h



Figure 3.4: The FBMR pressure vessel, showing dimensions of membrane panel, and arrangement of ports on each lateral flange cover where membrane panels are installed



Figure 3.5: Schematic of experimental setup to study steam reforming of propane in an FBMR



Figure 3.6: Experimental yields and temperature for propane steam reforming without membrane panels at average reactor temperature of 500°C and steam-to-carbon ratio molar ratio of 6.0. Total reactor feed = 0.673 mols/min



Figure 3.7: Parity plot of experimental hydrogen yield without membrane panels against local equilibrium values



Figure 3.8: Experimental yields and temperature for propane steam reforming at average reactor temperature of 485° C and steam-to-carbon molar ratio 5.0. One membrane panel installed, spanning from 0.95 to 1.16 m above distributor. Total reactor feed = 0.717 mols/min



Figure 3.9: Experimental yields and temperature for propane steam reforming at average reactor temperature of 500°C, pressure 600 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed. Total reactor feed = 0.614 mols/min



Figure 3.10: Experimental yields and temperature for propane steam reforming at average reactor temperature of 500°C, permeate pressure 25 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed. Total reactor feeds = 0.410, 0.614, and 0.819 mols/min



Figure 3.11: Experimental yields and temperature for propane steam reforming at average reactor temperature of 500°C, pressure 600 kPa, and permeate pressure 25 kPa. Six membrane panels installed. Total reactor feed = 0.614 mols/min



Figure 3.12: Experimental yields and temperature for propane steam reforming at pressure of 600 kPa, permeate pressure 25 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed. Total reactor feeds = 0.635, 0.614, and 0.595 mols/min for 475, 500, and 525° C respectively



Figure 3.13: Experimental yields and temperature for propane steam reforming at average reactor temperature of 500°C, pressure 600 kPa, permeate pressure 25 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed



Figure 3.14: Parity plot of experimental yields against equilibrium values at local temperatures if there was no hydrogen removal: (a) Hydrogen yield (b) Methane yield

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CHAPTER 4. STEAM REFORMING OF HEPTANE IN A FLUIDIZED BED MEMBRANE REACTOR*

4.1 Introduction

4.1.1 Background

Hydrogen demand is increasing in the petrochemicals and petroleum processing sectors¹⁻⁴ and for other industrial applications. It may also increase significantly in the energy and transportation sectors⁵⁻⁸. Being a carbon-free fuel, hydrogen can assist in mitigating global warming due to greenhouse gas emissions if CO_2 emissions can be minimized during hydrogen production⁹.

About 48% of industrial hydrogen is produced from natural gas as feedstock¹⁰, largely due to the widespread availability of natural gas, as well as having the highest hydrogen-tocarbon ratio. However, for onboard hydrogen generation for mobile applications, liquid hydrocarbons like gasoline, naphtha, kerosene or diesel are advantageous feedstocks^{11,12}, safely storable under ambient conditions, and with much higher volumetric energy density than natural gas¹³. Liquid feedstocks like naphtha are often used for hydrogen production when natural gas is not available, accounting for about 30% of hydrogen production^{10,14}. In refineries, feedstock versatility for steam reformers would be a great advantage due to fluctuating demand and supply of different feedstocks¹⁵.

Naphtha is the most common liquid hydrocarbon feedstock for hydrogen production. For steam reforming, low aromatic-content naphtha (LAN) is preferred. Recently, naphtha prices have been unstable due to fluctuations in oil prices. For places with access to both naphtha and natural gas, naphtha tends to be an unprofitable feedstock for hydrogen production during peaks, while being preferred during slumps. Many steam reforming facilities worldwide, especially in India and China, have installed pre-reformer units upstream of natural gas steam reformers to facilitate feedstock flexibility.

^{*} A version of this chapter has been published: **Rakib**, **M.A.**, Grace, J.R., Lim, C.J., and Elnashaie, S.S.E.H., Steam Reforming of Heptane in a Fluidized Bed Membrane Reactor, *Journal of Power Sources* (2010) 195, 5749-5760

For steam reforming of higher hydrocarbons, the major reactions can be written:

Higher hydrocarbons steam reforming

$$C_n H_m + nH_2 O \rightarrow nCO + \left(n + \frac{m}{2}\right) H_2$$
 $\Delta H^0_{298} = 1108 \text{ kJ/mol for } n=7$ (4.1)

Methanation and methane steam reforming

$$CO + 3 H_2 \leftrightarrows CH_4 + H_2O$$
 $\Delta H^{\circ}_{298} = -206 \text{ kJ/mol}$ (4.2)

Water gas shift

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad \qquad \Delta H^{\circ}_{298} = -41 \text{ kJ/mol} \qquad (4.3)$$

Methane overall steam reforming

$$CH_4 + 2H_2O \leftrightarrows CO_2 + 4H_2$$
 $\Delta H^{\circ}_{298} = 165 \text{ kJ/mol}$ (4.4)

Summing equation (4.1) and n times equation (4.3) leads to

$$C_nH_m + 2nH_2O = nCO_2 + \left(2n + \frac{m}{2}\right)H_2$$

For n = 7 (i.e. n-heptane):

$$C_7H_{16} + 14H_2O = 7CO_2 + 22H_2 \tag{4.5}$$

Since, under industrial operating conditions, excess steam is always used to minimize catalyst deactivation, the maximum hydrogen yield is 22 moles per mole of heptane fed.

4.1.2 Catalyst issues in steam reforming of higher hydrocarbons

Commercial catalysts for steam reforming of hydrocarbons are generally based on Ni, dispersed on a refractory support, due to its high activity and low cost. Other possible candidates include Co, Pt, Pd, Ru and Rh, the order of specific activities of metals supported on alumina or magnesia being Rh, Ru >Ni, Pd, Pt >Re >Co ¹⁶. Ni catalysts present major coking problems because of the formation, diffusion and dissolution of carbon.

Higher hydrocarbons show a greater tendency to form carbon on Ni than methane. Therefore, special catalyst formulations containing alkali or rare earths, or based on an active magnesia support, are required¹⁷. For higher hydrocarbons, there is a potential for various forms of carbon formation¹⁸⁻²³.

A common technique to reduce carbon formation is to employ a higher steam-to-carbon ratio than required stoichiometrically, the excess increasing with the number of carbons in the hydrocarbon chain. For example, in industrial naphtha steam reforming, steam-to-carbon ratios of 4 to 6 are common²⁴⁻²⁶ compared with ~3 for natural gas. However, a high steam-to-carbon ratio decreases the thermal efficiency of the process, and also leads to a larger reformer due to
the higher volumetric gas flow rates. On the other hand, in addition to resulting in higher rates of carbon formation, lower steam-to-carbon ratios also lead to higher methane leaving the reformer, which must then be compensated by maintaining a higher exit temperature. Intensive research on catalyst design is being carried out to decrease this ratio²⁷.

4.1.3 Naphtha steam reforming: Industrial practice

4.1.3.1 Conventional naphtha steam reforming

Since steam reforming of methane is endothermic and equilibrium-limited, industrial natural gas steam reformers operate at temperatures >850°C to achieve high conversions. However, the same operating conditions cannot be applied to higher hydrocarbon feedstocks like naphtha because such high temperatures would cause rapid catalyst deactivation due to carbon formation and shorter reformer tube life. A conventional naphtha steam reformer uses catalysts promoted with alkali compounds to suppress carbon formation²⁸. In many cases, two catalysts are provided, with the entrance of the reformer loaded with a more robust catalyst to handle heavier feeds. A high steam-to-carbon ratio, usually >4.0, is used to suppress catalyst deactivation^{29,30}. A lower average operating temperature is employed, with typical inlet and outlet temperatures of 485 and 850°C, respectively. Commercially available naphtha steam reforming catalysts have nickel loadings from 15% to ~25%, most again promoted by K₂O.

4.1.3.2 Steam reforming with pre-reformer

A modern hydrogen plant accepting naphtha feedstock starts with an additional unit, the prereformer, after feed desulfurization. Pre-reforming of the desulfurized hydrocarbon feedstock makes the gas feed to the primary reformer practically free of higher hydrocarbons, which are converted directly to C₁ components with no intermediate hydrocarbon products. Thus, while the pre-reformer operates with specially designed pre-reformer catalysts at temperatures from 450 to $550^{\circ}C^{23,29}$, the methane-rich gas from the pre-reformer can be heated to >650°C before entering the reformer operating at exit temperatures of ~950°C²⁹. Industrial pre-reformer catalysts are typically highly Ni-loaded, ~25-30% (by weight) for pre-reforming of lighter hydrocarbons up to LPG, and >50% for the naphtha range. The catalysts are characterized by high resistance to sulphur-poisoning and coke formation. At the practiced pre-reforming temperatures, undesired reactions like pyrolysis, steam cracking of higher hydrocarbons, and polymerization of alkenes are minimal. All forms of carbon formation can be avoided by properly choosing the temperature window for steam reforming^{23,28}. The higher hydrocarbon steam reforming reactions are practically irreversible, and thus the hydrogen yields are limited by the equilibrium of the methane steam reforming reactions. Downstream of the pre-reformer, the steam reformer therefore tends to operate at typical methane steam reforming operating conditions, and utilize regular methane steam reforming catalysts.

The first naphtha steam reformer dates back to 1962 at ICI, with an operating pressure of 15 bars^{28,31,32}. Some naphtha steam reformers have been operated at low temperatures to produce a methane-rich substitute natural gas. A Topsoe naphtha steam reformer was introduced in 1965, and a pre-reformer was first installed by Topsoe in 1986³¹. Figure 4.1 shows the block diagram of a modern higher hydrocarbon steam reforming set-up incorporating a pre-reformer. Pre-reforming catalysts have high nickel loadings, typically in excess of 25% by weight and some as high as 55%.

In the process for making hydrogen, the synthesis gas mixture leaving the steam reformer has few downstream units to purify the hydrogen. Traditionally, the shift conversion reaction following the reformer used to be conducted in two stages: a high-temperature shift (HTS) converter followed by a low-temperature shift (LTS) converter. With more recent steam reforming plants operating at low steam-to-carbon ratios, these reactors are replaced by a single medium-temperature shift (MTS) converter. A CO_2 removal section and a methanator (to remove CO traces) may follow the shift conversion. Recent developments also have CO_2 removal and methanation units replaced by pressure swing adsorption (PSA) to produce hydrogen of purity up to 99.999%³³.

4.1.3.3 Fluidized bed membrane reformer (FBMR)

Fine catalyst particles ideal for fluidization increase the catalyst effectiveness factor from as low as 0.01-0.001 in fixed bed reformers to almost unity^{34,35}. Better thermal uniformity in a fluidized bed can prevent hotspots. Selective removal of hydrogen from the reaction environment via permselective Pd alloy membranes drives the equilibrium methane steam reforming and water gas shift conversions forward, thereby significantly enhancing the hydrogen yield³⁶⁻³⁹. The fluidized bed and membrane reactor concepts developed at the University of British Columbia^{40,41}, has been commercialized by Membrane Reactor Technologies⁴². Rakib et al.⁴³ provided a FBMR model for steam reforming of heptane, and predicted that an FBMR for higher hydrocarbons can result in a compact reformer system, combining pre-reforming, reforming and hydrogen purification in a single unit. This paper focuses on the technical feasibility of such a reformer unit, with n-heptane as a surrogate for naphtha, as in some previous studies^{23,43-47}.

4.1.4 Thermodynamics of n-heptane steam reforming

A HYSYS steady state simulator, version Aspen HYSYS 7.1, was first used to examine the thermodynamics of heptane steam reforming for operating conditions spanning the experimental conditions. Figure 4.2 shows the dry gas compositions at a steam-to-carbon molar ratio of 5 for pressures of 400 and 800 kPa. Figure 4.3 shows dry gas compositions at a pressure of 400 kPa and steam-to-carbon molar ratios of 4 and 6. It is seen that heptane is fully consumed, indicating that heptane reforming is essentially irreversible for temperatures from 400 to 800°C. Irreversibility of steam reforming is a general feature for higher hydrocarbons having different degrees of reactivity²⁸. Industrial steam reforming of light gas oils and diesel fuels produces syngas with no traces of higher hydrocarbons in the product¹. Equilibrium predictions also show the absence of intermediate hydrocarbons other than methane, except for a trace of ethane (~0.1% typically).

Hydrogen production increases as temperature is increased, decreasing the equilibrium content of methane. This is because the steam reforming of methane is endothermic. Also, since the reactions involve a net increase in molar flow, Le Chatelier's principle requires that increasing pressure decreases the hydrogen production, as is evident from Figure 4.2. Higher steam partial pressure has a positive effect on hydrogen production, as seen in Figure 4.3.

4.2 FBMR for Steam Reforming of Heptane

4.2.1 FBMR experimental set-up

An FBMR pressure vessel, shown in Figure 4.4, was fabricated to allow experiments up to 10 barg and 621°C. A commercial naphtha steam reforming catalyst, RK-212 from Haldor Topsoe A/S, was crushed and sieved to a Sauter mean particle diameter of 179 μ m. Pd membranes are infinitely selective to hydrogen permeation due to the unique solution-diffusion mechanism of permeation^{48,49}. Hydrogen diffusion flux depends on the difference between the square roots of partial pressures on the two sides according to Sieverts' law, with diffusion as the rate-determining step⁵⁰:

$$Q_{H_2} = A_P \frac{P_{M0}}{\delta_{H_2}} \exp\left(\frac{-E_{H_2}}{RT}\right) (\sqrt{P_{H_2,R}} - \sqrt{P_{H_2,M}})$$
(4.6)

Pd is often alloyed with other metals like Ag, Cu and Ru to improve mechanical stability, resistance to hydrogen embrittlement and hydrogen permeation flux. In our study, double-sided

membrane panels, manufactured by Membrane Reactor Technologies⁵¹ with a 25 μ m thick Pd₇₇Ag₂₃ alloy foil layer, were inserted through six alternately arranged vertical slots on the wall of the reactor. These panels, shown schematically in Figure 4.5(a), are 231.8 mm x 73.0 mm x 6.35 mm thick. Accounting for welding and bonding space, the active area of each membrane is 206.4 mm x 50.8 mm on each side of the membrane panels to withdraw hydrogen along the reactor height. High-purity hydrogen, metered by mass flow meters, FMA-1818 from Omega Instruments, passed through the membrane panels to a spark-proof hydrogen vacuum pump. In some experiments, stainless steel dummies of the same dimensions as the active membrane panels were installed, as explained below. Figure 4.5(b) shows a membrane panel installed onto a supporting side flange cover.

Figure 4.6 depicts the experimental set-up. Before starting the experiments, the catalyst was reduced overnight at about 500°C. The required steady flow rate of steam was established before feeding heptane. The vapour head-space in the heptane storage tank was pressurized by helium, pushing the heptane through a liquid heptane Bronkhorst mass flow controller. Distilled water was pumped, metered by a Brooks mass flow controller, and flowed through an electrically-heated vaporizer. Heptane was mixed with the steam downstream of the vaporizer. The heptane/steam mixture was fed to the FBMR through a doughnut-shaped gas distributor, located inside and at the bottom of the FBMR, with six equally-spaced holes drilled on the inner side. This allowed spent catalysts to be discharged through a catalyst drain in the bottom head cover, without completely disassembling the bottom head. The steam-to-carbon ratio in the feed was maintained by adjusting the mass flow rates of water and heptane.

4.2.2 Experimental plan and performance characterization

Table 4.1 summarizes the steady reactor measurements made to characterize the reactor performance. Table 4.2 lists the location of the monitoring probes, and the location and height intervals covered by the membrane panels. The reactor performance was characterized by measuring the pure hydrogen produced and the gas compositions at different locations. The composition of the gas samples was analyzed by a Varian micro-GC CP-4900 (see Table 4.3). Table 4.4 gives key details of the experiments on the steam reforming of heptane. A steam-to-carbon ratio (SCR) of 5 was used for all experiments, except when SCR itself was a parameter. While most of these experiments maintained similar feed superficial velocities for parametric studies, some provided similar molar feeds. These experiments were conducted in three phases: Sets 1 to 3 were carried out with six membrane dummies, set 4 with five dummies and one active

membrane panel (at the 5th side opening from the bottom), and sets 5 to 9 with six active membranes installed. The fluidized bed reactor without membranes is comparable to a pre-reformer without removal of hydrogen. Experiments with one and six membrane panels help to elucidate the effect of hydrogen removal on the reactions inside the reactor.

Steam reforming of higher hydrocarbons is very rapid, and the conversion of the higher hydrocarbons is irreversible, limited only by equilibrium of methane steam reforming. Thus, conversion of the higher hydrocarbon fed becomes irrelevant, being essentially 100% from near the entrance of industrial setups²³, and also for an FBMR with heptane feed^{43,52}. Intermediate hydrocarbons were not detected, except for traces of ethane (less than 0.01% by volume in all cases). However, ethane was not considered in the performance calculations given their low levels. Since the objective is to produce pure hydrogen, pure hydrogen yield is the most relevant performance metric. To compare the reformer with and without membranes, the total hydrogen yield, including both permeated pure and retentate hydrogen, is calculated and plotted. The yield of carbon oxides, especially carbon dioxide, is an equivalent measure to describe the conversion of the hydrocarbons, including the intermediate. Carbon dioxide is a co-product from reactions (4.3) to (4.5). Based on the dry composition of gas samples withdrawn from the FBMR at different heights, local yields of retentate hydrogen, carbon oxides and methane are calculated:

Pure hydrogen yield =
$$\frac{\text{molar flow of pure hydrogen extracted via membranes}}{\text{molar heptane feed rate}}$$
 (4.7)
Retentate hydrogen yield = $\frac{\text{molar flow of hydrogen in retentate stream}}{\text{molar heptane feed rate}}$ (4.8)
Total hydrogen yield = pure hydrogen yield + retentate hydrogen yield (4.9)
Carbon oxides yield = $\frac{(\text{molar flow of CO} + \text{molar flow of CO}_2) \text{ in retentate stream}}{7 \text{ x molar heptane feed rate}}$ (4.10)
Mathema vield = $\frac{(\text{molar flow of methane in retentate stream}}{7 \text{ x molar heptane feed rate}}$ (4.11)

Methane yield =
$$\frac{100 \text{ at How of methane in retentate stream}}{7 \text{ x molar heptane feed rate}}$$
 (4.11)

4.3 **Results and Discussion**

4.3.1 FBMR experiments

In most experiments, two or three samples were analyzed at each location. Error bars, corresponding to the standard deviations $(\pm \sigma)$ for each sample gas location, are plotted below with some data points shifted very slightly sideways to allow clear display.

For each membrane panel there is one thermocouple close to the hydrogen removal port. An average bed temperature was calculated based on the temperatures recorded at all six membrane levels. For each parametric study, the time-average bed temperature was kept constant, except where the average bed temperature was itself the study parameter. Gas samples were withdrawn from two levels for each side opening. A cubic spline function was used to estimate the temperatures corresponding to these sampling port levels. For each parametric study, fitted temperature profiles are plotted with profiles of the carbon oxides yield, methane yield, and hydrogen yield. The heptane conversion exceeded 99% at the lowest sampling point, and was 100% for all samples above that. Hence, heptane conversion is not plotted here. For cases with one or more membranes present, the pure hydrogen and total hydrogen yields are plotted. The retentate hydrogen can be estimated from the difference between these two values.

4.3.2 Influence of key operating parameters

Figure 4.7 depicts the performance of heptane steam reforming with no in-situ hydrogen removal, representing experiments 1.a and 1.b in Table 4.4. Higher temperature is seen to favour the steam reforming of methane. This is also accompanied by higher hydrogen and carbon oxides yield by favouring reaction 4.2 in the backward, and 4.3 and 4.4 in the forward, direction. Carbon dioxide was the major carbon oxide, with carbon monoxide only \sim 1% of the dry gas.

Figure 4.8 examines the influence of reactor pressure by comparing results for experiments 2 and 1.a with identical total molar feed rates and average temperature. The experimental hydrogen yield was higher at the lower pressure of 460 kPa, as expected from thermodynamics. Correspondingly, the yield of carbon oxides was found to be higher, and of methane lower, for 460 kPa than for 725 kPa. This indicates that the experiments were thermodynamically, rather than kinetically, controlled.

Figure 4.9 plots information from experiments 2, 3.a, and 3.b to show the effect of varying the steam-to-carbon molar ratio (SCR), with the same total molar feed rates. In the range of operation of these experiments, increasing steam partial pressure positively affected the conversion of the intermediate component methane, resulting in a lower methane yield. This also gave higher yields of hydrogen and carbon oxides. Higher SCR also probably enhanced gasification of any deposited carbon, thereby reducing catalyst deactivation. However, for the maximum possible hydrogen yield (see equation 4.5), an SCR of 2 is required. Thus, a higher SCR is likely to decrease the energy efficiency of the process due to the energy required to raise excess steam.

Figure 4.10 plots the experimental hydrogen yield against the thermodynamic equilibrium values computed corresponding to the local temperatures for experiment sets 1 to 3. The experimental data closely follow the equilibrium values, indicating that the reactor without membranes is controlled by thermodynamic equilibrium.

Figure 4.11 corresponds to experiments 4.a through 4.d, where only one active membrane panel was installed with the active membrane length spanning from 1.21 to 1.41 m above the distributor. The shaded band in this figure denotes the zone where pure hydrogen is removed by the membrane. For structural similarity among all experiments, dimensionally identical stainless steel dummy plates were installed in the other five openings. Two reactor pressures were studied, with and without suction on the membrane permeation side for each level. The total molar feed rate was the same for these four runs, with identical average reactor temperatures, so that experiments 4.a and 4.b had lower residence times than 4.c and 4.d. It is seen that experiments 4.a and 4.c had similar performance. This is due to the higher driving force and higher residence time available for hydrogen permeation for 4.c, compared to 4.a, counteracted by a negative impact of the thermodynamic equilibrium for the higher reactor pressure of 4.c. This also applies to similar performance exhibited by 4.b and 4.d for the permeate side operated under vacuum (35 and 26 kPa respectively). The two runs with evacuated permeate (4.b and 4.d) showed better performances than without vacuum (4.a and 4.c). Note that the difference between these two pairs of runs became prominent after reaching the 5th flange where the single membrane panel was installed.

Figures 4.12 to 4.16 correspond to experiment sets 5 to 9, each conducted with six active membrane panels along the reactor. The shaded bands in these figures represent intervals where pure hydrogen was withdrawn by membrane panels.

Figure 4.12 presents the effect of reactor temperature, with increments of 25°C in the average reactor temperature. The most important reactions (reactions 4.1 to 4.4 as listed) are endothermic on an overall basis, with only the water gas shift reaction (equation 4.3) exothermic. In addition to the effect on equilibrium, an increase in membrane temperature increases hydrogen permeation (equation 4.6), shifting the reversible reactions in the forward direction. This is reflected in the higher yield of permeate hydrogen, contributing to the greater total hydrogen yield as the average reactor temperature increased. The methane yield decreased due to higher consumption of methane (equation 4.4). These trends are reflected in increased yield of carbon oxides.

Figure 4.13 portrays the effect of the reactor pressure (400, 600 and 800 kPa), with the average bed temperature maintained at 500°C. To keep the superficial gas velocities similar for all three pressures, the feed total molar flow rates were adjusted. The permeate side pressure was 25 kPa for all three cases, set by modulating the speed of the hydrogen vacuum pump. The total hydrogen yield decreased significantly when the pressure increased from 400 to 600 kPa, but a further increase from 600 to 800 kPa affected the hydrogen yield only marginally. Increased pressures negatively affect the equilibrium of the system, while also causing more hydrogen permeation flux due to increased pressure difference between the reactor and permeate sides. The thermodynamic effect is dominant at lower reactor pressures, but not at higher reactor pressures. This substantiates the fact that the fast kinetics of the steam reforming reactions makes the system reach local equilibrium rapidly so that the performance is limited by the membrane permeation capacity.

Figure 4.14 investigates the effect of the permeate side pressure with the reactor pressure and average bed temperature fixed at 600 kPa and 475°C respectively. The feed flow rates were the same for runs 5.a, 7.a and 7.b. Little hydrogen permeated through the membranes when the permeate side was at ambient pressure (vacuum pump not operated). The hydrogen permeation rate jumped significantly when the permeate side was evacuated to 50 or 25 kPa, reflected in increases in total hydrogen yield and carbon oxides yield, and a decreasing methane yield, with greater removal of hydrogen from the reactor. In these experiments, the feed steam-to-carbon molar ratio was 5.0, while stoichiometrically only 2 is required (equation 4.5). As a result, the bulk of the reactor gas stream consists of steam, and a higher reactor pressure does not necessarily translate to higher hydrogen partial pressure inside the reactor. When the permeate side pressure was atmospheric, the local partial pressure of hydrogen on the reactor side was estimated to be between 60 and 90 kPa, depending on the local conditions, with an average of 76 kPa. Thus, there was no driving force to promote hydrogen permeation through the membranes, and no hydrogen permeation was recorded. The average local hydrogen partial pressures were estimated to have been 67 kPa for $P_m = 50$ kPa, and 59 kPa for $P_m = 25$ kPa. Accordingly, hydrogen then permeated through the membranes, due to the positive driving force.

Figure 4.15 shows the effect of the steam-to-carbon molar ratio (SCR). As for the experiments with no hydrogen removal, higher steam partial pressure positively influenced the hydrogen yield. A similar effect is also seen with the six membranes installed. More methane was consumed, reflected in the dwindling methane yield with increasing SCR.

Figure 4.16 investigates the effect of superficial velocity. Gas superficial velocities increase as a result of the increasing molar flow provided by the steam reforming reactions, but decrease when hydrogen is removed from the system through the membranes. They are also affected by local temperature and pressure. Hence, the influence is described in terms of the feed molar flow rates, instead of the superficial velocity. Other operating conditions like average bed temperature, reactor pressure, permeate pressure and SCR were maintained constant for the two cases (5.b and 9) compared. Performance profiles are seen to differ near the entrance of the reactor, suggesting different hydrodynamic behaviour near the entrance. Beyond the entrance region, the performance shows only marginal differences, indicating that the overall reactor performance was dominated by the reaction equilibria. However, it is interesting to note that with an increase in the feed flow rate, the actual permeate hydrogen withdrawn also increased significantly (as the yields were almost the same at a 33% higher heptane feed). This was probably due to differences in temperature profile even though the average bed temperature was very nearly the same. It may also be due to weakening of any lateral concentration gradient, likely to be caused by hydrogen depletion near the membrane wall, at higher superficial gas velocities.

In Figure 4.17, experimental hydrogen and methane yields are plotted against the corresponding equilibrium values at local temperatures without hydrogen removal. The experimental data were obtained 1.64 m above the distributor, i.e. at the top of the sixth membrane panel. With no hydrogen removal corresponding to experiment sets 1 to 3, hydrogen yield was close to, but less than the equilibrium value, whereas methane slip was more than predicted by equilibrium. For the permeate side operating at ambient pressure, the performance did not improve much relative to cases without membranes, regardless of whether only one membrane or all six were installed. As expected, there was a significant improvement in the hydrogen and methane yields with six membranes compared with one, demonstrating that the reactor performance was dominated by the available membrane permeation area, as well as by the permeate side pressure.

The carbon oxides and methane yields generally follow the temperature profile along the length of the reactor, since the gas composition in the reactor is governed by the local thermodynamic equilibrium. This has been observed for most of the sampling points along the reactor length. For each membrane interval, the effect of hydrogen permeation was apparent, with a higher carbon oxides yield and a lower methane yield at the downstream location than at the upstream one. However, a discontinuity was often (e.g. Figure 4.15) observed for the

methane and carbon oxides yields just beyond the second membrane panel. The molar flow rate of gas was found to vary along the reactor height, probably as a result of the uneven temperature profile, which can significantly affect the reaction rate as well as the hydrogen permeation rate. The discontinuity in the methane and carbon oxides yields may have been due to hydrodynamic effects above the second membrane. A similar smaller discontinuity appears above the fourth membrane panel as well.

4.3.3 Hydrogen purity

Hydrogen purities were monitored separately for each membrane panel after each day of experiments. In most cases, the permeate stream was ~99.99% hydrogen. However, for the fourth and sixth membranes, the purity decreased to >99.95% towards the end of the series of experiments. The pure hydrogen production rate depended on the operating conditions and feed flow rates. The highest production rate was 0.39 Nm^3 /h in experiment 9.

4.3.4 Discussion

The experimental results show that an FBMR for heptane reforming can be operated at the industrial operating temperatures of naphtha pre-reformers, while achieving hydrogen yields comparable to a second stage steam reformer, which operates at temperatures as high as 850°C. This is because of the continuous shift of equilibrium limitation as hydrogen is progressively removed. In terms of total hydrogen yield, the FBMR gives the combined performance of a pre-reformer and a reformer. In addition, separate hydrogen purification is not needed, since pure hydrogen is available as a membrane permeate stream. Thus the FBMR combines the function of a pre-reformer, reformer, shift converter, and hydrogen purification section. However, some hydrogen is also lost in the off-gas retentate stream.

Since the FBMR operating temperature is moderate, ~550°C, catalyst deactivation is minimized, both in terms of carbon formation and sintering. Moderate temperature operation also avoids expensive alloys for high-temperature tubing used in conventional industrial steam reformers.

Heptane conversion exceeded 99% at the lowermost sampling point, and was complete (100%) above that. Except at the very bottom, the FBMR reaction zone sees practically no higher hydrocarbon during steam reforming of heptane. Similar behaviour was observed for steam reforming of propane⁵³. Thus the FBMR is flexible in feedstock, similar to what is achieved by addition of a pre-reformer prior to a conventional steam reformer. However, higher hydrocarbon feedstocks require high steam-to-carbon ratios, which can affect the pressure drop

in the steam reformer due to variations in volumetric flow rate. Fluidized beds operate with little or no variation of bed pressure drop, although variations of superficial gas velocity may change the hydrodynamic behaviour.

The FBMR process has been widely studied in the past for steam reforming of natural gas. In that case, operation at 550°C is sufficient to achieve high conversion, equivalent to that at temperatures above 800°C without membranes⁴¹. Temperatures >550°C, although not essential, could improve the hydrogen yield further by enhancing the equilibrium conversion, as well as the hydrogen permeation. The practical temperature limitation arises from the structural integrity of the membranes, which could develop pinholes or cracks. For steam reforming of liquid hydrocarbons like naphtha or its surrogate heptane, as employed in this study, the upper temperature limit is likely to be similar to that for a naphtha pre-reformer.

This study used a model component to emulate steam reforming of naphtha. However, the olefinic components (which must be less than 1% by volume³²) of naphtha can cause low temperature catalyst deactivation. To study the feasibility of the FBMR for naphtha steam reforming, the effects of naphthenes and aromatics must also be considered. Nevertheless, the current study provides valuable background information for higher hydrocarbon feedstocks like naphtha, gasoline, kerosene and diesel fuel.

4.4 Conclusions

Steam reforming of heptane was studied in a fluidized bed membrane reactor, providing insight into the feasibility of FBMR application for hydrogen production from liquid hydrocarbon feedstocks. Experiments were conducted without and with hydrogen removal. The composition of the reactor gas samples without membranes closely followed the equilibrium values at local temperatures and pressures. The reactor without membranes was equivalent to a pre-reformer for naphtha steam reforming. Effects of hydrogen removal were studied with one and six membrane panels installed. With hydrogen removal through selective membranes, the FBMR provides a compact reformer system, combining the pre-reformer, reformer, shift conversion and hydrogen purification steps into a single unit. The FBMR system is appropriate for steam reforming of higher hydrocarbons, since the temperature limitations of the Pd-Ag membranes closely match the usual pre-reformer temperatures to avoid catalyst deactivation by coking. The FBMR can also accept different hydrocarbon feedstocks. Hydrogen purifies as high as 99.99% were achieved from individual membrane panels. The reactor was tested under different

operating conditions and flow rates for parametric studies. A pure hydrogen production rate of 0.39 Nm^3 /h was achieved at an average bed temperature of 500°C, reactor pressure of 600 kPa, permeate pressure of 25 kPa, steam-to carbon molar ratio of 5, total feed rate of 0.819 mols/min, and a total membrane permeation area of 0.126 m². The maximum hydrogen yield was 14.7 moles of pure hydrogen (and 18.5 moles of total hydrogen) per mole of heptane fed, compared with the theoretical maximum of 22.

Quantity	Device and Location					
FBMR temperatures	One thermocouple just above distributor.					
	One thermocouple close to center of each membrane panel. One					
	thermocouple for freeboard just upstream of reformer exit.					
Gas composition	Two sampling ports for each of the six lateral flanges supporting a					
	membrane panel.					
	One sampling line for ROG.					
	Gas sampled from these sampling points are analyzed online by a					
	Varian micro-GC CP-4900 using sample selection valves.					
Permeate hydrogen	Flow rates of permeate hydrogen from each membrane panel are					
production	measured using FMA-1818 mass flow meters from Omega					
	Instruments.					
Purity of permeate	Hydrogen purity in permeate product from each membrane panel are					
hydrogen	analysed by the micro-GC.					
Pressures	Absolute pressures in the feed line, freeboard, and at the distributor					
	level in bed are determined using PX-309 absolute pressure					
	transducers from Omega Instruments.					
	Differential pressure between alternate levels of side flanges (i.e. pairs					
	1-3, 3-5, 2-4, and 4-6) and between distributor and freeboard are					
	measured using PX-2300 differential pressure transducers from					
	Omega Instruments.					

Table 4.2:
 Location of sampling ports, thermocouples and pure hydrogen withdrawal, and height intervals of active membrane surface

Description (Side opening	Location above	Height interval covered by		
counted from bottom)	distributor holes (m)	active membrane		
Thermocouple (Bottom)	0.01	-		
Thermocouple (Side opening 1)	0.32	-		
Thermocouple (Side opening 2)	0.52	-		
Thermocouple (Side opening 3)	0.78	-		
Thermocouple (Side opening 4)	1.08	-		
Thermocouple (Side opening 5)	1.29	-		
Thermocouple (Side opening 6)	1.59	-		
Thermocouple (Freeboard)	2.33	-		
Gas samples (Side opening 1)	0.22, 0.37	-		
Gas samples (Side opening 2)	0.47, 0.63	-		
Gas samples (Side opening 3)	0.73, 0.88	-		
Gas samples (Side opening 4)	0.98, 1.13	-		
Gas samples (Side opening 5)	1.24, 1.39	-		
Gas samples (Side opening 6)	1.49, 1.64	-		
Pure hydrogen (Side opening 1)	0.30	0.19 - 0.40		
Pure hydrogen (Side opening 2)	0.55	0.45 - 0.65		
Pure hydrogen (Side opening 3)	0.80	0.70 - 0.91		
Pure hydrogen (Side opening 4)	1.06	0.95 – 1.16		
Pure hydrogen (Side opening 5)	1.31	1.21 – 1.41		
Pure hydrogen (Side opening 6)	1.57	1.46 - 1.67		

Channel	Column Description	Carrier Gas	Gases Analyzed	Detection limits
1	10 m molsieve 5A with pre-column backflush	Argon	He, H_2 , O_2 , N_2 , CH_4 and CO	10 – 100 ppm
2	10 m PPU with pre-column backflush	Helium	$CO_2, C_2H_4, C_2H_6, C_2H_2, H_2S and COS$	10 – 100 ppm
3	8 m Silica PLOT with pre-column backflush	Helium	C ₃ and C ₄ isomers	10 – 100 ppm
4	8 m CP-Sil 5 with no pre-column	Helium	C_5 to C_{12} components	1 – 10 ppm

Table 4.3:
 Micro-GC column information for product gas analysis

Expt No.	Active Membranes	Total feed	T _{av}	P	P_m	SCR
	(Location)	rate				
		(mols/min)	(°C)	(kPa)	(kPa)	
1.a	Nono	0.673	520	460	NA	5.0
1.b	INDIRC	0.766	450	460	NA	5.0
2	None	0.673	520	725	NA	5.0
3.a	None	0.673	520	725	NA	4.0
3.b		0.673	520	725	NA	6.0
4.a		0.717	480	585	101	5.0
4.b	1	0.717	480	585	35	5.0
4.c	(#5)	0.717	480	720	101	5.0
4.d		0.717	480	720	26	5.0
5.a	6	0.635	475	600	25	5.0
5.b	6 (#1 to #6)	0.614	500	600	25	5.0
5.c		0.595	525	600	25	5.0
6.a	6	0.410	500	400	25	5.0
6.b	(#1 to #6)	0.819	500	800	25	5.0
7.a	6	0.635	475	600	101	5.0
7.b	(#1 to #6)	0.635	475	600	50	5.0
8.a	6	0.614	500	600	25	4.0
8.b	(#1 to #6)	0.614	500	600	25	6.0
9	6	0.819	500	600	25	5.0
	(#1 to #6)					

Table 4.4:
 Experimental runs for steam reforming of n-heptane



Figure 4.1: Key components in a modern steam reforming plant for hydrogen from higher hydrocarbon feedstock. (Adapted from Rostrup-Nielsen and Rostrup-Nielsen¹)



Figure 4.2: Dry gas equilibrium composition for steam-to-carbon molar ratio of 5.0: (a) P = 400 kPa; (b) P = 800 kPa. No membranes present



Figure 4.3: Dry gas composition for reactor pressure of 400 kPa: (a) Steam-to-carbon molar ratio = 4.0; (b) Steam-to-carbon molar ratio = 6.0. No membranes present



Figure 4.4: Drawing of FBMR pressure vessel supported on mobile stand



(b)

Figure 4.5: (a) Dimensions of membrane panel. (b) Ports arranged on each side-opening cover where membrane panels are installed



Figure 4.6: Schematic of experimental set-up to study steam reforming of n-heptane



Figure 4.7: Experimental yields and temperature for heptane steam reforming without active membrane panels at reactor pressure of 470 kPa and steam-to-carbon ratio molar ratio of 5.0. Total reactor feed = 0.673 and 0.766 mols/min at 520 and 450°C respectively



Figure 4.8: Experimental yields and temperature for heptane steam reforming without active membrane panels at average reactor temperature of 520° C and steam-to-carbon ratio molar ratio of 5.0. Total reactor feed = 0.673 mols/min



Figure 4.9: Experimental yields and temperature for heptane steam reforming without active membrane panels at average reactor temperature of 520° C and reactor pressure of 725 kPa. Total reactor feed = 0.673 mols/min



Figure 4.10: Parity plot of experimental yields without active membrane panels against local equilibrium values: (a) Hydrogen yield (b) Methane yield



Figure 4.11: Experimental yields and temperature for heptane steam reforming at average reactor temperature of 480°C and steam-to-carbon molar ratio 5.0. One membrane panel installed, spanning from 0.95 to 1.16 m above distributor. Total reactor feed = 0.717 mols/min



Figure 4.12: Experimental yields and temperature for heptane steam reforming at pressure of 600 kPa, permeate pressure 25 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed. Total reactor feeds = 0.635, 0.614, and 0.595 mols/min for 475, 500, and 525° C respectively



Figure 4.13: Experimental yields and temperature for heptane steam reforming at average reactor temperature of 500°C, permeate pressure 25 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed. Total reactor feeds = 0.410, 0.614, and 0.819 mols/min for P = 400, 600, and 800 kPa respectively



Figure 4.14: Experimental yields and temperature for heptane steam reforming at average reactor temperature of 475° C, pressure 600 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed. Total reactor feed = 0.635 mols/min



Figure 4.15: Experimental yields and temperature for heptane steam reforming at average reactor temperature of 500°C, pressure 600 kPa, and permeate pressure 25 kPa. Six membrane panels installed. Total reactor feed = 0.614 mols/min



Figure 4.16: Experimental yields and temperature for heptane steam reforming at average reactor temperature of 500°C, pressure 600 kPa, permeate pressure 25 kPa, and steam-to-carbon molar ratio 5.0. Six membrane panels installed



Figure 4.17: Parity plot of experimental yields against equilibrium values at local temperatures if there was no hydrogen removal: (a) Hydrogen yield (b) Methane yield

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CHAPTER 5. MODELING OF A FLUIDIZED BED MEMBRANE REACTOR FOR HYDROGEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS*

5.1 Introduction

5.1.1 Hydrogen from higher hydrocarbons feedstock

Industrial use of hydrogen is projected to increase due to rising fertilizer demand¹ and increased hydrotreating requirements of various feedstocks in refineries² as the available crude becomes heavier and increasingly sour. Hydrogen is also often foreseen as a major energy carrier, whose implementation could help to mitigate global warming due to greenhouse gas emissions from direct use of fossil fuels³. To make hydrogen readily available for automobiles, a distributed network of small-scale to medium-scale hydrogen production units is needed⁴.

Steam reforming of hydrocarbons is the major global pathway for hydrogen production^{2,5,6}. The feedstock consumptions for hydrogen production are 48% natural gas and 30% oil/ naphtha⁷. Compared to higher hydrocarbons like naphtha, natural gas is favored, mainly due to its widespread availability and lower cost. However, higher hydrocarbon feedstocks are used in places where natural gas is not available. Refineries also prefer flexible feedstock options to take advantage of seasonal surplus products or off-gases rich in higher hydrocarbons. For distributed small and medium scale hydrogen generation units, liquid hydrocarbon feedstocks may be advantageous due to (a) higher volumetric hydrogen density, (b) existing infrastructure of propane/ gasoline/ naphtha fuels, and (c) ease of storage and transportation at or near ambient conditions, compared to natural gas. Traditionally, higher hydrocarbon feedstocks were mainly naphtha, operated at feed temperatures of about 450 to 550°C, and a product temperature of \sim 750 to 850°C, in order to minimize catalyst deactivation by carbon formation, a problem which becomes more serious as the carbon number of the reforming feedstock increases.

^{*} A version of this chapter has been submitted for publication: **Rakib, M.A.,** Grace, J.R., Lim, C.J., and Elnashaie, S.S.E.H., Modeling of a Fluidized Bed Membrane Reactor for Hydrogen Production by Steam Reforming of Hydrocarbons (2010).

Recent versions of industrial naphtha-based steam reforming systems are installed with a pre-reformer, operated at relatively lower temperatures of 450 to 550°C, followed by a reformer at about 800 to 900°C. An important advantage of the pre-reformer is flexibility with relatively low impacts on the reformer operation, since the higher hydrocarbons are reformed in the pre-reformer to methane-rich gas feed for the reformer.

5.1.2 Fluidized Bed Membrane Reactors (FBMR)

Steam reforming reactions feature fast kinetics. High intra-particle diffusional limitations lead to very low effectiveness factors. Fine catalyst powders are therefore useful to reduce internal mass transfer limitations. These fine catalysts can be deployed in fluidized bed reactors, which also help to minimize heat transfer limitations for the highly endothermic reactions like steam reforming. Permselective Pd membranes enhance the hydrogen yield by shifting the equilibrium of the reaction. Fluidized bed membrane reactors have been studied experimentally for the production of pure hydrogen by steam reforming of methane or natural gas⁸⁻¹¹. Other processes studied experimentally in an FBMR, mostly in the bubbling flow regime, include oxidative dehydrogenation of ethane to ethylene¹², partial oxidation of butane to maleic anhydride¹³, and partial oxidation of methanol to formaldehyde¹⁴. FBMRs have also been modelled for hydrogen production and other processes. A comprehensive review has been provided by Deshmukh et al.¹⁵.

Fluidized bed membrane reactors for steam reforming of heptane in circulating fast fluidized bed mode of operation were modeled by Chen et al.¹⁶⁻¹⁹. Catalyst deactivation by carbon formation could be transformed into an advantage if the catalysts were regenerated by combustion in a separate regenerator, and the regenerated hot catalysts were recycled to the riser reformer, thereby enabling autothermal operation.

One-dimensional two-phase models are the most widely used to represent bubbling fluidized beds. A two-phase model originally proposed by Toomey and Johnstone²⁰ considers the dense fluidized bed comprised of two pseudo-phases: a bubble phase, containing very few particles, and a dense phase which contains most of the solids. The flow of gas required to maintain minimum fluidization velocity goes to the dense phase, while gas flow in excess of this amount appears as bubbles. FBMR models based on this approach have treated the two phases differently, with the bubble phase treated as a plug flow in most cases.

Rakib et al.²¹ wrote a one dimensional two-phase model for heptane steam reforming in an FBMR to size and predict its performance. Subsequently, the FBMR system was built,

installed and operated safely²². This paper deals with a modeling approach in order to understand the various phenomena taking place during steam reforming of higher hydrocarbons in an FBMR.

5.2 Description

Membrane panels or dummies were immersed vertically along the reactor height, the main section of which has a rectangular cross-section. Figure 5.1 gives a schematic of the reactor geometry. Table 5.1 provides key reactor physical details and membrane permeation parameters. A detailed description of the experimental setup, operating conditions and experimental results are provided elsewhere²²⁻²⁴. Figure 5.2 shows a schematic of the model considerations in this work.

5.2.1 Reactions and rate equations

The FBMR has been studied for steam reforming of heptane as a model component for naphtha, and propane as a key component of LPG.

Heptane steam reforming

$$C_7H_{16} + 7H_2O \rightarrow 7CO + 15H_2$$
 $\Delta H^{\circ}_{298} = 1108 \text{ kJ/mol}$ (5.1)

Propane steam reforming

$$C_{3}H_{8} + 3H_{2}O \rightarrow 3CO + 7H_{2}$$
 $\Delta H^{\circ}_{298} = 499 \text{ kJ/mol}$ (5.2)

With the appearance of CO and H₂ as products, the following reactions also occur:

Methanation (reverse of methane steam reforming)

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$
 $\Delta H^{\circ}_{298} = -206 \text{ kJ/mol}$ (5.3)

Water gas shift

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad \Delta H^{\circ}_{298} = -41 \text{ kJ/mol}$$
(5.4)

Methane overall steam reforming

$$CH_4 + 2H_2O \leftrightarrows CO_2 + 4H_2$$
 $\Delta H^{\circ}_{298} = 165 \text{ kJ/mol}$ (5.5)

Side reactions involving carbon formation which deactivates the catalyst are not considered in this model. The kinetic rate equations governing these reactions are listed in Tables 5.2 and 5.3.

5.2.2 Model simplifications

(1) Steady state conditions.

- (2) Ideal gas law.
- (3) Solids (catalyst) temperature identical to the local gas temperature.

- (4) Intra-particle gas diffusional limitations are ignored: Catalyst particles of Sauter mean diameter 179 μ m were used in the FBMR experiments, leading to effectiveness factors close to unity^{8,25,26}.
- (5) No energy balance is included in the model. Instead, the experimentally recorded temperatures were used to estimate axial temperature profiles, which were then imposed on the reactor in the model. The FBMR was heated by: (a) Four internal cable heaters above the feed distributor, (b) Six semi-circular external band heaters mounted opposite to each lateral flange opening, (c) Two external circular band heaters in the freeboard zone, and (d) Six external strip heaters mounted vertically on each lateral flange. The temperature at any position along the height of the reactor depended on the location and power output of each of the heaters, and non-uniform heat loss from different sections of the FBMR pressure vessel. Figure C.7 shows the arrangement of the external band heaters. The limited axial solids mixing due to relatively low superficial gas velocities (in the range of 0.06 to 0.12 m/s, see Appendix E) and slug flow was the probable reason for the temperature not being as uniform as would normally be expected in fluidized beds.
- (6) Permselective membrane, with infinite selectivity for hydrogen permeation: The poorest purity obtained in our experiments was 99.95% hydrogen.
- (7) A two-phase model is adopted, with the dense catalyst bed treated as two pseudo-phase compartments in parallel. Given the high aspect ratio of the bed, each phase is treated as a plug flow reactor with exchange between the two compartments. The membranes withdraw hydrogen from both phases.
- (8) Catalyst deactivation is neglected: A base case steam-to-carbon molar ratio of 5.0 was used for the experimental runs. As recommended by the supplier (Haldor Topsoe A/S) of the RK-212 catalyst, this is adequate to minimize catalyst deactivation by carbon formation.

5.2.3 Fluidized bed hydrodynamic model

Since the bubble size and local gas superficial velocities vary axially due to variations of temperature, pressure, total molar flow, and diffusive and convective mass transport, as described below, the bed expansion is calculated iteratively.

Researchers have often found that the two-phase theory overestimates the volume of gas passing through the bed as "visible" bubbles^{27,28}. The gas flow rate in the bubbles is often multiplied by a factor $Y (\leq 1.0)$ to allow for deviations observed experimentally from the two-phase theory, due to greater flow through the dense phase and/or increased flow through the

bubbles. *Y* has typically been found to be in the range 0.8 < Y < 1.0 for Group A powders and 0.6 < Y < 0.8 for Group B powders^{29,30}.

Gas split between the two phases at reactor inlet:

The entrance region close to the distributor is also treated by means of the two-phase model in this work, although separate treatment of this zone, referred to as the grid zone, is also common^{31,32}. Thus, the feed gas splits and distributes into the two phases at the entrance as:

$$Q_{b,in} = Y.A.(U - U_{mf})|_{in}$$
(5.6)

$$Q_{d,in} = A U_{in} - Q_{b,in} \tag{5.7}$$

with
$$U_{in} = \frac{\left(\sum_{i=1}^{n} F_{i,in}\right) R.T_{in}}{P_{in}.A}$$
 (5.8)

Hydrodynamic equations:

The minimum fluidization velocity is calculated to correspond to the local conditions based on the Wen & Yu correlation³³, with the constants as suggested by Grace³⁴:

$$U_{mf} = \left(\frac{\mu_g}{d_p \rho_g}\right) \left[(27.2)^2 + 0.0408 \, Ar \right]^{\frac{1}{2}} - 27.2$$
(5.9)

The fraction of bed occupied by bubbles is given by:

$$\varepsilon_b = \frac{Y.(U_0 - U_{mf})}{U_b}$$
(5.10)

where, the bubble velocity is given by:

$$U_{b} = Y (U_{0} - U_{mf}) + 0.711 (gd_{b})^{\frac{1}{2}}$$
(5.11)

In this work, Y = 1 is assumed.

Almost all particles are in the dense phase, with only a very small fraction in the bubbles. The solids content in the bubbles is commonly neglected, but their contribution to reaction in a fluidized bed reactor may be important for fast reaction kinetics. The bubbles may contain about 0.1-1.0% solids by volume^{30,35}. For this study, the solids volume fraction is taken³⁵ as:

$$\phi_b = 0.001\varepsilon_b \tag{5.12}$$

Assuming the dense phase voidage to be constant and equal to ε_{mf} , the volume fraction of solids in the dense phase is given by:

$$\phi_d = (1 - \varepsilon_b)(1 - \varepsilon_{mf}) \tag{5.13}$$

The bubble size is estimated from the semi-empirical equation of Darton et al.³⁶:

$$d_{b} = 0.54 \left(U - U_{mf} \right)^{0.4} \left(h + 4 \sqrt{\frac{A}{N_{or}}} \right)^{0.8} g^{-0.2}$$
(5.14)

with a maximum bubble size calculated ³⁷ as:

$$d_{bm} = 1.64 \Big[A \Big(U_0 - U_{mf} \Big) \Big]^{0.4}$$
(5.15)

The bubble surface area per unit volume of the bubble is then approximated by:

$$a_b = \frac{6}{d_b} \tag{5.16}$$

Interphase diffusional mass transfer:

The bubble phase contains very few catalyst particles, so that very little reaction usually takes place there. Most of the reaction takes place in the dense phase which is rich in catalyst. This can cause significant concentration differences between the phases, leading to an interphase diffusion mass transfer between the two phases. The interphase mass exchange coefficient is estimated by the correlation of Sit & Grace³⁸. For the *i*th component:

$$k_{iq} = \frac{U_{mf}}{3} + \left[\frac{4D_{ie}\varepsilon_{mf}U_b}{\pi d_b}\right]^{0.5}$$
(5.17)

where D_{ie} is the effective diffusivity of component *i* in the gas mixture, calculated based on the average composition of the bubble and the dense phases. Based on the correlation of Wilke³⁹:

$$\frac{(1-y_i)}{D_{ie}} = \sum_{i=1}^n \left(\frac{y_i}{D_{ij}}\right) \qquad i \neq j$$
(5.18)

where D_{ij} is the binary diffusivity of component *i* in *j*.

Interphase bulk mass convection:

Due to gas exchange between the two phases by diffusion due to a concentration gradient and simultaneous removal of one component (hydrogen) from both phases by permeation through membranes, flow rates in the dense phase could vary, becoming greater or less than required for minimum fluidization. If less, this could cause de-fluidization. We assume, however, that fluidization is maintained by bulk convection between the bubbles and dense phase so that the dense phase interstitial velocity always satisfies the minimum requirement. In modeling studies, this has been treated by introducing an inter-phase bulk convection term^{25,40,41}, equal in amount to the excess or deficit of the flow required to fluidize the dense phase. With U and U_{mf} calculated at a given height, the flow requirement in the dense phase at that position can be written as:

$$Q_{d,req} = U_{mf} A (1 - \varepsilon_b)$$
(5.19)

167

At a given height, the composition of the bulk inter-phase convective flow matches that of the source phase⁴². The volumetric exchange terms can be written as:

when
$$\frac{R.T}{P} \sum_{i=1}^{N_c} F_{i,d} > Q_{d,req}$$
, $Q_{d \to b} = \frac{R.T}{P} \sum_{i=1}^{N_c} F_{i,d} - Q_{d,req}$
 $Q_{b \to d} = 0$
(5.20)

when $\frac{R.T}{P} \sum_{i=1}^{N_c} F_{i,d} \le Q_{d,req}$, $Q_{b \to d} = Q_{d,req} - \frac{R.T}{P} \sum_{i=1}^{N_c} F_{i,d}$

when
$$\frac{R.I}{P} \sum_{i=1}^{c} F_{i,d} \leq Q_{d,req}$$
, $Q_{b \rightarrow d} = Q_{d,req} - \frac{R.I}{P} \sum_{i=1}^{c} F_{i,d}$
 $Q_{d \rightarrow b} = 0$ (5.21)

As a reasonable, though unproven, means of balancing the phase flows, any increase of flow of a species by bulk convection to a receiving phase is accounted for by a corresponding decrease in the species molar flow rate from the source phase.

Hydrogen removal from the catalyst bed:

Hydrogen permeation through Pd-based membranes occurs via a solution-diffusion mechanism ⁴³. When the diffusion of atomic hydrogen through the solution is the rate-limiting step, the hydrogen flux follows Sieverts' law⁴³, so that:

$$Q_{mH_{2},b} = \alpha . A_{p} \cdot \frac{P_{M0}}{\delta_{H_{2}}} \exp\left(\frac{-E_{H_{2}}}{RT}\right) \left(\sqrt{P_{H_{2},b}} - \sqrt{P_{H_{2},p}}\right)$$
(5.22)

$$Q_{mH_{2},d} = \alpha . A_{P} \cdot \frac{P_{M0}}{\delta_{H_{2}}} \exp\left(\frac{-E_{H_{2}}}{RT}\right) \left(\sqrt{P_{H_{2},d}} - \sqrt{P_{H_{2},p}}\right)$$
(5.23)

The permeation parameters, provided by the supplier of the membrane panels, based on permeation testing with helium/ hydrogen mixtures, are included in Table 5.1. The membranes are assumed to be impermeable to species other than hydrogen. The permeation effectiveness factor, α , accounts for blockage of the membranes by dust or foulant. It is treated below as an adjustable parameter to fit the simulated permeation hydrogen yields to the experimental results, with $1 \ge \alpha \ge 0$.

Mole balance equations for dense catalyst bed:

For each phase,

Mole balance for ith species in bubble phase:

$$\frac{dF_{i,b}}{dh} = k_{iq}a_b\varepsilon_bA(C_{i,d} - C_{i,b}) + \phi_b\rho_pA\sum_{j=1}^{N_g}\gamma_{ij}R_{j,b} - \varepsilon_bQ_{mi,b} - \frac{dQ_{b\to d}}{dh}C_{i,b} + \frac{dQ_{d\to b}}{dh}C_{i,d}$$

Internhase halancing mass

where
$$i = C_7 H_{16}$$
, $C_3 H_8$, CH_4 , $H_2 O$, CO , CO_2 , and H_2 , and $Q_{m_i h} = 0$ for $i \neq H_2$

Mole balance for ith species in dense phase:



where $i = C_7H_{16}$, C_3H_8 , CH_4 , H_2O , CO, CO_2 , and H_2 , and $Q_{m_{i,d}} = 0$ for $i \neq H_2$

Model equations for membrane permeate side:

The differential mole balance equation for the permeate hydrogen is:

$$\frac{dF_{H2,p}}{dh} = \varepsilon_b Q_{mH_2,b} + (1 - \varepsilon_b) Q_{mH_2,d}$$
(5.26)

Freeboard Calculations:

1---

Catalysts particles are entrained above the expanded dense bed surface into the freeboard after being ejected by bursting bubbles. The flux of entrained particles decreases with height in the freeboard, depending on the gas velocity, as well as the gas and particle properties.

In order to minimize catalyst loss due to entrainment of fines, a sintered metal filter (12.7 mm OD, 152 mm long, media grade 40) was located at the exit of the FBMR, attached to the top flange cover. A layer of catalyst fines could accumulate onto the filter medium surface, and in one case, as shown in Figure 5.3, a very loosely-bound cake of catalyst fines, retained on this filter, was retrieved intact. In most cases, however, no filter cake was found when the top cover of the FBMR was opened after operating the equipment. A thermocouple, installed close to the exit as seen in Figure 5.3, gives an indication of the temperature of the filter cake.

In order to make reasonable predictions of overall conversion and exit product distributions, it was found essential to account for catalytic reaction in the freeboard, due to the catalyst dispersion there. An amount of catalyst equivalent to 0.8 mm of static bed depth was assumed to be distributed uniformly in the freeboard region. This assumption was made on the basis of least squares error minimization with respect to the experimental yields of methane, CO₂, and H₂ in the reformer off-gas (ROG). The freeboard was then modeled as a single-phase dilute catalyst suspension. The inlet species flow rate to the freeboard region is estimated as the sum of species flow rates from the dense and bubble phase at the dense bed surface:

(5.24)

at
$$h_{fb} = 0$$
, $F_{i,fb} = F_{i,b} + F_{i,d}$ (5.27)

*Mole balance for i*th *species in freeboard*:

$$\frac{dF_{i,fb}}{dh_{fb}} = \phi_{fb}\rho_p A \sum_{j=1}^{NR} \gamma_{ij} R_{j,b}$$
(5.28)

5.3 Model Predictions versus Experimental Results

5.3.1 Experimental data for comparison with model predictions

An in-house code was written using Matlab, version 7.3 (2006), to solve the model equations. The differential equations were solved using a built-in variable order stiff ordinary differential equations solver, *ode15s*. A non-negativity criterion for the components molar flow rates was imposed on the solution to impart stability to the solutions. Relative and absolute tolerance values of 1×10^{-8} were used for the solver.

In our earlier experimental work, heptane²³, propane²⁴ and methane were steam reformed in an FBMR. The experiments with each hydrocarbon were conducted in three different combinations of dimensionally identical dummies and active membrane panels: (i) Six dummy panels, (ii) One active membrane panel installed in the fifth lateral opening from the bottom, the other five being dummies, and (iii) Six active membrane panels. Experimental results are tabulated in Appendix G. The experimental details of the runs used to compare the experimental profiles with the model predictions are listed in Table 5.4.

Experimental data were collected only after steady state operation was achieved. After fixing the operating conditions with respect to FBMR pressure, permeate side pressure, temperature profile, and feed flow rates, the sample gas concentration was monitored by the micro-GC. Steady state was assumed to be attained when the gas composition was seen to oscillate with absolute deviations less than 1%. Simulated dry molar gas compositions are compared with experimental gas compositions analyzed by the micro-GC after condensing the moisture from the sample gas streams.

The following quantities are calculated to assess the reactor performance:

Pure hydrogen yield =
$$\frac{\text{molar flow of pure hydrogen extracted via membranes}}{\text{molar flow of hydrocarbon in feed stream}}$$
 (5.29)
Retentate hydrogen yield = $\frac{\text{molar flow of hydrogen in retentate stream}}{\text{molar flow of hydrocarbon in feed stream}}$ (5.30)

Total hydrogen yield = Pure hydrogen yield + Retentate hydrogen yield (5.31)

Carbon oxides yield =
$$\frac{(\text{molar flow of CO} + \text{molar flow of CO}_2)\text{ in retentate stream}}{\text{Molar flow of carbon (in hydrocarbon) in feed stream}}$$
(5.32)
Methane yield =
$$\frac{\text{molar flow of methane in retentate stream}}{\text{Molar flow of carbon (in hydrocarbon) in feed stream}}$$
(5.33)

5.3.2 Membrane effectiveness factor

A genetic algorithm-based optimization routine was used to estimate the membrane permeation effectiveness factor, α , assumed to be the same for all 6 membrane panels. There is a probability that individual permeation effectiveness factors may differ from one membrane to another, e.g. due to thickness variations in the foil or hydrodynamic changes with height which could lead to variations in the thickness of any coating accumulated on the membrane foils (see Figure 5.4). The least squares fitted value of $\alpha = 0.248$ was used for the current model.

5.3.3 Test results with no membrane panels

Figure 5.5 shows the results for experiment 1.b where heptane was the feedstock²³ with no membranes present. Figure 5.6 depicts simulations for experimental conditions for experiment 1.b with propane as the feedstock²⁴. The conditions are similar to those of a pre-reformer used to reform higher hydrocarbons. For both feedstocks, the higher hydrocarbon is consumed almost completely, and methane appears in the reformer from right near the bottom, due to the methanation reaction, Eq. (5.3) above. Both propane and heptane are almost fully consumed right near the bottom, within 220 mm of the bottom, and hence their conversion profiles are not plotted here.

Figures 5.5 and 5.6 also indicate the corresponding yields of methane, carbon oxides and local hydrogen yield. These results indicate that, except for a very small zone near the entrance, the reactor behaves like a methane steam reformer. Model predictions of the local hydrogen yield show the effects of competing phenomena among higher hydrocarbon steam reforming, methanation, and methane steam reforming at the entrance of the FBMR. Since the by-products of steam reforming are CO and CO₂, the local yields of carbon oxides are indicators of conversion of the higher hydrocarbons as well as methane, the predominant intermediate. Figures 5.5 and 5.6 also show the simulated dry gas compositions for methane and hydrogen in the bubble and dense phases, and the experimental dry gas compositions. As seen, the predicted dry mole fractions in the dense phase are slightly higher than in the bubble phase for reaction products (e.g. hydrogen) and lower for reaction consumables (e.g. methane). Note that also that where there is a drop in temperature, there is a corresponding drop in yields of carbon oxides and

hydrogen, with an increase in methane yield due to reverse reaction, i.e. methanation. In such sections, the methane mole fraction is higher in the catalyst-rich dense phase. However, the gas compositions of both phases are very similar, indicating that the inter-phase mass transfer resistance is relatively unimportant for the operating conditions of the reactor. The simulated gas compositions for both phases are very close to the experimental composition profile in the reactor.

The model predictions closely match the experimental data, confirming its applicability for cases without hydrogen removal. The reversal in product distribution (yields of methane, hydrogen and carbon oxides) also indicates that without any hydrogen removal, the FBMR performance is overwhelmingly dictated by thermodynamic equilibrium.

5.3.4 Test results with one membrane panel present

Experiments with one membrane panel installed were simulated, as depicted in Figure 5.7, showing results for heptane experiment $4.b^{23}$, in Figure 5.8 for propane experiment $2.b^{24}$, and Figure 5.9 for experiment 2.c where methane was the feedstock. The shaded part indicates the span of the lone membrane panel installed in the 5th lateral opening from the bottom.

As depicted in these figures, the simulated yields for methane with higher hydrocarbons, and conversion of methane (with methane as feedstock), show changes in slope corresponding to the start and end of the lone membrane panel, indicating faster consumption of methane in the interval corresponding to the membrane panel. Since hydrocarbon consumption produces carbon oxides, the carbon oxides yield also show a corresponding increase in slope. Thus, the one-membrane case clearly shows an equilibrium shift due to hydrogen removal. These three figures also show the local hydrogen yields. At the bottom of the membrane panel, there is an increase in the total hydrogen yield due to removal of pure hydrogen, shown as permeate hydrogen yield. The retentate hydrogen yield, which is the difference between these two yields, also exhibited a drop in the span of the membrane panel, due to hydrogen removal.

Dry gas mole fractions for methane and hydrogen in the two phases, shown in these three figures, also indicate the effect of hydrogen removal. Compared to the immediately preceding or succeeding sections, in the interval occupied by the lone membrane panel, the difference in composition between the two phases increased for methane, and decreased for hydrogen. Membranes remove hydrogen from the dense phase as well as the bubble phase. Hydrogen is mostly produced in the dense phase where the vast majority of catalyst particles reside. However, the dense phase also occupies most of the volume, and hence covers most of the

membrane area. Hence the drop in hydrogen concentration is greater in the dense phase, even resulting in some crossing of the two profiles.

5.3.5 Test results with six membrane panels

With all six membrane panels installed, the full capacity of the membrane permeation flux in the reactor was available. Figures 5.10, 5.11 and 5.12 depict the reactor performance compared with experimental results from heptane²³, propane²⁴, and methane. Simulated axial profiles of methane yield (with higher hydrocarbons feed), methane conversion (with methane feed) and carbon oxides all clearly show the effects of hydrogen withdrawal. Reductions in slopes of these profiles are seen in the short sections between adjacent membrane panels, where there was no hydrogen removal. Similar behavior could be seen from the total hydrogen yield. The dry mole fractions of methane in the dense phase are seen to decrease more quickly than for the bubble phase, except in sections where there was a drop in temperature.

5.4 Discussion of Results

5.4.1 Comparison between model and experimental data

Parity plots comparing model predictions with experimental values reported for steam reforming of heptane²³, propane²⁴, and methane appear in Figures 5.13 to 5.15. Model estimates at a height of 1.64 m above the distributor are plotted against experimental data at the same location, which is the closest to the top (1.67 m) of the highest membrane panel.

Figure 5.13 compares permeate hydrogen yields predicted by the model against experimental values for all three hydrocarbon feedstocks. The maximum hydrogen yields per mole of hydrocarbon fed with steam in excess are 22, 10 and 4 respectively for heptane, propane and methane. In order to allow comparison on the same plot, the permeate hydrogen yields have been normalized so that the permeate hydrogen yields have been divided by 22, 10 and 4. Six membrane panels extract much more hydrogen than a single membrane panel. However, for the heptane 7.a and propane 3.a experiments, with the FBMR pressure at 600 kPa, and an ambient permeate side pressure, little permeate was produced due to the fact that the driving force for permeation is provided by the difference of square roots of hydrogen partial pressures on both sides, rather than the total pressures. This was predicted very closely by the model.

Figure 5.14 compares the methane yields from higher hydrocarbons estimated by the model with the experimental values. Regardless of whether the feed was heptane or propane, the

FBMR acts predominantly as a methane steam reformer, with the higher hydrocarbons fully consumed near the distributor. Removal of hydrogen in the permeate stream caused the equilibrium limited reactions to be shifted accordingly, by consuming more methane. Thus more membrane surface area leads to lower methane yields, as depicted in Figure 5.14.

Faster removal of hydrogen as permeate leads to higher consumption of methane, thereby yielding more carbon oxides via reactions (5.3), (5.4), and (5.5). Thus carbon oxides yield is an indirect measure of the conversion of any hydrocarbon in the process stream, including the higher hydrocarbon and the intermediate methane. In Figure 5.15, these have been plotted for the three hydrocarbon feeds for the three membrane configurations, i.e. without membranes, and with 1 and 6 membrane panels. As expected, more membrane area led to more carbon oxides.

In general, there is good agreement between model predictions and the experimental data. The model is therefore helpful in understanding the various phenomena taking place in the FBMR. Some deviation near the bottom of the reactor may be due a to more non-uniform temperature distribution in this region. In this model, the energy balance equation was not considered since the distribution of heaters dominates the temperature profile. However, in the entrance region, where highly endothermic steam reforming of higher hydrocarbons (Eqs.(5.1) and (5.2)) followed by exothermic methanation (Eq. (5.3)) are very important, some interesting heat effects may be occurring. This suggests that it would have been useful to have recorded temperature at more locations along the height of the FBMR, especially near the bottom.

5.4.2 Membrane permeation effectiveness factor

As noted above, the model used a membrane permeation effectiveness factor, $\alpha = 0.248$, to account for the rate of production of pure hydrogen extracted via the membranes. Various reasons can be postulated for the loss in membrane effectiveness:

(a) A cake persistently formed on the membrane surface during the fluidized bed operation, as shown in Figure 5.4. XRD and EDX analysis of this cake indicated that the source was mainly catalyst dust cemented (probably in the presence of steam) with traces of Pd (possibly from abrasion of membranes). Hydrogen must pass through this cake, before permeating selectively through the membrane foil. The remaining gas mixture components, predominantly steam, carbon dioxide and methane can form a diffusion layer between the cake and the membrane foil. Thus, fresh hydrogen produced from the steam reforming reactions faces two diffusional resistances: the cake, and an almost stagnant layer of gas mixture, before it can adsorb on the membrane surface.

- (b) The permeation equation was developed from experimental data based on hydrogen permeation from pure hydrogen streams and hydrogen-helium mixtures. Some previous research⁴⁴⁻⁴⁶ indicates that steam, CO or CO₂ can competitively adsorb on the membrane foil, thereby reducing the rate of permeation of hydrogen through the membrane, with steam adsorption being the most prominent.
- (c) Permeate side porous substrate resistance, and resistances from valves and fittings in the permeate line could also mean that the recorded permeation side pressure was actually slightly lower than actual.

To understand the influence of the membrane effectiveness factor, α was varied, for one of the experimental runs, heptane experiment 5.b. The simulated profiles for $\alpha = 0.15$, $\alpha = 0.248$ (the fitted value), and $\alpha = 0.35$ are shown in Figure 5.16. The same reactor temperature profile was implemented. Table 5.5 shows the key performance parameters at the top of the 6th membrane panel (1.67 m above distributor). As seen, the FBMR performance is heavily dependent on the permeability of the membranes. It also shows that a much smaller reactor length would be sufficient for higher membrane permeabilities for otherwise similar conditions.

5.4.3 Two-phase fluidization model

Phenomena captured in our model include maintenance of minimum fluidization conditions in the dense phase, change in the number of moles due to gas-solid catalytic reaction, mass transfer between the dense and bubble phases, removal of hydrogen from both phases by membranes, and interactions among all these phenomena.

The experiments without membranes assisted in determining the effects of hydrogen removal by membranes. For these experiments without membranes, using heptane or propane, the close agreement among experimental, simulated, and local equilibrium values indicates that (i) mass transfer between the dense and bubble phases is reasonably fast; (ii) the steam reforming kinetics are also relatively fast; and (iii) as a result of these two factors, the FBMR performance is governed closely by local equilibrium conditions.

As indicated by the simulation results, the two-phase fluidization model promotes nearequality of compositions due in part to mass transfer and convection between the phases. The two-phase fluidization model simulates the experimental performance of the FBMR well. A sensitivity analysis of the model to the reaction rate constants and to the interphase mass transfer rate as shown in Appendix F indicates that, for this particular process, the model is sensitive to accurately characterizing the chemical equilibrium and hydrogen permeation, but relatively insensitive to predicting the chemical kinetics, interphase mass transfer and hydrodynamics with precision.

5.4.4 FBMR performance

The FBMR performance is predominantly determined by local equilibrium. Any withdrawal of hydrogen therefore significantly influences the performance. This makes proper estimation of the membrane permeation very important. As outlined above, a permeation effectiveness factor was necessary to account for the decrease in hydrogen permeation relative to that predicted on the basis of permeation experiments in a permeation rig without particles.

The FBMR was operated with three different hydrocarbons, heptane, a model component for naphtha, propane, a key component of LPG, and methane, the major component in natural gas. Under the operating conditions of the experiments, satisfactory hydrogen yields were obtained for all three feedstocks. Since the higher hydrocarbons were fully consumed near the entrance of the reactor, the bulk of the reactor does not see the higher hydrocarbon, and an equilibrium-governed methane-rich gas composition occurs in the reactor. Removal of hydrogen steers the methane steam reforming and water gas shift reactions to produce more hydrogen, thereby enhancing the total hydrogen yield. Membrane-assisted reforming at relatively low temperatures of 500°C can achieve hydrogen yields comparable to a reformer operating at >750°C, and is thus compatible with higher hydrocarbons steam reforming, with minimal catalyst deactivation due to carbon formation or sintering.

Steam reforming of higher hydrocarbons starts with a low-temperature pre-reformer to produce a methane-rich feed gas for the steam reformer operated at high temperatures to achieve a desired methane conversion. This is followed by a shift reaction system, and finally pressure swing adsorption to generate pure hydrogen. The FBMR combines the functions of the pre-reformer, reformer, shift converter and purification system into a single unit due to in-situ removal of pure hydrogen.

5.5 Conclusions

A fluidized bed membrane reactor for steam reforming of hydrocarbons was modeled by a twophase fluidization model. With no membrane panels installed, the model closely predicted the reformer performance, which was dominated by equilibrium. Membrane panels immersed in the bed extracted pure hydrogen, enhancing conversion of the hydrocarbons including the key intermediate methane by favourably shifting the equilibrium. The model gave good predictions of the reactor behaviour, aided by a single fitted parameter, a membrane permeation effectiveness factor.

Development of durable membranes with higher hydrogen permeation flux would make the FBMR smaller for similar production capacities. Our FBMR was operated with three different hydrocarbon feeds, and the higher hydrocarbons were consumed close to the entrance of the reactor. Irrespective of the feedstock, the bulk of the FBMR operates as a methane steam reformer. Thus, an FBMR can be operated as a flexible reactor for hydrogen production. Compared to a traditional steam reformer, the FBMR offers a compact one-step reactor for producing hydrogen from higher hydrocarbons. Since membrane-assisted reforming enables high hydrogen yields at temperatures below 575°C, chances of catalyst deactivation are also minimized.

Quantity	Value	Description
Nor	6	Number of orifices in the distributor housing
	$1.88 \times 10^{-3} \mathrm{m}^2$	Main section of FBMR where membrane panels or
		dummies are not present
A	$2.31 \times 10^{-3} \text{ m}^2$	Main section of FBMR where membrane panels or
		dummies are present
	$4.26 \times 10^{-3} \text{ m}^2$	Expanded section above the main section
<i>h</i> _{static}	1.7 m	Static bed height
Lreactor	2.32 m	Total height of FBMR including the main rectangular
		section and the expanded circular section
d_p	179 μm	Mean size of catalyst particle
ρ_p	2600 kg/m ³	Particle density of catalysts powder
$\delta_{\scriptscriptstyle H_2}$	25 μm	Thickness of Pd-Ag membranes
P_{M0}	0.00207	Pre-exponential factor for membrane permeation
	mole/(m.min.atm ^{0.5})	equation
E_{H_2}	9180 J/mol	Activation energy for membrane permeation
		equation

 Table 5.1:
 Reactor physical details

Table 5.2 :	Reaction rate	equations
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Reaction number	Rate equation and kinetic parameters	Reference
(5.1)	$r_{1} = \frac{k_{1}P_{C_{7}H_{16}}}{\left[1 + K_{a}\left(\frac{P_{C_{7}H_{16}}P_{H_{2}}}{P_{H_{2}O}}\right) + K_{b}\left(\frac{P_{H_{2}O}}{P_{H_{2}}}\right)\right]^{2}}$	Tottrup ⁴⁷
(5.2)	$r_{2} = \frac{k_{2} P_{C_{3}H_{8}}^{'} 0.93}{1 + \theta P_{H_{2}}^{'} 0.86}$	Ma ⁴⁸
(5.3)	$r_{3} = k_{3} \frac{\left(\frac{P_{CO}P_{H_{2}}^{0.5}}{K_{3}} - \frac{P_{CH_{4}}P_{H_{2}O}}{P_{H_{2}}^{2.5}}\right)}{DEN^{2}}$	
(5.4)	$r_{4} = k_{4} \frac{\left(\frac{P_{CO}P_{H_{2}O}}{P_{H_{2}}} - \frac{P_{CO2}}{K_{4}}\right)}{DEN^{2}}$	Xu & Froment ⁴⁹
(5.5)	$r_{5} = k_{5} \frac{\left(\frac{P_{CH_{4}}P_{H_{2}O}^{2}}{P_{H_{2}}^{3.5}} - \frac{P_{CO_{2}}P_{H_{2}}^{0.5}}{K_{3}K_{4}}\right)}{DEN^{2}}$	
(5.3), (5.4), and (5.5)	$DEN = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + \frac{K_{H_2O}P_{H_2O}}{P_{H_2}}$	

Table 5.3:Kinetic parameters

Reaction number	Rate parameters	Units	Reference	
($k_1 = 8 \times 10^{-5} . e^{\frac{-67800}{RT}}$	$\left(\frac{\text{mol}}{g_{\text{catalyst}}.\text{h.bar}}\right)$	- 47	
(5.1)	<i>K_a</i> = 25.2	(bar^{-1})	l ottrup "	
	$K_{b} = 0.077$	(-)		
(5.2)	$k_2 = 2.1428 \times 10^{14} . e^{\frac{-189.63 \times 10^3}{RT}}$	$\left(\frac{\text{mol}}{\text{kPa}^{0.4}.\text{m}^2\text{Ni.h}}\right)$	Ma ⁴⁸	
	$\theta = 1$	$\left(\mathrm{kPa}^{-0.86}\right)$		
	$k_3 = 9.49 \times 10^{15} . e^{\frac{-240.1 \times 10^3}{RT}}$	$\left(\frac{\text{kmol.bar}^{0.5}}{\text{kgcat.h}}\right)$		
	$k_4 = 4.39 \times 10^6 . e^{\frac{-67.13 \times 10^3}{RT}}$	$\left(\frac{\text{kmol}}{\text{kgcat.h.bar}}\right)$		
	$k_5 = 2.29 \times 10^{15} . e^{\frac{-243.9 \times 10^3}{RT}}$	$\left(\frac{\text{kmol.bar}^{0.5}}{\text{kgcat.h}}\right)$		
(53) (54)	$K_{CO} = 8.23 \times 10^{-5} . e^{\frac{70.65 \times 10^3}{RT}}$	(bar^{-1})		
(5.5), (5.4), and (5.5)	$K_{CH_4} = 6.65 \times 10^{-4} . e^{\frac{38.28 \times 10^3}{RT}}$	(bar^{-1})	Xu & Froment ⁴⁹	
	$K_{H_2O} = 1.77 \times 10^5 . e^{\frac{-88.68 \times 10^3}{RT}}$	(bar^{-1})		
	$K_{H_2} = 6.12 \times 10^{-9} . e^{\frac{82.9 \times 10^3}{RT}}$	(-)		
	$K_3 = e^{\left(\frac{-26.83 \times 10^3}{T} + 30.114\right)}$	(bar ²)		
	$K_4 = e^{\left(\frac{4400}{T} - 4.036\right)}$	(-)		

Expt No.	Active Membranes	Total feed	Tav	Р	P_m	SCR
	(Location)	rate				
		(mols/min)	(°C)	(kPa)	(kPa)	
Heptane1.b	None	0.766	450	460	NA	5.0
Propane1.b	None	0.673	500	600	NA	6.0
Heptane4.b	1 (#5)	0.717	480	585	35	5.0
Propane2.b	1 (#5)	0.717	485	515	30	5.0
Heptane5.b	6 (#1 to #6)	0.614	500	600	25	5.0
Propane3.c	6 (#1 to #6)	0.614	500	600	25	5.0
Methane1.a	6 (#1 to #6)	0.819	500	800	50	5.0
Methane1.b	6 (#1 to #6)	0.614	500	600	50	5.0
Methane1.c	6 (#1 to #6)	0.614	500	600	25	5.0
	1 (115)	0.005	500	500	101	5.0
Methane2.a	1 (#5)	0.695	500	500	101	5.0
	1 (115)	0.005	500	750	101	5.0
Methane2.b	1 (#5)	0.695	500	750	101	5.0
Mathana2 a	1 (45)	0.005	500	500	20	5.0
ivietnane2.c	1 (#3)	0.695	500	500	30	5.0
Mathema 2 d	1 (#5)	0.605	500	75	20	5.0
Wietnane2.d	1 (#3)	0.093	300	/3	30	3.0

Table 5.4:
 Experimental conditions for runs where data are compared with model predictions

Table 5.5:
 FBMR performance with variations in permeation effectiveness factor

α	Methane Yield	Carbon Oxides Yield	Permeate H ₂ Yield	Retentate H ₂ Yield	Total H ₂ Yield
0.15	0.233	0.769	4.378	2.773	7.151
0.2484	0.112	0.890	6.561	2.041	8.602
0.35	0.031	0.972	8.161	1.356	9.517



FBMR Feed (Hydrocarbon + Steam)

Figure 5.1: Schematic of reactor geometry



Figure 5.2: Schematic of the FBMR kinetic model



Figure 5.3: A cake of catalyst formed around the ROG filter



(a)



(b)



(c)

Figure 5.4: Particulate coating formed on the membranes during FBMR operation: (a) A fresh membrane before installation (b) the membrane surface covered by the coating (c) a view of other side of the same membrane showing a clean shining membrane foil exposed after tapping off a part of the coating



Figure 5.5: FBMR performance for experiment Heptane1.b



Figure 5.6: FBMR performance for experiment Propane1.b



Figure 5.7: FBMR performance for experiment Heptane 4.b



Figure 5.8: FBMR performance for experiment Propane 2.b



Figure 5.9: FBMR performance for experiment Methane 2.c



Figure 5.10: FBMR performance for experiment Heptane 5.b



Figure 5.11: FBMR performance for experiment Propane 3.c



Figure 5.12: FBMR performance for experiment Methane 1.c



Figure 5.13: Parity plot for permeate hydrogen yields



Figure 5.14: Parity plot for methane yields


Figure 5.15: Parity plot for carbon oxides yields



Figure 5.16: Effect of membrane permeation effectiveness factor (Propane Experiment 3.c)

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CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusions

The demand for hydrogen is projected to increase in the energy sector, as well as for industrial processes. While natural gas is the most widely used feedstock for steam reforming, other hydrocarbon feedstocks may be desirable alternatives in refinery operations and in syngas production in locations where natural gas is not available or where the alternative feedstocks are in over-supply. This research deals with pure hydrogen production from higher hydrocarbons in a novel fluidized bed membrane reactor (FBMR).

In this project, an FBMR was designed, fabricated and installed with safety requirements adequately addressed. It was operated with methane, propane and heptane, representing different categories of hydrocarbon feedstock. Average bed temperatures up to of 550°C, and reactor pressures up to 800 kPa were studied. The following conclusions can be drawn from the experimental results:

(a) The FBMR produced pure hydrogen while enhancing overall hydrocarbon conversion.

As in several previous studies involving steam reforming of methane or natural gas in an FBMR, our experiments showed that FBMR operation achieves higher overall hydrogen yields for propane and heptane than predicted by equilibrium conditions, while simultaneously producing a pure hydrogen stream. These results were achieved at moderate temperatures (< 550°C).

(b) FBMR gives a compact reactor configuration for hydrocarbons steam reforming.

For higher hydrocarbon feedstocks, an industrial hydrogen production setup includes several units like pre-reformer, reformer, shift conversion section and purification section. The FBMR operation demonstrated that pure hydrogen can be produced in a single reactor, combining the functions of all these units. Thus a compact reactor configuration has been demonstrated, which could be useful for small to medium scale distributed hydrogen production at fuelling stations.

(c) FBMR is a suitable configuration for higher hydrocarbons.

FBMR operation can achieve high hydrogen yields and lower methane yields at the usual operating temperature of the pre-reformer, assisted by selective removal of hydrogen through

membranes, thereby continuously shifting the equilibrium limitation towards complete conversion of methane, the intermediate hydrocarbon.

(d) FBMR allows flexibility of feedstock.

The FBMR system can adapt to feedstock variations, with the bulk of the reactor behaving as a methane steam reformer and little influence of the actual feed hydrocarbon.

In addition to the major conclusions above, this research also achieved the following:

(a) The safety issues involving a laboratory scale reactor setup have been analyzed in detail. This can be useful for other small scale FBMR reactors. A Cause & Effect matrix has been developed to take care of any process upsets.

(b) In order to understand the phenomena occurring in the FBMR, a kinetic model of the reactor has been written, based on the two-phase model of fluidization, with the dense catalyst bed treated as two phases in parallel, each with plug flow of gas and with exchange between the two phases. Hydrogen is withdrawn from both phases in proportion to the volume fractions they occupy in the bed. Interphase diffusional mass transfer occurs due to the concentration difference of the various components in the two phases, and bulk convectional cross-flow is assumed to ensure that the gas flow corresponding to minimum fluidization conditions in the dense phase is maintained. The model provides a reasonably good fit between predicted and experimental yields of total hydrogen, carbon oxides and methane, for all three hydrocarbons tested, i.e. methane, propane and heptane.

6.2 Limitations of FBMR Steam Reforming

(a) Hydrogen at lower pressure

A major limitation for the process is that hydrogen is available at a very low pressure compared to hydrogen line pressure from a traditional steam reformer. The low pressure hydrogen then has to be compressed to meet downstream process requirements.

(b) Membrane cost

Palladium or its alloys are very expensive, augmenting the capital investment in the process. For the process to be economically attractive, the membranes must be thinner, as well as durable over extended periods of operation.

6.3 Recommendations for Future Work

As a follow-up of a proof-of-concept research presented in this dissertation, some directions are proposed:

(a) Energy balance equation in the reactor model

Due to the difficulty of accurate estimation of the heat lost from the FBMR through the insulation, the energy balance equation was not considered in the predictive reactor model, as described in Chapter 5. With the electrical energy input known, the heat lost can be estimated by heating the FBMR to the usual operating temperatures with no reactants being fed. Thereby, a complete predictive model can be developed with the incorporation of the energy balance equation.

(b) Further sophistications of the model

An axial dispersion model for the two phase model would be able to capture the phenomenon of gas back-mixing which occurs in fluidized beds. Such a model would likely offer better predictions than a plug flow model.

The model used in this work is one-dimensional model. A two- or three-dimensional model can capture the local recirculation and back mixing phenomena due to the presence of membrane panels and intermittent widening of the cross-sectional area between the panels. It may also be able to analyze any lateral concentration gradient due to hydrogen withdrawal via the vertical membrane panels. A computational fluid dynamics (CFD) model may be a useful tool to describe the complex phenomena and geometry. CFD calculations should be able to predict the interphase balancing mass transfer when flow rate in the dense phase differs from that under the minimum fluidization conditions¹.

(c) Real hydrocarbon feedstock

Model hydrocarbon compounds were used in this study, so that the main underlying concept of steam reforming of higher hydrocarbons could be proved in a step-by-step approach. However, real hydrocarbon feedstocks like naphtha, kerosene or diesel contain naphthenic, aromatic or olefin components, which may promote carbon formation, causing catalyst deactivation. Steam reforming of such real feedstocks is therefore required to study any effect on the membranes, e.g. possible fouling due to coke deposition.

(d) CO₂ capture

With the ills of climate change being clearly visible, control of greenhouse gas emissions is becoming increasingly more important. Hydrogen extraction from fossil fuels by steam reforming produces large quantities of CO_2 as a byproduct. This CO_2 is usually released to the atmosphere. In-situ CO_2 capture in a steam reforming process can enhance hydrogen yield by promoting equilibrium shift, in a manner similar to withdrawal of hydrogen through membranes. This has been extensively studied for methane steam reforming. In principle, this could also be extended to steam reforming of higher hydrocarbons.

(e) Lowering of steam-to-carbon molar ratio

Keeping in view the main scope of the research presented in this thesis as a proof-of-concept, the base steam-to-carbon molar ratio was maintained as 5.0 for these experiments. A lower steam-to-carbon ratio could improve the energy efficiency of the process, and also decrease the reactor volume due to decreased volumetric flow. With high hydrogen yields achieved at temperatures of 550°C or lower, a lower steam-to-carbon ratio may be able to achieve deactivation-free operation. This needs to be investigated experimentally.

(f) Autothermal reforming

A major limitation of industrial steam reformers is heat supply to the highly endothermic steam reforming reactions. Hundreds of catalyst filled tubes need to be housed in a furnace to decrease the radial non-uniformity of temperature. Autothermal reforming introduces a controlled amount of oxygen which consumes some of the hydrocarbon, supplying the heat requirement. Fluidized bed operation reduces this radial non-uniformity of temperature. In addition, in-situ supply of heat due to autothermal reforming eliminates the heat transfer barrier. Autothermal reforming of methane or natural gas could also be extended to steam reforming of higher hydrocarbons.

(g) Other configurations: Ex-situ membranes

One of the main challenges for this process to be commercially implemented is the durability of the membranes against abrasion in a particulate environment and with temperature cycling during start-ups and shut-downs. This could be avoided by placing the membranes downstream in a separate vessel, and recycling the retentate partially to the FBMR for further reaction.

(h) Catalyst improvement: Fluidizable catalyst development

Fluidizable catalysts prepared by crushing commercial catalyst pellets are liable to further breakage in an FBMR due to particle-particle and particle-wall collisions. This can affect the fluidization characteristics, as well as leading to loss of fines by entrainment. Attrition-resistant fluidizable catalysts need to be developed.

(i) Long-term durability tests

Resistance of the membranes against development of pinholes for continuous operation over long periods of time needs to be established. Effect of the olefins and aromatic content in the feed may cause membrane fouling by coke deposition, thereby decreasing the hydrogen recovery.

(j) Scale-Up: Hydrogen filling stations as a first target

As Deshmukh et al.² observed, FBMRs show greater promise of commercialization than fixed bed membrane reactors for steam reforming. Further studies on scale-up for this newly developed process are required for higher hydrocarbon feedstocks.

6.4 Specific Recommendations for Reactor Built in the Current Study

(a) A better temperature control scheme should be implemented, with an individual temperature controller for each heater to provide more uniform temperature profiles, and better safeguards against overheating some zones while leaving some zones significantly colder. Additional rope heaters could be placed in locations where heat losses are greater (e.g. at the flanges).

(b) Two additional ports are available per rectangular flange on the side openings. Utilizing these to record bed temperatures could improve the reactor performance monitoring.

(c) One or two additional off-gas filters should be installed in parallel to the existing one, with proper bypass capabilities. Fine catalyst cakes build-up on the filters could then be dislodged during operation with periodic reverse injection of inert gas, while the other filters are still available for off-gas venting. Filters need to be cleaned in rotation, so that the catalyst particles can drop back onto the bed, and also to ensure that these lines are not blocked.

(d) This set-up could also be used to investigate other reactions, e.g. propane dehydrogenation or the water-gas shift reaction.

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APPENDIX A. KINETIC SIMULATION OF A COMPACT REACTOR SYSTEM FOR HYDROGEN PRODUCTION BY STEAM REFORMING OF HIGHER HYDROCARBONS^{*}

A.1 Introduction

Hydrogen is frequently discussed as a future energy carrier. Key applications are as a carbonfree fuel, and as a fuel for hydrogen fuel cells for automotive and other applications. Hydrogen has been used effectively in a number of internal combustion engine vehicles mixed with natural gas (Hythane)¹. Hydrogen can also be combined electrochemically with oxygen without combustion to produce direct-current electricity in fuel cells, and is used in a growing number of fuel cell vehicles.

As a feedstock in chemical processes, the demand for hydrogen is increasing, both for the petrochemical industries and for petroleum refining processes. Synthesis gas, a mixture of hydrogen, carbon monoxide and carbon dioxide in various proportions, is used by Fisher Tropsch catalytic technology to produce a wide range of chemicals from methanol up to diesel. Steam-reforming-based hydrogen plants are installed in refineries to meet the fast-rising demand-supply gap in their daily operations².

Hydrogen is used in the metallurgical industry to create a reducing atmosphere in metal extraction³, and in annealing of steel. It is also used in the electronics industry to manufacture semiconductor devices, and in the food industries for hydrogenation of fats and oils^{3,4}.

Thus the demand of hydrogen is projected to increase, and this has motivated research into improving methods of hydrogen production, separation, purification, storage and transportation. Many of the hydrogen uses put special demand on the purity of the hydrogen from these reformers.

Steam reforming remains the leading pathway of hydrogen from hydrocarbon sources, especially natural $gas^{2,5}$. The greatest advantage of the steam reforming pathway is that hydrogen is extracted not only from a hydrocarbon, but from steam as well, thereby enhancing H₂ production, giving the maximum H₂ production per mole of hydrocarbon. The presence of

^{*} A version of this Appendix has been published: **Rakib, M.A.**, Grace, J.R., Elnashaie, S.S.E.H., Lim, C.J., and Bolkan Y.G. Kinetic Simulation of a Compact Reactor System for Hydrogen Production by Steam Reforming of Higher Hydrocarbons, *Canadian Journal of Chemical Engineering* (2008) 86, 403-412.

excess steam in the reaction mixture suppresses coking reactions, the extent of which depends largely on the reaction temperature and the type of hydrocarbon.

Currently methane is the major feedstock for production of synthesis gas, as well as pure hydrogen. However, compared to liquid hydrocarbons, the volumetric hydrogen density remains low even after natural gas is compressed to liquid for transportation, although the H/C ratio of methane is high⁶. Therefore, an easily deliverable and safely storable hydrogen source, such as gasoline and diesel, is preferred for mobile applications⁷. On-board hydrogen generation systems prefer liquid hydrocarbon feedstocks, such as gasoline, kerosene and diesel oil, which have a higher energy density and a wider distribution network, compared to methanol⁸. In addition, many refineries benefit from flexibility in feedstocks, taking advantage of the surplus of various hydrocarbons in the refinery.

Traditional steam reforming plants have a fixed bed steam reformer. For naphtha steam reforming, the desulfurized hydrocarbon is fed to a pre-reformer, which is operated adiabatically, where the higher hydrocarbons are directly converted to methane, giving a methane-rich gas feed for the reformer⁹. In the primary reformer there are hundreds of externally fired catalyst-packed tubes, in which steam reforming of methane takes place. The fixed bed reformer is followed by the shift reactorS (HTS and LTS reactors) section for further reaction of carbon monoxide with steam to enhance hydrogen yield. The gas purification system consists of a CO₂ removal unit, a Methanator, and finally a Pressure Swing Adsorption unit to produce pure hydrogen.

Steam reforming is limited by diffusional resistances inside the catalyst pellet, resulting in very low effectiveness factors, of the order of 10⁻² to 10⁻³ ¹⁰⁻¹². In addition, with external firing needed for the highly endothermic reactions, formation of hot spots can lead to problems related to temperature control. Pressure drop limitations block attempts to improve the effectiveness factor by using smaller diameter particles. Adris et al.¹³ and Elnashaie et al.¹⁰ proposed a novel Fluidized Bed Steam Reformer, with the heat supplied through immersed heat transfer tubes. Heat transfer limitations of the fixed bed reactor are also minimized in the fluidized bed because of better mixing characteristics.

The other major limitation for the steam reforming reactions is thermodynamic equilibrium. Removal of the main products can drive the reaction towards completion, following Le Chatelier's principle. Permselective membranes of Pd or Pd-based alloys can remove H_2 , thus serving dual objectives: enhancing the hydrocarbon conversion by favourably shifting the equilibrium conversion, and producing a stream of pure H_2 as permeate¹⁴⁻¹⁶.

This study deals with modeling a fluidized bed membrane reactor for steam reforming of higher hydrocarbons, carried out to size an experimental reformer setup. Typically, naphtha consists predominantly of saturated hydrocarbons (>90% by volume), the balance being made mainly of aromatics, and some unsaturated hydrocarbons¹⁷. *n*-Heptane is treated in the current simulations as a model compound for steam reforming of naphtha, as also earlier assumed by Chen^{17,18}, Tøttrup¹⁹, Christensen⁹, and Darwish et al.²⁰. Others have assumed it to be a model component for gasoline^{6,8,21}. A hydrocarbon feed mixture composed of *n*-heptane and *n*-hexane (in a weight ratio of $C_7/C_6 = 2$) was taken as a synthetic feed for steam reforming of naphtha by Melo et al.⁷.

A.2 Irreversibility of Steam Reforming of Higher Hydrocarbons

Equilibrium calculations, in Figure A.1 show that the steam reforming of heptane is practically irreversible, indicated by its complete consumption at the representative conditions of reaction. The temperature was varied from 400 to 800°C at four different pressures from 1 to 20 bars, and equilibrium compositions were predicted using a Gibbs Reactor in HYSYS simulation software. The feed composition, consisting of *n*-heptane, steam and H_2 , used for the equilibrium predictions are listed in Table A.1, and is the same as employed for the base simulation conditions in the kinetic model.

For higher hydrocarbons, the reaction can be written as^{2,17,18,22},

$$C_n H_m + nH_2 O \to nCO + \left(n + \frac{m}{2}\right) H_2 \quad \dots \quad r_1 \qquad \Delta H^0_{298} = 1108 \text{ kJ/mol} \quad \text{(for n=7)} \quad (A.1)$$

Once H_2 and CO are available by steam reforming of higher hydrocarbons, a reverse steam reforming reaction (reverse of Equation A.2) produces CH_4 (methanation reaction), and thereafter the process proceeds as simple steam reforming of methane^{2,17,18,22}.

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2$$
 r_2 $\Delta H^0_{298} = 206.1 \text{ kJ/mol}$ (A.2)

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$
 r_3 $\Delta H^0_{298} = -41.1 \text{ kJ/mol}$ (A.3)

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2$$
 r_4 $\Delta H^0_{298} = 165 \text{ kJ/mol}$ (A.4)

Although methane is not present in the feed, it immediately starts to appear in the system due to the methanation reactions (reverse of reactions (2) and (4)), once H_2 , CO and CO₂ appear in the system by reactions (1) and (3). The methane yield decreases with increasing temperature due to the endothermicity of the steam reforming reaction of methane. As a result, H_2 yield continues to increase. If this H_2 is selectively removed from the system, CH_4 yield will decrease further, due to forward equilibrium shift of reaction (2).

The irreversibility for steam reforming applies to all higher hydrocarbons with different degrees of reactivity. The higher hydrocarbons are generally more reactive than methane, with aromatics showing the lowest reactivity, approaching that of methane²³. Industrially, with proper desulfurization, it has been possible to convert light gas oils and diesel fuel into syngas with no trace of higher hydrocarbons in the product gas². Pilot scale experiments on adiabatic prereforming of natural gas, which also contained higher hydrocarbons in the range C₂-C₇, showed that the concentration of all higher hydrocarbons decreased continuously through the bed and that no intermediate compounds were observed⁹.

A.3 Kinetic Modeling of a Fluidized Bed Membrane Reactor

A two-phase model of a fluidized bed membrane reactor (FBMR) was prepared to assist with the sizing of an experimental reactor. The bubbling bed regime of operation has been adopted for the simulations for this paper since the experimental reformer will be focused mainly on this regime. Pd-based membrane panels supplied by Membrane Reactor Technologies Limited, a Vancouver based company, will be used in the reactor immersed in the fluidized bed of the catalyst. A distributor design has been adopted in the experimental design which minimizes any effect of jetting. The geometry and reaction base conditions are tabulated in Table A.1. Simulations were performed for a 1 m membrane length. Figure A.2 shows a schematic of the model developed. Double-sided membrane panels are inserted through vertical slits along the height of the reformer shell. The membrane panels pass through the centerline of the reformer, dividing the cross-section into two communicating sections. Thus, the membranes will be in contact with the bubble and dense phases nearly proportionally to the fractions they occupy in the fluidized bed.

A.3.1 Model assumptions

- 1. Steady-state reactor conditions.
- 2. Isothermal bed. The experimental reactor setup will be externally heated to overcome the high endothermicity of the reaction in addition to allowing isothermal operation.
- 3. Only the lower dense catalyst bed is simulated; the lean freeboard regime is not treated in this paper.
- 4. The lower dense catalyst bed is treated as two parallel phases made up of a dense phase and a bubble phase.

- 5. Plug flow behaviour is assumed for the dense phase as well as the bubble phase. The high aspect ratio of the FBMR simulated justifies this assumption.
- 6. Catalyst diffusion resistance is taken to be negligible. Very fine catalyst particles with a mean particle size of 100 μ m will be used for the experiments.
- 7. Catalyst deactivation is neglected in this paper.
- 8. Any jetting just above the distributor is neglected.

A.3.2 Model equations for reactor side

Mole Balance for ith Species in the Bubble Phase.

$$\frac{dF_{ib}}{dL} = k_{iq}a_b\varepsilon_b A(C_{id} - C_{ib}) + \phi_b\rho_p A\sum_{j=1}^4 \gamma_{ij}R_{jb} - \varepsilon_b Q_{ib}$$
(A.5)

 $i = CH_4, H_2O, CO, CO_2, H_2, and C_7H_{16}$

*Mole Balance for i*th *Species in the Dense Phase.*

$$\frac{dF_{id}}{dL} = k_{iq}a_b\varepsilon_b A(C_{ib} - C_{id}) + \phi_d \rho_p A \sum_{j=1}^4 \gamma_{ij}R_{jd} - \varepsilon_d Q_{id}$$

$$i = CH_4, H_2O, CO, CO_2, H_2, \text{ and } C_7H_{16}$$
(A.6)

Subscripts *b* and *d* refer to the bubble and dense phases, respectively; γ_{ij} is the stoichiometric coefficient of component *i* in the *j*th reaction (negative for species consumed and positive for products); Q_{ib} and Q_{id} are the permeation rates per unit length from the reactor side to the permeation side for the bubble phase and the dense phases, respectively, for species *i*.

A.3.3 Model equations for separation side

The differential mole balance equation for the permeate hydrogen is written as:

$$\frac{dF_{H2,p}}{dL} = \varepsilon_b Q_{H_2,b} + \varepsilon_d Q_{H_2,d} \tag{A.7}$$

The hydrogen permeation rate from each phase is calculated from Sieverts' law:

$$Q_{H_2,b} = A'_{p} \frac{P_{M0}}{\delta_{H_2}} \exp\left(\frac{-E_{H_2}}{RT}\right) (\sqrt{P_{H_2,b}} - \sqrt{P_{H_2,p}})$$
(A.8)

$$Q_{H_{2,d}} = A'_{p} \frac{P_{M0}}{\delta_{H_{2}}} \exp\left(\frac{-E_{H_{2}}}{RT}\right) (\sqrt{P_{H_{2,d}}} - \sqrt{P_{H_{2,p}}})$$
(A.9)

The membranes are assumed to be impermeable to all other species.

where P_{M0} = Pre-exponential factor for permeation = 0.00207 mole/(m.min.atm^{0.5})

and E_{H2} = Activation energy for permeation = 9180 J/mol

A.3.4 Interphase mass exchange coefficient

The interphase mass exchange coefficient is calculated based on the correlation by Sit and Grace^{24} . For the *i*th component:

$$k_{iq} = \frac{U_{mf}}{3} + \left[\frac{4D_{ie}\varepsilon_{mf}U_b}{\pi d_b}\right]^{\frac{1}{2}}$$
(A.10)

where D_{ie} is the effective diffusivity of component *i* in the gas mixture and is calculated based on the average composition of the bubble and the dense phases, using the correlation²⁵:

$$\frac{\left(1-y_{i}\right)}{D_{ie}} = \sum_{i=1}^{n} \left(\frac{y_{i}}{D_{ij}}\right) \qquad \qquad i \neq j$$
(A.11)

where D_{ij} is the binary diffusivity of components *i* and *j*.

A.4 Results and Discussion

Figure A.3 shows the predicted species concentrations for the 2 phases for operation at 650°C (close to the current maximum temperature of palladium membrane) and 10 bars absolute pressure. As can be seen, although the reaction occurs predominantly in the dense phase, and there is almost no reaction in the bubble phase, the species concentrations in the two phases are almost identical. This is attributable to the relatively fast mass transfer between the two phases at the temperature of the reformer.

Figure A.4 shows that as hydrogen is withdrawn from the reaction mixture, the methane yield decreases, enhancing the hydrogen production. Thus, while on the one hand pure hydrogen is produced due to membrane separation, on the other hand, overall hydrogen yield increases, which is a measure of the reactor performance in this case. Retentate hydrogen yield, which represents the hydrogen left inside the reactor, goes on decreasing as more and more hydrogen permeates through the membranes.

Figure A.5 shows that heptane conversion is completed within a few centimetres after the entrance, especially for higher steam-to-carbon ratios. The rest of the reactor then proceeds as in steam reforming of methane.

As seen from Figure A.6, with increasing steam-to-carbon ratio, the hydrogen permeate yield is predicted to be enhanced, correspondingly increasing the overall hydrogen yield.

Based on these observations, as shown in Figure A.7, the fluidized bed membrane reactor (FBMR), can be considered to be composed of two overlapping zones: Zone 1, a short zone,

where steam reforming of heptane is completed, and Zone 2, for steam reforming of methane. Thus, in this bi-functional reaction and separation set-up, a separate pre-reformer is not needed, since with hydrogen permeation, the reaction can proceed towards completion in the same unit. In view of the pure hydrogen permeation, PSA units are also not required.

The main challenge for the competitiveness of this technology lies with membrane issues, in particular in assuring pin-hole-free high-flux perm-selective membranes. Figure A.8 shows the effects of decreasing the membrane thickness for a reformer operating at 650°C and 10 bars. Thinner membranes minimize the residual methane and hydrogen in the reformer, and maximize the pure (permeate) hydrogen yield.

Figure A.9 shows the increase of hydrogen permeate yield with increasing specific membrane surface area for a reformer operating at 650°C and 10 bars. Steam reforming reactions being very rapid, and hydrogen permeation being slow, an important parameter is the membrane packing factor, 'a', defined as the membrane surface area per unit volume of reactor. As this factor is increased, the reformer performance as measured in terms of pure hydrogen yield, is significantly enhanced, and a significantly smaller reformer can be used.

Thus this multifunctional reactor is predicted to be able to combine the units from a pre-reformer, reformer and hydrogen purifier into a single unit. The sequence of events can be considered to be:

- i. Steam reforming of higher hydrocarbon, depicted in Figure A.5.
- ii. Methanation, indicated in Figure A.4a when the peak is attained for the methane yield.
- iii. Steam reforming of methane, depicted in Figure A.4a, when the methane conversion becomes zero, thus completing the full conversion of the hydrocarbons.
- iv. Hydrogen permeation until the hydrogen partial pressure in the retentate equalizes with that in the permeate stream, evident from Figure A.4b.
- v. In parallel with step (iv), net interphase mass transfer between the bubble and dense phases is also completed.

When this sequence of events is complete, the species concentrations in the two phases do not change any further, and the concentration profiles remain flat thereafter, as in Figure A.3. The reformer heights corresponding to this sequence of events depend on the operating parameters including reformer pressure, membrane permeate side pressure, reformer temperature, steam-to-carbon ratio in the feed, and superficial velocity.

A.5 Conclusions

n-Heptane was used as a model component for higher hydrocarbons, close to the naphtha cut. Insitu permselective membranes should be able to produce ultra-pure hydrogen as required by some sectors like the fuel cell industry. Higher conversion of methane (produced by the methanation reaction) allows the reformer to be operated at much lower temperature to achieve the same hydrogen yield as for much higher temperatures without membranes. A FBMR system for higher hydrocarbons can result in a compact reformer system combining the units from a prereformer, reformer and hydrogen purification into a one single unit.

However, for the system to be economically viable and competitive, major challenges remain for the membranes. Desirable membrane features are:

- High flux.
- High selectivity to hydrogen.
- Low cost.
- Longevity.
- Higher membrane packing, while maintaining a minimum separation requirement in a fluidized space to prevent solids bridging and gas bypassing.

Challenges specific to higher hydrocarbons include catalyst deactivation and possible membrane fouling. These have not been considered in this paper, but will be key factors to be examined in the experimental work.

The model considers the bubbling bed mode of operation, as this will be the main operating regime in the forthcoming experiments. However, many industrial fluidized bed reactors are operated in the turbulent regime in view of the higher throughput and advantageous features²⁶. The transition from bubble to turbulent flow happens earlier for powders with smaller mean particle diameter and wider particle size distributions²⁷. The experimental work will include determination of this transition at the temperature and pressure of the reformer, and investigate how it affects the hydrogen yield.

A.A Appendices

A.A.1 Kinetic expressions for reactions in reformer

• <u>Steam Reforming of Higher Hydrocarbons:</u>		(Tottrup ¹⁹)	
$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2$	r_1	For Heptane, $n = 7$, $\Delta H_{298}^o = 1108 \frac{kJ}{mol}$	
$r_{1} = \frac{k_{1}P_{C_{7}H_{16}}}{\left[1 + K_{a}\left(\frac{P_{C_{7}H_{16}}P_{H_{2}}}{P_{H_{2}O}}\right) + K_{b}\left(\frac{P_{H_{2}O}}{P_{H_{2}}}\right)\right]^{2}}$			
$k_1 = 8 \times 10^{-5} \exp\left(-\frac{67800}{RT}\right)$		mol g _{catalyst} .hr.bar	
$K_a = 25.2$		bar ⁻¹	
$K_{b} = 0.077$		[-]	
• <u>Steam Reforming of Methane:</u>		(Xu and Froment ²⁸)	
$CH_4 + H_2O \Leftrightarrow CO + 3H_2$	<i>r</i> ₂	$\Delta H_{298}^{o} = 206.1 \frac{kJ}{mol}$	
$CO + H_2O \Leftrightarrow CO_2 + H_2$	<i>r</i> ₃	$\Delta H_{298}^{o} = -41.1 \frac{kJ}{mol}$	
$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2$	<i>r</i> ₄	$\Delta H_{298}^{o} = 165.0 \frac{kJ}{mol}$	
$r_{2} = k_{2} \frac{\left(\frac{P_{CH_{4}}P_{H_{2}O}}{P_{H_{2}}^{2.5}} - \frac{P_{CO}P_{H_{2}}^{0.5}}{K_{1}}\right)}{DEN^{2}}$			
$r_{3} = k_{3} \frac{\left(\frac{P_{CO}P_{H_{2}O}}{P_{H_{2}}} - \frac{P_{CO2}}{K_{2}}\right)}{DEN^{2}}$			

$$r_{4} = k_{4} \frac{\left(\frac{P_{CH_{4}}P_{H_{2}O}^{2}}{P_{H_{2}}^{3.5}} - \frac{P_{CO_{2}}P_{H_{2}}^{0.5}}{K_{1}K_{2}}\right)}{DEN^{2}}$$
$$DEN = 1 + K_{CO}P_{CO} + K_{H_{2}}P_{H_{2}} + K_{CH_{4}}P_{CH_{4}} + \frac{K_{H_{2}O}P_{H_{2}O}}{P_{H_{2}}}$$

The equation parameters are available in Xu and Froment 28 .

A.A.2 Hydrodynamic equations for the 2-phase model

Bubble Size Distribution:

$$d_{b} = d_{bm} - (d_{bm} - d_{b0})e^{-0.3h/D}$$

$$d_{bm} = 1.64[A(U_{0} - U_{mf})]^{0.4}$$

$$d_{b0} = \frac{1.38}{g^{0.2}} \left[\frac{A(U_{0} - U_{mf})}{N_{or}}\right]$$
(Mori and Wen²⁹)
$$U_{0} = U_{-1}$$

Fraction of Bed Occupied by Bubbles:

 $\varepsilon_b = \frac{U_0 - U_{mf}}{U_b}$

Bubble Rise Velocity:

$$U_b = U_0 - U_{mf} + 0.711 (gd_b)^{1/2}$$

(Davidson and Harrison³⁰)

Minimum Fluidization Velocity:
$$\text{Re}_{mf} = [(33.7)^2 + 0.0408 \, Ar]^{1/2} - 33.7$$

(Wen and Yu^{31,32})

Volume Fraction of Solids:

$$\phi_d = (1 - \varepsilon_b)(1 - \varepsilon_{mf}) \qquad \phi_b = 0.001\varepsilon_b$$

Table A.1: Reactor geometry and base simulation parameters

Reformer empty cross-sectional area	$2.0 \times 10^{-3} \text{ m}^2$	
Specific membrane area	$64 \text{ m}^2/\text{m}^3$ of reactor	Reformer
	volume	
Total membrane length (along height of	1 m	
reformer)		
Catalyst type	Ni-Al ₂ O ₃	
Catalyst particle mean diameter	100 <i>µ</i> m	Catalyst
Catalyst particle density	2270 kg/m ³	
Steam:Carbon ratio in feed	3	
<i>n</i> -Heptane mole fraction in feed	0.0454	
Steam mole fraction in feed	0.9538	Process operating
H ₂ mole fraction in feed	0.0008	conditions
Feed temperature	650°C	
Feed pressure	10 bars abs	
Membrane permeate side pressure	0.3 bars abs	
Reactor inlet gas superficial velocity	0.23 m/s	



Figure A.1: Equilibrium compositions in n-heptane steam reforming at varying temperatures and pressures



Figure A.2: Schematic diagram of the kinetic model





Figure A.3: Predicted species concentrations in the two phases at 650°C, 10 bars: (a) Dense phase (b) Bubble Phase





(b)

Figure A.4: Predicted methane and hydrogen yields at 650°C, 10 bars: (a) Methane (b) Hydrogen



Figure A.5: Predicted heptane conversions at 650°C, 10 bars



Height above Distributor, m







Figure A.6: Predicted effect of S/C ratios on yields at 650°C, 10 bars: (a) Permeate hydrogen (b) Retentate hydrogen



Figure A.7: Reaction zones in FBMR system for higher hydrocarbons: Pre-reforming, reforming and purification in a single unit



Height above distributor, m

(a)



(b)

Figure A.8: Dependence of hydrogen yields on membrane thickness at 650°C, 10 bars: (a) Permeate hydrogen (b) Retentate hydrogen



(b)

Figure A.9: Dependence of hydrogen yields on specific membrane area at 650°C, 10 bars: (a) Permeate hydrogen (b) Retentate hydrogen

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APPENDIX B. FBMR OPERATING MANUAL³

B.1 Introduction

This document outlines the start-up strategy, experimentation, emergency and normal shutdown processes to ensure safe operation. It is assumed at this stage that the reactor system has already been tested for the basic safety requirements, and that commissioning has been completed successfully. However, routine checks must be done before every start-up.

B.2 Steam Reforming Experiments: Reactor Start-up

The MAWP of the reactor pressure vessel is 1020.5 kPag at 621°C. The maximum heating rate for any part of the pressure vessel is to be 5°C/min. The temperature is increased using electrical heaters and decreased gradually to allow for compression/expansion of parts. Keeping in view the personnel safety issues, temperature tolerance of the membranes, and catalyst stability, it was decided to use a maximum temperature of 575°C, and a maximum pressure of 1000 kPa for any combination of operating conditions.

Step 1: Prior Preparations (Inventory Check)

(1.a) <u>Catalysts</u>

 Install membrane dummies or membrane panels as applicable. Fill the reactor with RK-212 catalyst powder to be able to just submerge the topmost membrane/dummy. The reactor must be leak tested by pressurization every time the reactor is started. Put on the insulation jackets.

(1.b) <u>Desulfurizer sorbent</u>

• When operated with natural gas, replace sorbent in desulfurizer every 48 hours of operation.

(1.c) <u>Water</u>

- Fill water tank.
- Prime the water pump by opening V-515.2, and allowing water to flow out until no air bubbles are detected at the outlet.

³ Input was received from Ali Gulamhusein (Membrane Reactor Technologies Limited) while preparing this document.
• Close V-515.2 and cap line to prevent leakage.

(1.d) <u>Gases & liquid hydrocarbons</u>

- Check gas pressures (nitrogen, hydrogen, and natural gas or helium cylinder for liquid hydrocarbon headspace). Cylinders must be changed/ refilled if pressure close to 550 psi.
- Open valve on nitrogen cylinder. Set PI-101.2 to 150 psig.
- Open valve on hydrogen cylinder. Set PI-301.2 to 150 psig.
- If performing natural gas steam reforming, start natural gas compressor, and set it on AUTO mode, which starts itself to refill cylinder and stops when a preset pressure value is reached in the cylinder.
- If performing natural gas steam reforming, start warm water flow for irrigating PR-401.2.
- If performing liquid hydrocarbons steam reforming, set PI-1201.2 to 250 psig.
- Make sure that there is enough liquid hydrocarbons storage in the respective tanks.

Step 2: Prior Preparations (System Purging)

(2.a) <u>Purge the hydrogen feed line with nitrogen</u>

- Close V-421.2 to prevent N₂ purge to reactor
- Open XV-315.1 (H₂ solenoid)
- Fully open V-115.1 and partially open the mass flow controller FICV-301.1 (~3 slpm).
- Partially open the mass flow controller FICV-101.1 (~3 slpm)
- Gradually open nitrogen supply via V-101.1.
- Allow pressure to build-up.
- Gradually release N₂ via V-311.1
- Close V-311.1 and allow pressure to rebuild, then gradually release via V-311.1
- Repeat 2 or 3 times
- Close V-101.1, FICV-301.1, V-115.1, and XV-315.1

(2.b) <u>Purge the reactor fully with nitrogen</u>

This is done automatically, while fluidizing the reactor during process heaters start-up, in Step 3.

(2.c) <u>Purge the permeate section with nitrogen</u>

If membrane panels are installed, purge the permeate lines including the hydrogen pump.

- Ensure V-015.1 is closed
- Open V-010.1

- Gradually open V-015.1, avoid sudden spikes in flow as this will hamper control of PCV-600.3 (uses same N₂ supply)
- Allow purge to continue for 15 minutes. Also, repeat this, with pump bypass valve V-718.4 open.

Step 3: Heating up the FBMR and Catalyst Reduction

(3.a) <u>Fluidizing with nitrogen</u>

- Close V-101.1.
- Open V-421.2 and the solenoid valve XV-119.1.
- Set nitrogen flow rate on FICV-101.1. Recommended nitrogen flow rate = 6 slpm, for good fluidization behaviour. (Also monitor via the differential pressure transducers along the FBMR height).

(3.b) <u>Turning on the heaters</u>

- Prepare the connections for the external heaters: Turn on the main power supply, turn on the voltage transformer. Next, turn on the heaters switch on the power distribution box on the FBMR rig. Reset Emergency Stop button, if engaged.
- On the HMI program, start the External Heaters, and the Internal Heaters.
- Heat up the reactor, with only nitrogen flowing.
 - Specify 30% of full-scale heating rate for the internal as well as the external heaters. Adjust the settings to ensure heating rate of 5°C/min to 500°C. The skin temperature of the reactor vessel at any point should not exceed 600°C.
- Gradually ramp up vaporizer heaters to maintain a maximum feed line temperature of 450°C (TT-1001.2), while not exceeding 500°C skin temperature (TT-1000.2)

(3.c) <u>Introducing hydrogen</u>

- Reduce the catalyst overnight (12 hours) with hydrogen-nitrogen mix.
 - Hydrogen should not be introduced at temperatures below 350°C, especially when membranes are in use.
 - Open hydrogen solenoid valve XV-315.1.
 - Set nitrogen and hydrogen flow rates on FICV-101.1 and FICV-301.1 respectively. Both of these are controlled by a stand-alone Brooks read-out box. For hydrogennitrogen mix, recommended flow rates are hydrogen and nitrogen are 1.5 slpm and 4.5 slpm respectively.

Step 4: Introducing Steam and Hydrocarbon Feeds

The hydrocarbons are to be sequentially used as desulfurized natural gas, propane, and finally heptane. This stage of steam reforming experiments is similar for all three types of hydrocarbons, and is described only for natural gas here.

(4.a) <u>Steam introduction</u>

- Start cooling water to ROG vent condenser line, and to gas sampling condenser line.
- After overnight catalyst reduction, the reactor is ready for steam introduction. Ramp up or down the FBMR temperature to the initial desired operating temperature.
- Pressurize the FBMR to the initial desired operating pressure, by setting the PCV-600.3.
- Set the nitrogen flow rate to be 3 slpm (FICV-101.1); however, stop the nitrogen solenoid valve XV-101.1. Set the hydrogen flow rate to 6 slpm.
- Open the water solenoid valve XV-501.2.
- Start water pump, and gradually increase the water flow to the required value, and correspondingly decrease the hydrogen flow rate so as to give a superficial velocity of 6 cm/s. At no time (while there is no hydrocarbon feed), should the steam-hydrogen ratio exceed 6. The recommended steam-hydrogen ratio would be 4.
- After steam flow stabilizes (indicated by a stable temperature for the ROG exit temperature TT-1002.3, introduce the hydrocarbon feed.

(4.b) <u>Natural gas introduction</u>

- Before initiating NG flow, ensure that cooling water to the NG regulator is on.
- After period of stability, establish NG flow:
 - Open XV-419.2 (NG solenoid)
 - Set set-point on FICV-401.2 to required set-point.
- Monitor reactor temperatures. Increase in heater duty may be required due to reforming action
- Shut off hydrogen upon GC confirmation of reaction (presence of CO₂ detected) by closing solenoid XV-315.1.

Now the reformer is fully operational!!!

B.3 During Steam Reforming Experiments

The permeate gas flow rates, temperatures, and bed pressures are logged into the computer automatically, and are also recorded manually every 10 minutes.

Once the hydrocarbon has been introduced, one of the sample gas lines is monitored for gas composition. When the gas composition variation is within absolute deviations of $\sim \pm 1\%$, and verified with another gas sampling line, steady state is assumed to have reached. Gas samples are analyzed at various locations, repeated as required.

B.4 Keep-Warm Mode of Operation

(1.a) <u>Transition from experiments mode to keep-warm mode</u>

- Set Internal Heaters to 20%
- Set External Heaters to 20%
- Adjust above two power input rates, so as to avoid temperature overshoot, and triggering ESD, which may happen feeds are turned off.
- Release FBMR pressure by slowly opening PCV-600.
- Gradually ramp down the hydrocarbon and water flows and ramp up nitrogen flows, maintaining the superficial velocity at 6 cm/s. The SCR should never fall below 4.
- Stop NG flow by closing solenoid valve XV-419.2.
- Stop water flow by closing solenoid valve XV-501.2.
- Monitor reactor temperatures, further decrease in heater duty may be required due to no reforming action. Maintain temperatures to 500°C, and fully open the PCV-600.
- Maintain 10% hydrogen and 90% nitrogen flow rate to maintain a superficial velocity of 5 cm/s.

(1.b) <u>Transition from keep-warm mode to experiments mode</u>

- Continue with Step 4 as described in Section B
- Resume experiments when operating conditions are reached

B.5 Normal Shutdown

(1.a) Depressurize FBMR, shut off feeds and introduce purge gas

- Reduce temperature to 450°C
- Open shunt valves for the differential pressure transducers
- Release FBMR pressure by slowly opening PCV-600.
- Gradually ramp down hydrocarbon and water flows and ramp up nitrogen flows, maintaining the superficial velocity at 6 cm/s. The SCR should never fall below 4.
- Stop hydrocarbon flow, and start hydrogen flow. A steam/hydrogen molar ratio of 4 should be maintained to keep the catalyst reduced.
- Continue steaming for 10 minutes.
- Stop steam and hydrogen. Close water (XV-501.2) and hydrogen (XV-315.1) solenoid valves.
- Close steam feed isolation valve. Close manual and solenoid valve on feed delivery from water tanks.
- Maintain nitrogen flow rate to maintain a superficial velocity of 5 cm/s.

(1.b) <u>Reduce temperature</u>

- Shut down hydrogen pump
- Turn off the internal heaters
- Reduce power input to external heaters to allow FBMR cooling at the rate of 5°C/min
- Continue nitrogen purging till the temperature falls below 100°C.
- Shut down all heaters completely.
- It is important that all steam be purged from the vaporizer and reactor. Maintain nitrogen flow for at least 2 hours after steam shutoff. Shut off nitrogen flow.

(1.c) If shutting down for a lengthy period

- If shutting down for a lengthy period, isolate helium pad from the liquid hydrocarbon tanks and vent pressure.
- Isolate all gas cylinders and feed valve.
- Empty the water tank.
- Reduce and stop process nitrogen via the HMI controller. Close process nitrogen supply valve and isolate cylinders.
- Close purge nitrogen supply valve and isolate cylinders.

B.6 Emergency Shutdown

- Push the STOP button on the PLC Panel door, and confirm the shutdown from the Control Computer adjacent to the Control Panel OR
 Click the HMI Emergency Shutdown button on the Control Computer and confirm the action.
- Press the red Emergency Shutdown button on the FBMR heaters power distribution box, and turn off the external heaters switch.
- Close all hydrogen bottles in flammables storage area outside east exit of the building.
- Close natural gas compressor located outside north east corner of the building. Close both natural gas tanks in flammables storage area outside east exit of the building.
- Shut off natural gas feed (V-420.2) and higher hydrocarbon feed (V-1206.2) adjacent to small window (east wall) where all gas/liquid lines enter the building.
- Shut off propane valve (V-1202.2) and heptane valve (V-1203.2) in liquid flammables storage area outside east exit of the building.
- Contact concerned persons as per emergency contact list in sheet above.
- Pressing the red Emergency Shutdown button on the PLC panel does the following:
 - shuts off the feed flow solenoid valves
 - opens nitrogen solenoid for purge
 - stops the water pump, and hydrogen pump
 - turns off all heaters
 - opens PCV-600.3

APPENDIX C. FBMR ASSEMBLY DRAWINGS

This Appendix shows some of the representative and important FBMR assembly drawings. The full set of fabrication drawings and design calculations are available from M. Rakib and J. Grace as electronic files in a folder Rakib_FBMR_Assembly_Drawings.



Figure C.1: FBMR assembly: Shell weldment



Figure C.2: FBMR pressure vessel assembly



Figure C.3: Typical rectangular cover for side opening



Figure C.4: Assembly of rectangular cover and membrane panel



Figure C.5: Assembly of inlet head, showing feed distributor



Figure C.6: General arrangement of FBMR on reactor stand



Figure C.7: Location of band heaters (denoted in brown) mounted on the FBMR

APPENDIX D. CATALYST EVALUATION UNIT

This Appendix shows the main process flow diagrams for the catalyst evaluation unit (microreactor set-up). These were prepared in collaboration with Alexandre Vigneault, a fellow graduate student.



Figure D.1: Catalyst evaluation unit: Micro-reactor feeding system, Part I



Figure D.2: Catalyst evaluation unit: Micro-reactor feeding system, Part II



Figure D.3: Catalyst evaluation unit: Micro-reactor and gas analysis

APPENDIX E. HYDRODYNAMIC BEHAVIOUR IN A PLEXIGLAS COLUMN AND THE FBMR

E.1 Fluidizability of the Catalyst Particles

A commercial naphtha steam reforming catalyst RK-212 manufactured by Haldor Topsoe A/S was used for the experiments. The catalyst, available in the form of 7-holed cylindrical catalyst pellets, was crushed and sieved to obtain the desired size ranges of the particles.

During the commissioning stage, the reactor was loaded with particles of the size cut +90 μ m -125 μ m. In another trial, the FBMR was loaded with a mixture of equal fractions of particles of size cuts +63 μ m -90 μ m, +90 μ m -125 μ m, and +125 μ m -150 μ m. The gas superficial velocities was varied up to 0.18 m/s, using dry nitrogen gas (Industrial grade nitrogen, supplied by Praxair Inc.). In all these cases, the pressure transducers along the height of the FBMR (as shown in Figure 2.5) indicated very poor quality of fluidization, with different degrees of bed activity indicated along the FBMR height, some locations even indicating no fluidization at all.

A Plexiglas column, shown in Figure E.1, was constructed for cold hydrodynamic studies to understand, by better visualization, the hydrodynamics in the FBMR unit. The dimensions of this cold model, provided in Figure E.2, are similar to, but not identical to the FBMR vessel due to constraints of materials availability. Bed activity trends monitored by pressure transducers for the cold column were similar to those for the FBMR, the reason attributed to channelling in the long vertical column equipped with the membrane panels. The particles exhibited behaviour similar to Group C particles, with occasional lifting of the whole bed with a horizontal gap translating upwards, as seen in Figure E.3.

On the contrary, spent FCC particles of mean size 100 μ m exhibited smooth fluidization. Crushed RK-212 particles of size cuts +150 μ m -180 μ m, and +180 μ m -212 μ m were tested separately in the cold column, and good fluidization was achieved in both cases. However, in both cases for the RK-212 particles, initially there were small vertical bridges of un-fluidized zones, which disappeared in about two hours.

Alumina-supported nickel and/or precious metal catalysts were used in previous research¹, with mean particle sizes in the range of 108 μ m or lower. However, those catalysts were prepared by a catalyst manufacturer by impregnating the active material on high-quality

alumina powder supplied to them. As such these particles with higher sphericity or on-purpose fluidizable catalyst particles, e.g. FCC particles, would demonstrate easier and better fluidizability than those of irregular shape prepared by crushing commercial catalyst pellets .

Figure E.4 shows enlarged views of fresh catalyst particles (after crushing and sieving); Figure E.5 shows enlarged views of catalyst particles unloaded at the end of a series of experiments. These show that the freshly loaded particles were very irregular and jagged, whereas the used catalyst is much more rounded and regular, the sphericity going from ~0.3 to ~0.8.

While particles smaller than 125 μ m remained stagnant in general, initial mobilization of bigger particles in the cold model column was still found to be difficult, which could have been due to entanglement of the jagged surfaces of the fresh particles, aggravated by Van der Waals forces as well as by moisture absorbed while stored after crushing. However, once mobilized, the hydrodynamic activity improved in general, possibly due to drying of the catalyst particles while fluidizing with dry nitrogen gas, as well as rounding of the particles during operation.

E.2 Superficial Gas Velocities in the FBMR

The cold column also gave an understanding of the bubble behaviour in the range of the superficial gas velocities encountered in the FBMR. Working at ambient conditions of temperature and pressure, superficial velocities higher than $\sim 0,08$ m/s led to big bubbles or slugs in the upper half of the bed. This indicates that in the high-temperature tests, the FBMR operated in the bubbling bed flow regime in some cases, and formed slugs in others, especially with the superficial velocities varying widely along height as shown below. However, caution is needed as behaviour could differ at elevated temperatures and pressures in the FBMR operation.

Figures E.6 to E.11 plot the superficial gas velocities for representative cases of steam reforming experiments with no membranes, one membrane panel, and six membrane panels installed for propane and heptane. The temperature profiles for the experiments are also shown with each plot. Four factors caused the changes in superficial velocity:

- (1) Intermittent abrupt variations of the superficial gas velocity occur due to changes in crosssectional area in the spaces between adjacent membrane panels (or dummies), compared to the spans covered by these panels.
- (2) In general the superficial gas velocity follows the trend of the temperature variations.

- (3) The steam reforming reactions led to a net increase in the molar flow rate in the FBMR. This caused steep increases in the superficial velocity near the FBMR entrance, where the higher hydrocarbon (propane or heptane) conversion is completed. Colder sections in the FBMR can also encounter methanation reactions leading to decrease in superficial velocity, while a temperature increase can increase the molar flow rate due to methane steam reforming, as well as increasing the molar volumetric flow.
- (4) Volumetric flow, and hence superficial velocity, is also affected by the hydrogen removal via membranes. Especially in regions with an increasing temperature, a decrease in the gas superficial velocity can be seen in the spans occupied by active membrane panels.

E.3 Future Work with Cold Model

Experiments with the cold Plexiglas replica of the FBMR were conducted to understand the difficulties of fluidizing the RK-212 catalyst particles, and to select a suitable catalyst particle size for good fluidizability. The column can be used in future to study the degree of gas backmixing in the fluidized bed of such a high aspect ratio. It could also be used to study the hydrodynamics in a column with an unusual fluidized bed geometry, as well as to provide guidance on reactor modelling.



Figure E.1: Plexiglas column for hydrodynamic studies



Figure E.2: Plexiglas column dimensions



Figure E.3: Catalyst bed being lifted by the gas



Figure E.4: Fresh catalyst particles



Figure E.5: Used catalyst particles



Figure E.6: Gas superficial velocities for experiment Propane 1.a



Figure E.7: Gas superficial velocities for experiment Propane 2.d



Figure E.8: Gas superficial velocities for experiment Propane 3.c



Figure E.9: Gas superficial velocities for experiment Heptane 1.a



Figure E.10: Gas superficial velocities for experiment Heptane 4.d



Figure E.11: Gas superficial velocities for experiment Heptane 5.b

E.4 References

 Boyd, T.; Grace, J.; Lim, C. J.; Adris, A. E. M., Hydrogen from an internally circulating fluidized bed membrane reactor. *International Journal of Chemical Reactor Engineering* 2005, 3, A58.

APPENDIX F. MODEL SENSITIVITY ANALYSIS

This appendix examines the sensitivity of the reactor model described in Chapter 5 in order to understand the relative importance of the various resistances to reaction inside the FBMR, as well as the effect of uncertainties in estimating different parameters in the model. Experiment Propane 3.c is taken as a basis for estimating the effects.

F.1 Model Sensitivity to Reaction Rate Constants

The kinetic rate constants for all reactions involved in the FBMR were first varied by a factor of 10 upwards and downwards compared with those based on earlier studies in the literature.

Figure F.1 shows the reactor performance with these major variations in rate constants. Some variations in the performance can be seen near the entrance of the reactor, affected mainly by the propane steam reforming kinetics. However, in general, it can be seen that in the bulk of the bed, there was very little difference in the local yields of methane, carbon oxides or hydrogen for these variations in the reaction rate constants.

Figures F.2 and F.3 show the methane and hydrogen concentrations in the dense and bubble phases. The model considers a very lean concentration of catalyst particles in the bubble phase (Equation 5.12). While reduced catalyst rate constants (multiplication by a factor of 0.1) do not appreciably change the deviation between the dense and bubble phase concentrations, multiplying by a factor of 10 lowers the concentration difference between these two phases for methane and hydrogen.

F.2 Model Sensitivity to Interphase Mass Transfer

The rates of diffusional and convective mass transfer of components between the bubble and dense phases were varied by a factor of 10 lower and higher compared with those obtained from the Sit and Grace (1981) correlation.

Figure F.4 shows the reactor performance with variations of the interphase mass transfer. Propane fed to the distributor also goes to the bubble phase, and higher mass transfer (factor of 10) transfers the propane almost immediately to the dense phase. However, slower mass transfer (factor of 0.1) retains more propane in the bubbles, thereby delaying the overall conversion of propane, which can only occur where there are catalyst particles, i.e. in the dense phase. Since methane is an intermediate component, it appear more slowly in the reactor, and its overall conversion is also delayed compared to the actual mass transfer rate case. This is explained from the methane concentrations in the bubble and dense phases as seen from Figure F.5, with a cross-over occurring between the two concentration curves.

While the tenfold changes in interphase mass transfer are discernible, the effects are not very significant. Hence, interphase mass transfer, while not a negligible factor, plays a secondary role with respect to the overall reaction model. Since the hydrodynamics of the bed mostly enter the model through the interphase mass transfer, one may also conclude that accurate portrayal of the bed hydrodynamics is of secondary importance for this particular process and the operating conditions investigated.

F.3 Conclusions

The model sensitivity studies with respect to reaction rate, show that in general for this FBMR, the kinetics are fast enough at all temperatures tested for the role of chemical kinetics to be insignificant in determining the FBMR performance. Interphase diffusional mass transfer rate is shown to be somewhat more significant in affecting the reactor performance, but to nevertheless still play a secondary role. Given these findings, it is evident from these studies that the FBMR performance is primarily controlled by chemical equilibrium and by hydrogen permeation through the membranes. Hence the model is sensitive to accurately characterizing the chemical equilibrium and hydrogen permeation, but relatively insensitive to predicting the chemical kinetics, interphase mass transfer and hydrodynamics with precision.



Figure F.1: FBMR performance with variations of reaction rate constants for experiment Propane 3.c



Figure F.2: Methane concentrations with variations of reaction rate constants for experiment Propane 3.c



Figure F.3: Hydrogen concentrations with variations of reaction rate constants for experiment Propane 3.c



Figure F.4: FBMR performance with variations of interphase mass transfer for experiment Propane 3.c


Figure F.5: Methane concentrations with variations of interphase mass transfer for experiment Propane 3.c



Figure F.6: Hydrogen concentrations with variations of interphase mass transfer for experiment Propane 3.c

F.4 References

1. Sit, S. P.; Grace, J. R., Effect of bubble interaction on interphase mass transfer in gas-fluidized beds. *Chemical Engineering Science* **1981**, 36, 327-335.

APPENDIX G. EXPERIMENTAL DATA TABULATION (FBMR)

FBMR Temperature (°C)		
0.01 m	400	
0.32 m	487	
0.52 m	471	
0.78 m	502	
1.08 m	497	
1.29 m	514	
1.59 m	525	
Bed Average	499	
2.26 m	423	

Time Averaged Conditions		
P (kPa abs)	803	
P _m (kPa abs)	52	
Feed CH ₄ (slpm)	3.059	
Feed Water (g/h)	737.4	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	1.169	
Permeate 2	0.832	
Permeate 3	0.610	
Permeate 4	0.350	
Permeate 5	0.943	
Permeate 6	1.403	

Experiment: Methane 1.a				
Usight (m)	Sample Gas Dry Composition			
fieight (m)	H ₂	CH ₄	CO	CO ₂
0.219	37.39	52.15	0	10.46
0.219	37.10	52.63	0	10.28
0.371	40.91	35.32	0.53	23.24
0.371	41.27	34.62	0.55	23.56
0.473	29.63	34.81	0.27	35.28
0.473	29.05	35.19	0.27	35.49
0.625	29.01	25.32	0.51	45.16
0.727	45.42	37.16	0.40	17.01
0.727	44.63	36.66	0.43	18.28
0.879	45.20	28.16	0.90	25.73
0.981	41.63	30.47	0.70	27.20
0.981	41.25	30.38	0.71	27.66
1.133	41.43	30.45	0.70	27.42
1.235	47.27	26.29	1.02	25.43
1.387	48.15	22.65	1.36	27.84
1.489	43.50	24.59	1.10	30.81
1.489	43.27	24.33	1.15	31.25
1.489	43.28	24.03	1.14	31.54
1.489	43.02	23.19	1.17	32.62
1.489	42.20	22.49	1.33	33.99
1.641	40.20	26.02	1.05	32.74
2.327	35.45	29.91	0.58	34.05
2.327	35.27	29.57	0.59	34.57

FBMR Temperature (°C)		
0.01 m	402	
0.32 m	486	
0.52 m	470	
0.78 m	494	
1.08 m	499	
1.29 m	515	
1.59 m	538	
Bed Average	500	
2.26 m	440	

Time Averaged Conditions		
P (kPa abs)	610	
P _m (kPa abs)	52	
Feed CH ₄ (slpm)	2.29	
Feed Water (g/h)	553	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	0.793	
Permeate 2	0.643	
Permeate 3	0.434	
Permeate 4	0.245	
Permeate 5	0.695	
Permeate 6	1.051	

Experiment: Methane 1.b				
Hoight (m)	Sample Gas Dry Composition			
fieight (iii)	H ₂	CH ₄	СО	CO ₂
0.219	40.29	47.78	0	11.93
0.219	41.29	46.25	0	12.46
0.371	41.45	32.91	0.47	25.17
0.371	41.71	33.23	0.49	24.57
0.473	32.22	34.63	0.30	32.86
0.473	32.25	34.26	0.31	33.18
0.625	32.70	26.66	0.63	40.01
0.727	47.49	34.48	0.48	17.55
0.727	46.27	35.56	0.47	17.71
0.727	47.15	34.73	0.48	17.65
0.879	44.60	29.87	0.79	24.74
0.981	43.96	26.22	0.91	28.91
0.981	44.70	27.53	0.88	26.88
1.133	42.60	21.54	1.20	34.67
1.235	46.09	27.78	0.87	25.26
1.387	47.24	24.04	1.09	27.63
1.387	46.26	25.35	1.06	27.33
1.489	45.14	19.63	1.56	33.67
1.489	45.50	19.18	1.56	33.75
1.489	45.22	19.54	1.51	33.73
1.489	45.74	20.03	1.52	32.71
1.489	46.03	20.16	1.51	32.30
1.489	46.14	20.02	1.55	32.30
1.489	45.85	20.66	1.52	31.97
1.489	45.52	20.67	1.50	32.31
1.489	45.59	19.82	1.49	33.10
1.489	45.35	19.65	1.46	33.54
1.489	45.13	20.54	1.43	32.89
1.489	45.87	19.49	1.55	33.09
1.641	44.00	23.63	1.31	31.06
2.327	40.08	25.08	0.88	33.96
2.327	40.70	24.93	0.86	33.51

FBMR Temperature (°C)		
0.01 m	405	
0.32 m	482	
0.52 m	463	
0.78 m	490	
1.08 m	496	
1.29 m	515	
1.59 m	545	
Bed Average	498	
2.26 m	450	

Time Averaged Conditions		
P (kPa abs)	608	
P _m (kPa abs)	25	
Feed CH ₄ (slpm)	2.29	
Feed Water (g/h)	553	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	1.331	
Permeate 2	0.991	
Permeate 3	0.697	
Permeate 4	0.377	
Permeate 5	0.894	
Permeate 6	1.409	

Experiment: Methane 1.c				
Hoight (m)	Sample Gas Dry Composition			
fieight (iii)	H_2	CH ₄	CO	CO ₂
0.219	38.00	49.58	0.00	12.41
0.219	37.29	50.63	0.00	12.08
0.371	36.69	31.66	0.47	31.18
0.371	36.34	32.10	0.47	31.09
0.473	29.38	28.04	0.37	42.21
0.473	29.02	29.24	0.35	41.40
0.625	28.45	16.42	0.67	54.45
0.727	44.98	35.06	0.45	19.50
0.727	43.18	36.25	0.42	20.14
0.879	42.66	27.78	0.82	28.74
0.981	41.49	23.76	0.96	33.79
0.981	41.21	24.38	0.99	33.42
0.981	41.94	24.72	0.97	32.37
1.133	39.04	17.61	1.25	42.11
1.235	42.45	24.71	0.96	31.88
1.387	41.81	20.65	1.19	36.34
1.387	41.36	20.39	1.22	37.04
1.489	40.47	13.10	1.82	44.61
1.489	39.53	12.85	1.74	45.87
1.489	39.68	13.65	1.75	44.91
1.489	39.86	14.13	1.70	44.30
1.641	35.97	18.84	1.40	43.79
2.327	35.57	17.56	1.11	45.75
2.327	35.09	18.11	1.08	45.72

FBMR Temperature (°C)		
0.01 m	402	
0.32 m	442	
0.52 m	457	
0.78 m	537	
1.08 m	512	
1.29 m	523	
1.59 m	524	
Bed Average	499	
2.26 m	457	

Time Averaged Conditions		
P (kPa abs)	498	
P _m (kPa abs)	101	
Feed CH ₄ (slpm)	2.596	
Feed Water (g/h)	625	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	0.181	
Permeate 6	NA	

Experiment: Methane 2.a					
Hoight (m)	Sample Gas Dry Composition				
fieight (m)	H ₂ CH ₄		СО	CO ₂	
0.219	29.79	63.03	0.00	7.18	
0.219	30.46	62.29	0.00	7.25	
0.219	30.85	61.65	0.00	7.49	
0.371	38.36	52.25	0.00	9.39	
0.371	38.69	51.81	0.00	9.50	
0.473	47.34	40.51	0.00	12.15	
0.473	46.81	41.78	0.00	11.41	
0.727	57.33	27.42	0.83	14.42	
0.727	57.52	27.11	0.84	14.54	
0.981	59.88	23.74	1.05	15.34	
0.981	58.84	25.87	1.01	14.28	
1.235	57.87	27.00	0.84	14.29	
1.235	57.49	27.31	0.77	14.43	
1.235	56.98	28.18	0.79	14.05	
1.235	56.80	28.47	0.75	13.99	
1.235	57.16	27.89	0.77	14.18	
1.235	56.80	28.25	0.76	14.19	
1.235	56.70	28.38	0.75	14.18	
1.235	56.88	27.83	0.79	14.50	
1.235	56.97	28.03	0.77	14.24	
1.387	54.97	29.93	0.72	14.37	
1.387	55.38	29.20	0.72	14.70	
1.489	59.82	23.87	1.13	15.18	
1.489	59.77	23.64	1.14	15.44	
1.641	57.77	26.13	0.94	15.16	
1.641	57.68	26.43	0.92	14.96	
1.641	54.87	29.99	0.73	14.41	
2.327	56.25	28.01	0.80	14.95	
2.327	56.57	27.61	0.79	15.03	
2.327	55.82	28.63	0.83	14.72	

FBMR Temperature (°C)			
0.01 m	407		
0.32 m	446		
0.52 m	461		
0.78 m	541		
1.08 m	506		
1.29 m	520		
1.59 m	528		
Bed Average	500		
2.26 m	460		

Time Averaged Conditions			
P (kPa abs)	747		
P _m (kPa abs)	102		
Feed CH ₄ (slpm)	2.596		
Feed Water (g/h)	625		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	0.723	
Permeate 6	NA	

e (°C)	Experiment: Methane 2.b				
407	Hoight (m)	Samp	le Gas Dry	[,] Compo	sition
446	Height (m)	H ₂	CH ₄	СО	CO ₂
461	0.219	34.08	57.91	0.00	8.01
541	0.371	36.98	54.59	0.00	8.43
506	0.473	43.65	45.86	0.00	10.49
520	0.727	54.43	31.26	0.68	13.63
528	0.727	54.53	31.16	0.69	13.61
500	0.981	57.20	27.86	0.92	14.03
460	0.981	57.24	27.69	0.90	14.17
	1.235	53.24	32.19	0.63	13.95
ditions	1.235	53.09	32.68	0.60	13.64
747	1.235	53.23	32.33	0.60	13.84
102	1.387	49.45	34.47	0.67	15.40
2.596	1.387	48.63	34.67	0.68	16.02
625	1.387	48.15	35.98	0.70	15.17
0	1.387	49.87	32.83	0.68	16.62
	1.387	50.40	32.51	0.66	16.42
	1.387	50.43	32.49	0.66	16.42
m)	1.387	50.22	32.54	0.66	16.58
NA	1.387	49.55	33.29	0.66	16.51
NA	1.387	50.05	32.98	0.64	16.34
NA	1.387	49.84	33.20	0.64	16.31
NA	1.489	55.39	26.90	1.04	16.68
0.723	1.489	55.30	26.91	1.03	16.76
NA	1.641	52.63	30.48	0.82	16.07
	2.327	49.46	34.30	0.62	15.62
	2.327	49.57	34.22	0.59	15.62

FBMR Temperature (°C)		
0.01 m	407	
0.32 m	446	
0.52 m	461	
0.78 m	541	
1.08 m	515	
1.29 m	521	
1.59 m	525	
Bed Average	501	
2.26 m	458	

Time Averaged Conditions			
P (kPa abs)	495		
P _m (kPa abs)	29		
Feed CH ₄ (slpm)	2.596		
Feed Water (g/h)	625		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	1.645	
Permeate 6	NA	

Experiment: Methane 2.c				
Hoight (m)	Sample Gas Dry Composition			
fieight (iii)	H_2	CH ₄	СО	CO ₂
0.219	34.26	57.05	0.00	8.69
0.219	34.24	57.41	0.00	8.35
0.371	39.22	51.69	0.00	9.08
0.371	39.00	51.86	0.00	9.14
0.473	47.73	40.58	0.00	11.70
0.473	47.47	40.88	0.00	11.64
0.727	57.79	26.52	0.87	14.82
0.727	57.69	26.68	0.88	14.75
0.981	60.66	23.22	1.10	15.03
0.981	59.65	24.34	1.06	14.94
1.235	55.51	27.53	0.79	16.17
1.235	55.58	27.00	0.82	16.60
1.235	55.00	27.94	0.81	16.25
1.387	48.89	26.52	1.04	23.56
1.387	48.66	25.85	1.00	24.49
1.387	48.64	25.24	0.98	25.15
1.387	48.75	25.54	0.99	24.72
1.387	48.22	25.05	1.02	25.72
1.387	48.40	24.46	1.00	26.14
1.387	49.25	25.77	0.96	24.03
1.489	56.11	20.79	1.46	21.64
1.489	56.95	21.06	1.39	20.60
1.641	54.23	23.35	1.21	21.21
1.641	54.46	23.71	1.16	20.68
2.327	52.85	25.58	0.95	20.62
2.327	53.02	25.30	0.96	20.72
2.327	52.62	26.15	0.95	20.29

FBMR Temperature (°C)		
0.01 m	406	
0.32 m	449	
0.52 m	468	
0.78 m	542	
1.08 m	507	
1.29 m	518	
1.59 m	530	
Bed Average	502	
2.26 m	457	

Time Averaged Conditions			
P (kPa abs)	756		
P _m (kPa abs)	29		
Feed CH ₄ (slpm)	2.596		
Feed Water (g/h)	625		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	NA	
Permeate 6	NA	

Experiment: Methane 2.d				
Height (m) Sample Gas Dry Composition				
fileight (m)	H ₂	CH ₄	СО	CO ₂
0.219	33.64	58.35	0.00	8.01
0.371	37.75	53.23	0.00	9.02
0.473	43.61	45.91	0.00	10.49
0.727	54.63	31.09	0.73	13.56
0.981	57.62	27.28	0.96	14.15
1.235	51.90	32.76	0.64	14.70
1.235	51.99	32.85	0.63	14.53
1.387	44.72	30.16	0.80	24.33
1.387	44.48	29.96	0.80	24.77
1.387	44.65	29.86	0.78	24.72
1.387	43.77	30.88	0.82	24.53
1.387	44.29	29.97	0.79	24.94
1.387	44.65	30.12	0.82	24.41
1.489	52.22	24.90	1.30	21.58
1.489	52.66	24.50	1.26	21.58
1.641	48.85	27.03	1.14	22.98
1.641	49.23	28.13	1.03	21.62
2.327	47.63	30.34	0.77	21.27
2.327	47.50	30.42	0.75	21.32

FBMR Temperature (°C)		
0.01 m	418	
0.32 m	443	
0.52 m	467	
0.78 m	483	
1.08 m	508	
1.29 m	537	
1.59 m	554	
Bed Average	499	
2.26 m	442	

Time Averaged Conditions		
P (kPa abs)	410	
P _m (kPa abs)	NA	
Feed C_3H_8 (g/h)	93.6	
Feed Water (g/h)	688.9	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	NA	
Permeate 6	NA	

Experiment: Propane 1.a					
Stream Logation (m)	Sample Gas Dry Composition (%)				
Stream Location (III)	H ₂	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	50.10	26.54	0.37	20.63	2.74
0.219	53.71	21.79	0.25	22.01	2.49
0.371	52.59	23.94	0.37	20.93	1.55
0.371	53.50	23.36	0.38	20.73	1.02
0.473	47.82	32.49	0.39	19.68	0.00
0.473	51.54	26.83	0.27	21.04	0.00
0.473	49.90	29.47	0.37	20.03	0.00
0.473	49.35	30.48	0.39	19.52	0.00
0.473	50.87	28.95	0.39	19.41	0.00
0.727	53.08	25.39	0.27	21.01	0.00
0.727	53.59	26.22	0.29	20.19	0.00
0.981	57.77	20.89	0.37	21.34	0.00
0.981	58.88	19.66	0.29	21.46	0.00
1.235	62.29	16.28	0.50	21.43	0.00
1.235	61.96	16.79	0.37	21.25	0.00
1.489	67.43	11.18	0.38	21.38	0.00
1.489	66.69	11.24	0.28	22.06	0.00
1.641	63.49	14.29	0.29	21.94	0.00
1.641	64.58	13.54	0.80	21.88	0.00
2.327	59.62	18.83	0.50	21.55	0.00
2.327	59.58	18.12	0.37	22.30	0.00
2.327	59.28	18.59	0.28	22.13	0.00
2.327	59.45	18.94	0.45	21.61	0.00

FBMR Temperature (°C)		
0.01 m	403	
0.32 m	439	
0.52 m	469	
0.78 m	485	
1.08 m	507	
1.29 m	546	
1.59 m	560	
Bed Average	501	
2.26 m	462	

Time Averaged Conditions		
P (kPa abs)	598	
P _m (kPa abs)	NA	
Feed C_3H_8 (g/h)	93.6	
Feed Water (g/h)	688.9	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	NA	
Permeate 6	NA	

Experiment: Propane 1.b					
Stream Location (m)	Sample Gas Dry Composition (%)				
	H ₂	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	51.96	25.94	0.37	22.10	0.00
0.219	48.02	30.18	0.25	21.78	0.02
0.371	47.51	31.16	0.37	21.27	0.06
0.371	48.57	30.74	0.38	20.69	0.00
0.473	45.39	34.66	0.39	19.85	0.00
0.473	45.32	34.51	0.27	20.10	0.00
0.473	45.49	34.64	0.37	19.87	0.00
0.473	45.74	33.94	0.39	20.29	0.00
0.473	48.93	30.99	0.39	20.03	0.00
0.727	48.71	30.36	0.27	20.84	0.00
0.727	49.69	29.35	0.29	20.54	0.00
0.981	54.90	23.32	0.37	21.69	0.00
0.981	55.51	23.03	0.29	21.34	0.00
1.235	58.31	19.88	0.50	21.66	0.00
1.235	59.03	19.11	0.37	21.80	0.00
1.489	63.90	14.46	0.38	21.54	0.00
1.489	64.24	13.95	0.28	21.69	0.00
1.641	61.32	17.25	0.37	21.37	0.00
1.641	61.71	16.31	0.80	21.90	0.00
2.327	55.02	23.49	0.50	21.46	0.00
2.327	55.42	22.96	0.37	21.60	0.00
2.327	55.56	23.11	0.28	21.27	0.00
2.327	55.22	23.24	0.45	21.51	0.00

FBMR Temperature (°C)		
0.01 m	386	
0.32 m	436	
0.52 m	464	
0.78 m	484	
1.08 m	505	
1.29 m	548	
1.59 m	562	
Bed Average	500	
2.26 m	467	

Time Averaged Conditions			
P (kPa abs)	703		
P _m (kPa abs)	NA		
Feed C_3H_8 (g/h)	93.6		
Feed Water (g/h)	688.9		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	NA	
Permeate 6	NA	

Experiment: Propane 1.c					
Stream Location (m)	Sample Gas Dry Composition (%)				
	H ₂	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	50.75	27.59	0.37	21.41	0.25
0.219	59.72	16.62	0.25	22.58	1.08
0.371	49.40	29.55	0.37	20.82	0.22
0.371	51.59	27.08	0.38	21.18	0.16
0.473	46.67	32.85	0.39	20.37	0.00
0.473	47.04	32.07	0.27	20.72	0.00
0.473	44.05	36.25	0.37	19.44	0.00
0.473	43.97	35.62	0.39	20.16	0.00
0.727	45.12	35.43	0.39	19.46	0.00
0.727	49.21	29.48	0.27	21.22	0.00
0.981	53.38	25.46	0.29	20.89	0.00
0.981	56.80	21.33	0.37	21.63	0.00
1.235	58.13	20.30	0.29	21.30	0.00
1.235	59.04	19.89	0.50	20.94	0.00
1.489	63.75	14.15	0.37	21.84	0.00
1.489	64.81	13.07	0.38	21.89	0.00
1.641	60.71	16.92	0.28	22.16	0.00
1.641	62.55	16.16	0.37	21.20	0.00
2.327	56.43	22.07	0.80	21.41	0.00
2.327	56.30	21.81	0.50	21.80	0.00
2.327	56.95	21.16	0.37	21.67	0.00
2.327	56.56	23.32	0.28	20.12	0.00

FBMR Temperature (°C)		
0.01 m	410	
0.32 m	453	
0.52 m	462	
0.78 m	490	
1.08 m	492	
1.29 m	502	
1.59 m	504	
Bed Average	484	
2.26 m	443	

Time Averaged Conditions			
P (kPa abs)	518		
$P_{\rm m}$ (kPa abs)	101		
Feed C ₃ H ₈ (g/h)	118.3		
Feed Water (g/h)	725.8		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	0.015	
Permeate 6	NA	

Experiment: Propane 2.a					
Stucen I costion (m)	Sample Gas Dry Composition (%)				
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	46.74	27.46	0.14	18.67	6.99
0.219	42.30	31.21	0.12	17.98	8.38
0.219	39.66	33.56	0.12	17.54	9.12
0.219	42.12	30.68	0.14	18.34	8.72
0.371	50.82	13.15	0.22	18.96	3.40
0.371	50.68	12.49	0.24	18.32	2.10
0.371	50.95	12.84	0.21	18.52	2.10
0.625	50.26	19.46	0.49	22.14	0.00
0.625	48.89	21.52	0.46	22.07	0.00
0.625	47.44	22.93	0.49	21.45	0.00
0.727	46.59	31.74	1.04	20.63	0.00
0.727	53.83	23.33	0.91	21.92	0.00
0.727	49.30	28.03	0.97	21.70	0.00
0.981	47.20	32.63	0.84	19.12	0.00
0.981	44.16	36.49	0.86	18.23	0.00
0.981	51.97	26.89	0.80	20.33	0.00
1.133	56.14	22.29	0.82	20.75	0.00
1.133	44.44	35.13	1.03	19.26	0.00
1.133	54.44	23.93	0.88	20.68	0.00
1.235	54.90	23.62	0.93	20.54	0.00
1.235	52.62	26.03	1.01	20.34	0.00
1.235	53.43	24.70	1.01	20.86	0.00
1.235	52.37	25.92	0.99	20.72	0.00
1.235	52.46	26.00	0.99	20.49	0.00
1.235	48.34	30.70	1.06	19.90	0.00
1.235	55.02	22.91	1.05	21.02	0.00
1.235	51.73	26.36	1.11	20.80	0.00
1.387	54.18	23.74	1.11	20.96	0.00
1.387	51.79	26.73	1.30	20.18	0.00
1.387	53.29	24.64	1.28	20.79	0.00
1.387	52.87	25.27	1.22	20.64	0.00
1.489	47.22	33.08	0.99	18.71	0.00
1.489	53.96	24.35	0.97	20.71	0.00
1.489	52.80	26.07	0.93	20.20	0.00
1.641	49.40	28.76	0.84	21.00	0.00
1.641	49.24	29.28	0.89	20.59	0.00
1.641	49.30	28.83	0.87	21.00	0.00
2.327	45.50	35.03	0.77	18.70	0.00
2.327	50.59	28.32	0.73	20.35	0.00
2.327	50.16	27.86	0.80	21.18	0.00

FBMR Temperature (°C)		
0.01 m	414	
0.32 m	453	
0.52 m	464	
0.78 m	494	
1.08 m	496	
1.29 m	505	
1.59 m	509	
Bed Average	487	
2.26 m	446	

Time Averaged Conditions			
P (kPa abs)	515		
P _m (kPa abs)	29		
Feed C ₃ H ₈ (g/h)	118.3		
Feed Water (g/h)	725.8		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	1.377	
Permeate 6	NA	

Experiment: Propane 2.b					
Stream Logation (m)	Stream Location (m) Sample Gas Dry Composition (%)				ion (%)
Stream Location (m)	H_2	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	41.78	31.76	0.11	19.67	6.68
0.219	41.06	32.50	0.12	20.46	5.85
0.219	39.01	34.41	0.10	19.52	6.96
0.473	38.40	36.61	0.15	21.35	3.49
0.473	39.01	36.34	0.15	22.22	2.28
0.473	37.73	38.10	0.15	21.51	2.51
0.727	52.57	27.52	0.75	18.90	0.26
0.727	46.60	31.53	0.92	20.95	0.00
0.727	48.93	28.03	0.94	22.09	0.00
0.727	46.16	32.24	0.89	20.71	0.00
1.133	53.87	24.96	0.82	20.26	0.09
1.133	56.14	21.50	0.83	21.52	0.00
1.133	51.80	26.13	0.91	21.17	0.00
1.235	52.66	23.59	1.10	22.64	0.00
1.235	52.47	23.62	1.12	22.79	0.00
1.235	51.73	25.13	1.13	22.01	0.00
1.235	52.23	24.50	1.14	22.13	0.00
1.387	49.78	20.32	1.58	28.32	0.00
1.387	49.00	21.16	1.57	28.27	0.00
1.387	46.83	24.46	1.63	27.09	0.00
1.387	51.04	17.05	1.54	30.37	0.00
1.387	53.25	16.18	1.33	29.24	0.00
1.387	52.06	19.97	1.33	26.63	0.00
1.489	49.41	25.20	1.29	24.10	0.00
1.489	49.73	25.44	1.26	23.56	0.00
1.489	52.71	20.47	1.28	25.54	0.00
1.641	46.87	27.83	0.94	24.36	0.00
1.641	47.04	27.12	0.93	24.90	0.00
1.641	46.95	27.29	0.97	24.79	0.00
2.327	53.34	14.88	1.37	30.41	0.00
2.327	52.52	17.24	1.33	28.91	0.01
2.327	51.88	19.21	1.34	27.57	0.00

FBMR Temperature (°C)		
0.01 m	414	
0.32 m	448	
0.52 m	459	
0.78 m	494	
1.08 m	494	
1.29 m	505	
1.59 m	509	
Bed Average	485	
2.26 m	456	

Time Averaged Conditions			
P (kPa abs)	706		
P _m (kPa abs)	101		
Feed C ₃ H ₈ (g/h)	118.3		
Feed Water (g/h)	725.8		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	0.273	
Permeate 6	NA	

Experiment: Propane 2.c					
Stream Location (m)	cation (m) Sample Gas Dry Composition (%)				
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	36.35	35.82	0.00	17.17	6.66
0.219	39.83	33.41	0.00	19.14	7.62
0.219	36.34	33.79	0.12	17.73	5.50
0.371	47.20	18.67	0.21	19.72	2.10
0.371	48.54	15.42	0.21	17.85	1.00
0.371	45.35	17.90	0.21	17.38	0.56
0.625	46.60	26.77	0.29	21.27	0.00
0.625	44.57	28.01	0.29	20.33	0.00
0.625	44.30	28.89	0.27	21.19	0.00
0.727	46.68	32.35	0.70	20.24	0.00
0.727	49.42	29.44	0.68	20.41	0.00
0.727	48.77	29.04	0.73	21.41	0.00
0.981	45.47	34.09	0.86	19.51	0.00
0.981	49.36	30.37	0.80	19.38	0.00
0.981	44.60	35.37	0.81	19.10	0.00
1.133	48.86	30.20	0.76	20.16	0.00
1.133	49.21	27.77	0.82	22.18	0.01
1.133	47.95	32.05	0.81	19.18	0.00
1.235	54.02	25.01	0.84	20.11	0.00
1.235	50.15	28.52	0.86	20.42	0.00
1.235	47.91	31.27	0.93	19.84	0.00
1.235	51.46	26.74	0.94	20.84	0.00
1.235	52.17	26.64	0.92	20.26	0.00
1.235	48.11	30.73	0.98	20.17	0.00
1.235	52.72	25.57	0.91	20.75	0.00
1.235	50.12	28.28	0.91	20.63	0.00
1.235	49.75	30.04	0.89	19.30	0.00
1.387	53.02	24.15	1.00	21.71	0.00
1.387	50.45	28.07	1.01	20.38	0.00
1.387	49.08	27.09	1.12	22.62	0.00
1.489	46.98	32.11	0.97	19.88	0.00
1.489	51.30	27.04	0.93	20.67	0.00
1.489	49.17	28.34	0.96	21.37	0.00
1.641	46.21	31.05	0.75	21.96	0.00
1.641	45.58	31.99	0.75	21.64	0.00
1.641	47.48	31.21	0.69	20.59	0.00
2.327	47.45	29.79	0.62	22.01	0.00
2.327	45.34	33.06	0.61	20.98	0.00
2.327	45.96	32.21	0.58	21.23	0.00

FBMR Temperature (°C)		
0.01 m	415	
0.32 m	449	
0.52 m	460	
0.78 m	496	
1.08 m	496	
1.29 m	505	
1.59 m	510	
Bed Average	486	
2.26 m	455	

Time Averaged Conditions		
P (kPa abs)	698	
P_{m} (kPa abs)	28	
Feed C_3H_8 (g/h)	118.3	
Feed Water (g/h)	725.8	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	1.600	
Permeate 6	NA	

Experiment: Propane 2.d					
Stream Location (m)	m) Sample Gas Dry Composition (%)				
Stream Location (m)	H_2	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	40.60	32.55	0.00	18.75	8.09
0.219	39.18	33.88	0.00	19.17	7.76
0.219	38.36	34.59	0.00	18.99	8.06
0.473	36.50	40.05	0.12	20.40	0.05
0.473	37.62	39.05	0.00	20.89	0.02
0.473	36.58	42.40	0.00	21.01	0.01
0.727	51.30	26.74	0.70	21.24	0.00
0.727	50.90	27.30	0.70	20.98	0.00
0.727	51.28	26.51	0.71	21.34	0.00
1.133	49.60	28.75	0.77	20.86	0.00
1.133	48.30	30.74	0.74	20.22	0.00
1.133	49.44	29.31	0.77	20.49	0.00
1.235	49.26	28.29	0.83	21.43	0.18
1.235	49.76	27.22	0.91	22.03	0.00
1.235	48.46	29.67	0.91	20.87	0.00
1.387	48.81	22.48	1.26	27.40	0.00
1.387	43.74	26.89	1.31	27.98	0.00
1.387	46.10	25.15	1.25	27.37	0.00
1.387	43.73	26.20	1.33	28.64	0.00
1.387	49.69	18.51	1.23	30.51	0.00
1.387	50.50	18.00	1.27	30.11	0.00
1.489	48.67	26.13	0.98	24.13	0.00
1.489	48.21	26.54	1.04	24.11	0.00
1.489	46.30	29.56	1.04	23.00	0.00
1.641	47.88	24.47	0.83	26.73	0.00
1.641	46.56	25.40	0.85	27.17	0.00
1.641	46.76	26.56	0.83	25.80	0.00
2.327	43.35	28.26	0.79	27.59	0.01
2.327	42.49	30.71	0.79	26.00	0.01
2.327	41.99	30.86	0.75	26.39	0.01

FBMR Temperature (°C)		
0.01 m	438	
0.32 m	483	
0.52 m	472	
0.78 m	515	
1.08 m	494	
1.29 m	506	
1.59 m	531	
Bed Average	500	
2.26 m	480	

Time Averaged Conditions			
P (kPa abs)	610		
P _m (kPa abs)	101		
Feed C_3H_8 (g/h)	101.4		
Feed Water (g/h)	622.1		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	0.036	
Permeate 2	0.026	
Permeate 3	0.088	
Permeate 4	0.019	
Permeate 5	0.110	
Permeate 6	0.237	

Experiment: Propane 3.a					
Stream Location (m)	Sample Gas Dry Composition (%)			ion (%)	
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	42.19	37.42	0.42	19.93	0.04
0.219	39.05	42.58	0.35	18.02	0.00
0.219	42.87	36.32	0.36	20.43	0.01
0.371	50.14	28.80	0.58	20.47	0.00
0.371	44.42	35.84	0.63	19.10	0.00
0.371	50.18	27.84	0.65	21.32	0.00
0.473	36.29	43.94	0.30	19.38	0.07
0.473	43.14	36.65	0.29	19.84	0.02
0.625	42.24	37.35	0.42	19.94	0.05
0.625	39.20	42.45	0.42	17.92	0.01
0.625	42.13	37.42	0.44	19.97	0.04
0.727	46.91	31.79	0.76	20.53	0.02
0.727	45.33	34.34	0.79	19.53	0.02
0.727	45.40	33.85	0.80	19.92	0.03
0.879	43.99	34.53	0.68	20.76	0.05
0.879	45.02	33.25	0.68	20.98	0.06
0.981	43.99	35.71	0.64	19.64	0.01
0.981	45.71	33.00	0.64	20.63	0.01
0.981	43.18	36.94	0.64	19.23	0.01
1.133	47.39	31.05	0.76	20.80	0.00
1.133	47.21	31.35	0.74	20.70	0.00
1.133	46.31	32.15	0.75	20.79	0.00
1.133	46.96	31.64	0.75	20.65	0.00
1.235	47.21	30.65	0.71	21.40	0.03
1.235	47.23	31.17	0.69	20.89	0.02
1.235	46.61	31.66	0.71	21.01	0.01
1.387	45.70	33.28	0.79	20.21	0.02
1.387	47.42	30.50	0.79	21.27	0.01
1.489	49.99	27.40	1.10	21.46	0.05
1.489	50.17	26.94	1.11	21.71	0.08
1.489	50.51	27.05	1.08	21.36	0.00
1.489	50.55	27.23	1.12	21.02	0.07
1.489	50.62	26.69	1.10	21.55	0.05
1.489	49.43	27.42	1.17	21.94	0.04
1.489	49.75	26.56	1.19	22.44	0.06
1.641	49.92	27.24	1.15	21.68	0.00
1.641	48.86	28.34	1.18	21.62	0.00
2.327	49.08	27.49	1.12	22.32	0.00
2.327	49.90	26.37	1.13	22.59	0.00
2.327	49.25	26.68	1.13	22.94	0.00

FBMR Temperature (°C)		
0.01 m	443	
0.32 m	475	
0.52 m	464	
0.78 m	520	
1.08 m	502	
1.29 m	513	
1.59 m	539	
Bed Average	502	
2.26 m	484	

Time Averaged Conditions			
P (kPa abs)	609		
P _m (kPa abs)	48		
Feed C ₃ H ₈ (g/h)	101.4		
Feed Water (g/h)	622.1		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	0.993	
Permeate 2	0.942	
Permeate 3	0.459	
Permeate 4	0.238	
Permeate 5	0.585	
Permeate 6	0.928	

Experiment: Propane 3.b					
Stream Location (m)	Stream Location (m) Sample Gas Dry Composition (%)				ion (%)
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	38.98	39.01	0.36	21.66	0.00
0.219	40.30	37.29	0.34	22.05	0.01
0.219	40.12	38.11	0.35	21.41	0.01
0.219	41.33	35.29	0.36	23.01	0.02
0.371	47.82	24.68	0.65	25.55	0.05
0.371	40.32	34.10	0.66	23.42	0.01
0.371	49.87	22.13	0.61	25.63	0.04
0.473	33.25	41.99	0.31	24.00	0.06
0.473	37.04	39.03	0.32	23.60	0.01
0.473	38.66	36.98	0.38	23.98	0.00
0.625	39.89	32.80	0.51	26.78	0.01
0.625	39.21	32.49	0.56	27.71	0.02
0.625	35.79	38.62	0.57	25.01	0.01
0.727	42.49	23.83	1.09	32.54	0.05
0.727	39.04	28.53	1.12	31.30	0.01
0.879	38.56	23.21	1.04	37.17	0.02
0.879	37.54	23.13	1.11	38.17	0.05
0.981	39.86	24.24	1.07	34.83	0.00
0.981	40.12	22.09	1.07	36.72	0.01
1.133	37.78	18.51	1.37	42.34	0.00
1.133	37.44	16.74	1.42	44.40	0.00
1.235	40.89	24.47	1.18	33.44	0.01
1.235	41.39	22.15	1.17	35.29	0.01
1.387	39.33	21.67	1.36	37.64	0.01
1.387	39.59	20.92	1.28	38.21	0.00
1.489	41.66	15.29	1.78	41.26	0.01
1.489	40.24	16.80	1.83	41.11	0.02
1.489	41.04	15.83	1.82	41.27	0.03
1.489	40.43	16.95	1.70	40.88	0.03
1.489	41.20	16.48	1.70	40.58	0.04
1.641	39.53	20.32	1.58	38.57	0.00
1.641	38.57	21.26	1.63	38.55	0.00
2.327	42.03	17.33	1.66	38.98	0.00
2.327	41.01	18.13	1.65	39.20	0.00
2.327	41.50	17.56	1.65	39.28	0.00

FBMR Temperature (°C)			
0.01 m	443		
0.32 m	469		
0.52 m	451		
0.78 m	517		
1.08 m	499		
1.29 m	510		
1.59 m	540		
Bed Average	498		
2.26 m	486		

Time Averaged Conditions			
P (kPa abs)	605		
P_{m} (kPa abs)	25		
Feed C_3H_8 (g/h)	101.4		
Feed Water (g/h)	622.1		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.511	
Permeate 2	1.280	
Permeate 3	0.633	
Permeate 4	0.321	
Permeate 5	0.763	
Permeate 6	1.108	

Experiment: Propane 3.c					
Stream Leastion (m)	Stream Location (m) Sample Gas Dry Composition (%)				ion (%)
Stream Location (m)	H_2	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	36.21	39.69	0.33	23.75	0.02
0.219	35.95	40.47	0.35	23.22	0.01
0.219	39.70	36.43	0.32	23.54	0.01
0.371	40.19	29.18	0.45	27.32	0.05
0.371	39.70	29.56	0.48	27.43	0.04
0.371	36.31	34.36	0.43	26.17	0.01
0.473	32.89	37.30	0.30	29.48	0.03
0.473	32.45	38.58	0.31	28.65	0.02
0.473	33.99	36.07	0.32	29.60	0.01
0.625	37.04	30.92	0.49	31.48	0.07
0.625	33.78	35.47	0.50	30.23	0.03
0.625	33.96	36.01	0.48	29.53	0.02
0.727	36.68	23.53	1.19	38.54	0.01
0.727	37.01	21.03	1.22	40.64	0.02
0.879	34.57	15.50	1.13	48.75	0.05
0.879	32.77	18.05	1.19	47.98	0.02
0.981	35.43	18.76	1.12	44.67	0.02
0.981	34.02	21.08	1.19	43.71	0.00
1.133	31.07	12.30	1.33	55.30	0.00
1.133	30.96	12.80	1.41	54.83	0.00
1.235	37.43	19.76	1.25	41.54	0.02
1.235	37.20	20.40	1.23	41.10	0.03
1.387	35.99	16.06	1.33	46.59	0.03
1.387	34.90	16.56	1.36	47.15	0.02
1.489	36.33	11.63	1.90	50.13	0.01
1.489	35.97	10.88	1.86	51.28	0.01
1.489	35.39	11.23	1.81	51.55	0.01
1.489	36.22	13.96	1.76	48.02	0.04
1.489	36.39	13.36	1.90	48.33	0.02
1.641	31.52	16.05	1.51	50.92	0.00
1.641	31.50	17.33	1.58	49.59	0.00
2.327	36.54	12.00	1.73	49.72	0.00
2.327	36.77	12.60	1.78	48.84	0.00
2.327	35.94	13.14	1.82	49.11	0.00

FBMR Temperature (°C)		
0.01 m	402	
0.32 m	480	
0.52 m	460	
0.78 m	515	
1.08 m	490	
1.29 m	499	
1.59 m	544	
Bed Average	498	
2.26 m	458	

Time Averaged Conditions			
P (kPa abs)	406		
P _m (kPa abs)	25		
Feed C_3H_8 (g/h)	67.6		
Feed Water (g/h)	414.8		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.034	
Permeate 2	1.097	
Permeate 3	0.435	
Permeate 4	0.266	
Permeate 5	0.488	
Permeate 6	0.689	

Experiment: Propane 4.a					
Stream Location (m)	Sample Gas Dry Composition (%)				
Stream Location (m)	H_2	CH ₄	СО	CO ₂	C ₃ H ₈
0.219	40.91	22.94	0.69	35.36	0.09
0.219	38.99	25.85	0.69	34.45	0.02
0.219	39.08	25.19	0.70	35.04	0.00
0.371	41.14	20.60	0.83	36.31	0.22
0.371	36.38	17.62	0.85	44.85	0.08
0.371	36.69	18.32	0.86	43.75	0.05
0.473	41.48	31.27	0.38	26.53	0.05
0.473	40.51	32.41	0.39	26.28	0.12
0.473	41.74	30.59	0.38	26.74	0.03
0.625	38.83	26.90	0.64	33.48	0.00
0.625	38.85	27.35	0.66	33.05	0.00
0.727	40.62	16.06	1.19	42.13	0.00
0.727	40.15	16.87	1.27	41.71	0.00
0.727	39.92	15.49	1.25	43.34	0.00
0.879	34.71	11.04	1.21	53.05	0.00
0.879	34.30	11.67	1.25	52.78	0.00
0.981	37.29	17.94	1.05	43.72	0.00
0.981	37.95	18.33	1.03	42.70	0.00
0.981	38.11	17.30	1.00	43.59	0.00
1.133	34.90	12.14	1.28	51.68	0.00
1.133	35.15	11.36	1.27	52.16	0.06
1.235	38.85	15.64	1.23	44.27	0.00
1.235	39.83	15.20	1.15	43.80	0.03
1.235	39.15	15.02	1.18	44.65	0.00
1.387	38.23	13.37	1.39	47.01	0.00
1.387	38.74	13.81	1.35	46.10	0.00
1.489	37.51	9.69	1.84	50.97	0.00
1.489	37.22	9.33	1.88	51.54	0.02
1.489	37.34	8.68	1.81	52.17	0.00
1.489	37.91	9.13	1.83	51.13	0.00
1.489	37.97	9.12	1.85	51.06	0.00
1.489	37.40	8.88	1.84	51.88	0.00
1.641	33.79	12.67	1.77	51.77	0.00
1.641	34.52	13.56	1.76	50.16	0.00
2.327	37.39	9.00	1.78	51.83	0.00
2.327	38.11	8.84	1.77	51.28	0.00
2.327	38.91	8.48	1.73	50.88	0.00
2.327	38.23	8.25	1.72	51.80	0.00

FBMR Temperature (°C)		
0.01 m	413	
0.32 m	472	
0.52 m	460	
0.78 m	509	
1.08 m	503	
1.29 m	509	
1.59 m	544	
Bed Average	500	
2.26 m	491	

Time Averaged Conditions			
P (kPa abs)	802		
P _m (kPa abs)	25		
Feed C ₃ H ₈ (g/h)	135.2		
Feed Water (g/h)	829.5		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.668	
Permeate 2	1.661	
Permeate 3	0.793	
Permeate 4	0.625	
Permeate 5	0.977	
Permeate 6	1.519	

Experiment: Propane 4.b					
Stream Logation (m)	Stream Location (m) Sample Gas Dry Composition (%)				ion (%)
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	30.39	36.13	0.47	31.60	1.41
0.219	31.22	35.06	0.48	32.30	0.94
0.371	31.93	30.05	0.58	36.28	0.95
0.371	34.11	27.84	0.62	37.25	0.17
0.473	30.65	34.63	0.45	31.62	0.12
0.473	29.74	38.31	0.36	29.34	0.03
0.473	31.52	36.25	0.37	30.48	0.00
0.625	34.69	32.93	0.46	30.49	0.00
0.625	34.23	33.95	0.46	30.08	0.00
0.727	34.55	30.05	0.96	33.16	0.30
0.727	36.55	26.00	0.94	36.22	0.00
0.879	30.96	19.66	1.00	46.36	0.00
0.879	30.07	21.45	1.07	47.21	0.00
0.981	35.88	25.54	0.95	35.77	0.00
0.981	36.14	25.05	0.96	36.23	0.00
1.133	30.99	18.90	1.30	47.63	0.00
1.133	31.26	17.87	1.31	48.61	0.95
1.235	35.63	24.41	1.08	38.65	0.23
1.235	35.14	22.51	1.11	40.25	1.00
1.387	34.41	20.00	1.21	43.31	0.00
1.387	33.13	21.03	1.27	43.68	0.88
1.489	32.62	18.72	1.38	45.83	0.00
1.489	32.84	18.20	1.42	46.09	0.00
1.489	32.40	17.88	1.39	46.93	0.00
1.489	32.71	17.84	1.53	46.62	0.00
1.489	33.14	17.39	1.48	46.86	1.13
1.641	30.99	20.70	1.52	45.82	0.00
1.641	31.37	21.35	1.53	45.46	0.28
2.327	35.99	17.53	1.62	44.81	0.05
2.327	36.40	16.44	1.64	45.32	0.20
2.327	35.27	16.62	1.66	46.10	0.05

FBMR Temperature (°C)		
0.01 m	419	
0.32 m	473	
0.52 m	457	
0.78 m	510	
1.08 m	501	
1.29 m	509	
1.59 m	544	
Bed Average	499	
2.26 m	490	

Time Averaged Conditions			
P (kPa abs)	603		
P _m (kPa abs)	25		
Feed C ₃ H ₈ (g/h)	124.78		
Feed Water (g/h)	612.58		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.522	
Permeate 2	1.415	
Permeate 3	0.649	
Permeate 4	0.481	
Permeate 5	0.828	
Permeate 6	1.314	

Experiment: Propane 5.a					
Stream Leastion (m)	Sample Gas Dry Composition (%)				ion (%)
Stream Location (m)	H_2	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	28.56	36.52	0.52	29.80	0.28
0.219	29.73	32.13	0.54	31.89	0.24
0.219	26.45	39.31	0.57	29.39	0.14
0.371	35.32	30.70	0.67	25.51	0.13
0.371	42.03	24.77	0.64	25.36	0.14
0.371	37.55	25.32	0.58	27.89	0.01
0.371	35.38	28.86	0.57	27.51	0.05
0.473	28.58	45.87	0.32	23.94	0.00
0.473	35.68	37.30	0.30	24.66	0.00
0.473	29.60	45.29	0.34	23.40	0.00
0.473	32.25	41.43	0.33	24.35	0.00
0.625	31.55	35.73	0.50	28.34	0.00
0.625	33.56	33.68	0.48	28.00	0.00
0.625	30.03	38.55	0.52	27.87	0.00
0.727	30.03	30.04	1.10	32.79	0.00
0.727	33.13	27.12	1.01	32.58	0.00
0.727	31.23	28.91	1.07	32.41	0.00
0.879	26.01	23.57	1.11	39.43	0.00
0.879	28.94	19.90	1.05	40.14	0.00
0.879	26.80	25.45	1.14	37.57	0.00
0.981	29.43	27.99	1.07	34.72	0.00
0.981	29.37	28.99	1.05	34.32	0.00
1.133	25.79	21.25	1.40	41.82	0.00
1.133	28.25	16.74	1.26	42.31	0.00
1.235	30.54	24.49	1.28	35.48	0.00
1.235	31.93	22.59	1.21	36.23	0.00
1.387	28.49	22.60	1.40	38.29	0.00
1.387	30.11	18.62	1.32	39.29	0.00
1.387	28.89	21.99	1.33	38.29	0.00
1.489	28.09	17.14	1.70	42.17	0.00
1.489	28.20	16.17	1.70	42.96	0.00
1.489	28.31	15.51	1.65	43.21	0.19
1.489	28.37	16.36	1.67	43.08	0.17
1.489	28.43	18.03	1.68	41.92	0.00
1.489	28.77	15.95	1.77	42.47	0.00
1.489	28.98	14.22	1.69	44.18	0.10
1.641	27.50	19.19	1.69	41.56	0.00
1.641	27.40	21.01	1.77	39.98	0.00
1.641	27.54	17.70	1.72	42.14	0.00
2.327	30.02	15.57	1.93	41.95	0.00
2.327	31.39	14.33	1.89	40.66	0.00
2.327	31.14	15.58	1.92	41.05	0.00

FBMR Temperature (°C)			
0.01 m	416		
0.32 m	473		
0.52 m	455		
0.78 m	509		
1.08 m	499		
1.29 m	506		
1.59 m	543		
Bed Average	498		
2.26 m	478		

Time Averaged Conditions			
P (kPa abs)	605		
P _m (kPa abs)	25		
Feed C_3H_8 (g/h)	85.38		
Feed Water (g/h)	628.7		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.349	
Permeate 2	1.263	
Permeate 3	0.553	
Permeate 4	0.421	
Permeate 5	0.631	
Permeate 6	0.975	

Experiment: Propane 5.b					
Stream Logation (m)	Stream Location (m) Sample Gas Dry Composition (%)				ion (%)
Stream Location (m)	H_2	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	37.61	24.79	0.51	30.96	0.02
0.219	36.98	27.90	0.51	30.01	0.05
0.219	38.01	25.22	0.53	30.79	0.08
0.219	38.19	24.65	0.51	31.51	0.10
0.371	36.71	19.28	0.61	35.02	0.05
0.371	38.06	18.80	0.58	34.68	0.10
0.473	35.32	36.62	0.31	25.68	0.00
0.473	39.55	28.78	0.33	27.88	0.00
0.625	35.70	27.29	0.51	30.74	0.00
0.625	34.51	30.05	0.47	30.54	0.00
0.727	34.96	17.95	1.02	36.85	0.00
0.727	36.02	15.09	0.98	38.86	0.11
0.879	31.54	13.73	0.95	42.71	0.00
0.879	32.07	12.81	0.94	42.37	0.00
0.981	37.92	16.93	0.99	35.88	0.16
0.981	38.18	16.83	0.97	36.36	0.00
1.133	35.17	12.62	1.10	40.66	0.04
1.133	35.51	11.35	1.06	41.19	0.02
1.235	35.92	14.10	1.06	39.40	0.10
1.235	35.55	13.92	1.06	39.85	0.11
1.387	33.08	11.81	1.16	43.09	0.14
1.387	33.25	11.97	1.13	43.00	0.02
1.489	32.61	8.03	1.40	45.28	0.06
1.489	32.34	7.72	1.43	45.43	0.11
1.489	32.26	7.80	1.44	46.36	0.07
1.489	32.68	7.78	1.44	44.75	0.08
1.489	32.96	8.10	1.48	45.51	0.00
1.641	29.67	10.99	1.30	46.25	0.00
1.641	30.40	10.25	1.30	45.38	0.00
2.327	33.31	7.65	1.48	44.97	0.00
2.327	32.94	7.84	1.43	45.67	0.00
2.327	33.43	7.39	1.38	44.59	0.00

FBMR Temperature (°C)		
0.01 m	409	
0.32 m	460	
0.52 m	445	
0.78 m	487	
1.08 m	477	
1.29 m	480	
1.59 m	508	
Bed Average	476	
2.26 m	475	

Time Averaged Conditions			
P (kPa abs)	601		
P _m (kPa abs)	25		
Feed C_3H_8 (g/h)	104.78		
Feed Water (g/h)	642.94		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)			
Permeate 1	1.176		
Permeate 2	1.374		
Permeate 3	0.530		
Permeate 4	0.412		
Permeate 5	0.626		
Permeate 6	0.981		

Experiment: Propane 6.a					
Stream Location (m)	Sample Gas Dry Composition (%)				
Stream Location (m)	H_2	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	31.03	31.78	0.39	31.38	0.03
0.219	29.17	35.26	0.37	30.12	0.01
0.219	29.62	34.41	0.39	30.51	0.03
0.371	30.99	26.36	0.53	34.23	0.18
0.371	32.99	19.79	0.50	37.98	0.00
0.371	28.72	30.64	0.57	33.59	0.02
0.473	37.11	32.72	0.28	25.04	0.04
0.473	36.08	33.17	0.23	25.35	0.03
0.473	35.71	32.71	0.26	26.31	0.05
0.625	35.60	32.44	0.36	27.32	0.01
0.625	35.99	33.10	0.33	26.82	0.01
0.625	39.78	24.98	0.35	29.89	0.01
0.727	32.76	25.04	0.76	34.43	0.05
0.727	32.08	25.48	0.78	34.29	0.02
0.879	29.35	22.72	0.73	38.21	0.11
0.879	29.44	21.75	0.73	38.62	0.10
0.981	33.39	24.72	0.63	34.15	0.11
0.981	33.54	24.85	0.63	33.66	0.07
1.133	32.07	24.14	0.77	36.14	0.02
1.133	31.64	22.75	0.80	36.35	0.02
1.235	31.55	24.34	0.75	36.10	0.03
1.235	31.17	25.04	0.74	35.55	0.05
1.235	31.40	23.69	0.78	36.28	0.04
1.387	30.61	21.31	0.75	37.82	0.11
1.387	32.30	17.49	0.73	39.17	0.05
1.387	31.57	20.35	0.75	38.67	0.00
1.387	30.89	19.84	0.75	38.47	0.05
1.489	30.51	17.42	0.81	40.10	0.04
1.489	30.09	17.79	0.80	40.09	0.13
1.489	31.35	16.41	0.74	41.15	0.09
1.489	31.38	15.93	0.74	40.67	0.00
1.489	29.57	17.09	0.80	41.44	0.08
1.489	30.03	17.24	0.84	41.54	0.07
1.489	30.14	17.91	0.94	40.99	0.07
1.489	31.19	14.27	0.90	42.26	0.06
1.489	30.36	1/.10	0.96	41.27	0.10
1.641	29.37	19.54	0.87	40.56	0.00
1.641	27.92	23.06	0.89	38.96	0.00
2.327	30.31	11.44	1.55	40.11	0.00
2.327	37.00	10.5/	1.33	39.77	0.00
2.327	35.90	12.93	1.40	40.27	0.00
2.327	24.04	13.4/	1.44	29.99	0.00
2.327	34.94	14.04	1.44	38.03	0.00

FBMR Temperature (°C)		
0.01 m	417	
0.32 m	498	
0.52 m	479	
0.78 m	532	
1.08 m	523	
1.29 m	533	
1.59 m	579	
Bed Average	524	
2.26 m	485	

Time Averaged Conditions			
P (kPa abs)	600		
P _m (kPa abs)	25		
Feed C ₃ H ₈ (g/h)	98.21		
Feed Water (g/h)	602.66		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.418	
Permeate 2	1.693	
Permeate 3	0.723	
Permeate 4	0.585	
Permeate 5	0.779	
Permeate 6	1.223	

Experiment: Propane 6.b					
Stream Location (m)	Sample Gas Dry Composition (%)				
Stream Location (III)	H ₂	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	33.06	19.38	0.76	36.45	0.18
0.219	30.72	26.94	0.64	33.96	0.09
0.219	32.32	25.39	0.77	33.66	0.07
0.219	32.58	23.67	0.77	35.21	0.09
0.371	33.69	16.53	0.93	38.60	0.95
0.371	33.30	21.35	0.86	35.55	0.02
0.371	35.48	18.17	0.87	36.39	0.02
0.371	33.24	23.73	0.88	33.28	0.02
0.473	38.61	30.68	0.38	27.08	0.00
0.473	37.53	31.46	0.40	27.19	0.16
0.473	34.11	35.28	0.40	27.12	0.10
0.625	35.05	27.82	0.67	30.57	0.07
0.625	33.85	28.02	0.68	32.15	0.03
0.727	35.84	15.64	1.28	37.42	0.02
0.727	35.05	17.95	1.32	36.76	0.04
0.879	30.35	11.32	1.32	45.30	0.12
0.879	30.35	13.01	1.39	43.78	0.15
0.879	29.30	11.77	1.42	45.12	0.17
0.981	36.76	16.18	1.42	37.00	0.19
0.981	37.16	14.75	1.41	36.71	0.17
1.133	32.76	12.24	1.60	42.41	0.01
1.133	32.76	14.13	1.62	41.20	0.00
1.235	33.45	15.07	1.54	39.88	0.04
1.235	33.48	13.53	1.55	40.97	0.01
1.387	31.22	11.31	1.74	44.23	0.01
1.387	30.88	9.77	1.67	45.63	0.00
1.489	29.01	7.94	1.94	46.99	0.09
1.489	28.72	7.78	1.92	47.90	0.01
1.489	28.42	7.24	1.90	48.74	0.00
1.489	28.68	7.06	1.93	48.10	0.03
1.641	29.16	8.15	2.11	46.99	0.00
1.641	29.58	7.13	2.06	47.07	0.00

FBMR Temperature (°C)			
0.01 m	421		
0.32 m	473		
0.52 m	480		
0.78 m	498		
1.08 m	503		
1.29 m	512		
1.59 m	522		
Bed Average	498		
2.26 m	490		

Time Averaged Conditions			
P (kPa abs)	600		
P _m (kPa abs)	25		
Feed C_3H_8 (g/h)	135.2		
Feed Water (g/h)	829.53		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.442	
Permeate 2	1.802	
Permeate 3	0.649	
Permeate 4	0.513	
Permeate 5	0.864	
Permeate 6	1.590	

Experiment: Propane 7					
Stream Location (m)	Stream Location (m) Sample Gas Dry Composition (%)				ion (%)
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C ₃ H ₈
0.219	31.44	28.80	0.53	33.20	0.14
0.219	31.79	28.37	0.55	32.80	0.00
0.219	30.89	29.80	0.54	33.47	0.00
0.371	28.87	18.82	0.75	41.67	0.00
0.371	27.76	19.67	0.79	42.09	0.00
0.473	31.88	41.27	0.33	24.98	0.03
0.473	35.57	34.77	0.33	26.79	0.02
0.473	30.33	43.25	0.35	24.66	0.02
0.473	35.30	35.48	0.36	26.62	0.04
0.625	32.63	33.92	0.54	28.63	0.01
0.625	35.11	28.98	0.55	30.14	0.01
0.625	35.43	29.62	0.54	30.20	0.02
0.727	36.02	24.12	0.89	33.09	0.02
0.727	35.82	24.94	0.88	32.19	0.01
0.879	28.85	20.68	0.99	39.84	0.06
0.879	30.85	17.69	0.97	41.18	0.05
0.981	35.91	21.97	1.10	34.22	0.09
0.981	36.25	19.45	1.12	35.91	0.02
1.133	33.06	16.32	1.27	40.02	0.02
1.133	34.41	12.87	1.15	40.62	0.02
1.235	36.93	19.20	1.24	34.87	0.02
1.235	35.54	22.07	1.26	34.64	0.05
1.387	35.88	16.55	1.39	37.53	0.10
1.387	35.56	15.63	1.39	38.53	0.08
1.489	33.55	14.54	1.65	39.68	0.00
1.489	33.33	13.31	1.67	41.67	0.00
1.489	34.03	12.71	1.66	41.00	0.00
1.489	34.29	12.25	1.64	40.83	0.00
1.489	33.51	11.67	1.71	40.90	0.00
1.489	34.00	11.63	1.72	40.47	0.00
1.641	32.44	15.15	1.61	39.91	0.00
1.641	34.33	13.03	1.66	40.68	0.00
2.327	35.62	12.14	1.60	39.44	0.00
2.327	35.40	11.99	1.62	40.43	0.00
2.327	35.88	13.64	1.67	39.24	0.00

FBMR Temperature (°C)		
0.01 m	452	
0.32 m	479	
0.52 m	496	
0.78 m	514	
1.08 m	531	
1.29 m	548	
1.59 m	553	
Bed Average	520.2	
2.26 m	464	

Time Averaged Conditions		
P (kPa abs)	460	
P _m (kPa abs)	NA	
Feed C_7H_{16} (g/h)	113	
Feed Water (g/h)	707	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	NA	
Permeate 6	NA	

Experiment: Heptane.1a					
Stream Location (m)	Sample Gas Dry Composition (%)				
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	52.88	23.59	0.44	23.10	0
0.219	43.10	35.10	0.49	21.30	0
0.219	42.15	35.89	0.46	21.50	0
0.219	52.78	22.92	0.51	23.79	0
0.371	49.24	26.29	0.56	23.91	0
0.371	48.95	27.91	0.56	22.58	0
0.371	43.77	33.80	0.60	21.82	0
0.371	50.18	26.54	0.56	22.72	0
0.371	46.39	31.25	0.56	21.80	0
0.371	43.84	32.97	0.59	22.60	0
0.371	44.87	32.18	0.56	22.39	0
0.473	43.65	34.33	0.61	21.40	0
0.473	45.21	32.57	0.60	21.63	0
0.473	45.66	30.81	0.57	22.96	0
0.727	52.12	25.28	1.02	21.59	0
0.727	55.22	20.76	0.99	23.04	0
0.727	53.81	21.79	1.04	23.36	0
0.727	55.01	21.29	0.99	22.71	0
0.981	57.74	17.96	1.84	22.45	0
0.981	60.58	13.52	1.75	24.15	0
0.981	55.66	20.14	1.92	22.28	0
0.981	57.45	17.80	1.89	22.87	0
1.235	60.61	13.99	1.72	23.68	0
1.235	56.18	19.49	1.72	22.61	0
1.235	59.36	13.97	1.62	25.06	0
1.235	56.03	19.66	1.71	22.60	0
1.235	60.04	15.84	1.60	22.52	0
1.235	56.49	19.79	1.72	22.01	0
1.235	57.90	17.87	1.72	22.51	0
1.235	57.58	17.53	1.78	23.12	0
1.489	66.14	8.89	2.15	22.83	0
1.489	60.71	15.00	2.57	21.72	0
1.489	63.32	11.70	2.42	22.56	0
1.641	54.28	22.70	1.98	21.04	0
1.641	62.54	13.59	1.67	22.20	0
1.641	56.29	20.53	1.94	21.24	0
1.641	60.44	15.28	1.77	22.51	0
2.327	56.44	19.00	1.50	23.05	0
2.327	54.44	22.05	1.56	21.95	0
2.327	55.20	20.33	1.56	22.92	0
2.327	56.44	19.74	1.51	22.30	0

FBMR Temperature (°C)		
0.01 m	414	
0.32 m	419	
0.52 m	432	
0.78 m	449	
1.08 m	459	
1.29 m	467	
1.59 m	470	
Bed Average	449.3	
2.26 m	432	

Time Averaged Conditions			
P (kPa abs)	463		
P _m (kPa abs)	NA		
Feed C_7H_{16} (g/h)	127		
Feed Water (g/h)	804		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	NA	
Permeate 6	NA	

Experiment: Heptane.1b					
Stream Leastion (m) Sample Gas Dry Composition (%)					
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	45.67	32.39	0.31	21.78	0.12
0.219	35.39	43.20	0.28	21.01	0.165
0.219	41.13	36.92	0.26	21.80	0.116
0.371	37.49	41.01	0.35	21.42	0.041
0.371	39.55	36.29	0.35	24.07	0.042
0.371	44.29	32.88	0.37	22.74	0.043
0.473	38.96	40.31	0.74	20.67	0.013
0.473	39.26	39.78	0.76	20.93	0.009
0.473	37.64	41.24	0.79	20.86	0.007
0.727	36.95	40.59	0.32	22.39	0
0.727	54.18	20.29	0.45	24.88	0
0.727	40.62	36.63	0.21	22.58	0
0.981	47.84	28.96	0.48	23.11	0
0.981	45.07	31.98	0.47	22.66	0
0.981	44.37	32.39	0.45	23.19	0
1.235	47.16	29.64	0.00	22.97	0
1.235	44.59	32.19	0.34	23.00	0
1.235	48.54	26.66	0.62	24.67	0
1.235	41.17	36.91	0.55	21.84	0
1.235	39.59	38.06	0.82	22.25	0
1.235	46.96	30.90	0.31	21.83	0
1.235	44.14	33.88	0.54	21.83	0
1.235	43.71	33.09	0.67	23.02	0
1.235	47.58	27.34	0.00	24.88	0
1.489	43.71	33.62	0.89	22.50	0
1.489	48.71	28.36	0.97	22.66	0
1.489	47.22	30.27	0.53	22.41	0
1.641	40.72	36.27	1.20	23.00	0
1.641	41.88	34.47	1.05	23.60	0
1.641	43.94	33.38	0.68	22.45	0
2.327	44.34	34.14	1.30	21.49	0
2.327	47.12	31.05	1.21	21.68	0
2.327	55.54	20.55	1.06	23.86	0

FBMR Temperature (°C)		
0.01 m	448	
0.32 m	479	
0.52 m	494	
0.78 m	513	
1.08 m	531	
1.29 m	550	
1.59 m	558	
Bed Average	520.8	
2.26 m	476	

Time Averaged Conditions		
P (kPa abs)	726	
P _m (kPa abs)	NA	
Feed C_7H_{16} (g/h)	112	
Feed Water (g/h)	707	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	NA	
Permeate 6	NA	

Experiment: Heptane.2					
Stream Location (m) Sample Gas Dry Composition (%)					
Stream Location (III)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	49.21	26.92	0.31	23.56	0
0.219	35.56	43.17	0.28	20.98	0
0.219	49.26	26.89	0.26	23.59	0
0.371	38.22	33.24	0.53	28.01	0
0.371	48.73	29.15	0.39	21.72	0
0.371	41.26	34.25	0.43	24.06	0
0.371	48.01	28.34	0.43	23.22	0
0.473	38.85	38.05	0.38	22.72	0
0.473	40.42	38.10	0.36	21.11	0
0.473	36.33	42.19	0.37	21.10	0
0.727	51.99	24.30	0.82	22.89	0
0.727	50.63	26.85	0.83	21.69	0
0.727	53.59	21.79	0.85	23.78	0
0.981	55.41	20.06	1.58	22.95	0
0.981	55.65	19.99	1.53	22.83	0
0.981	57.13	18.72	1.51	22.64	0
1.235	52.21	24.18	1.43	22.17	0
1.235	57.20	17.69	1.33	23.78	0
1.235	53.33	21.58	1.40	23.69	0
1.235	53.73	22.86	1.36	22.05	0
1.235	52.75	24.40	1.38	21.47	0
1.235	52.28	21.32	1.59	24.82	0
1.235	52.86	24.32	1.44	21.38	0
1.489	58.15	16.48	2.13	23.23	0
1.489	58.62	17.21	2.15	22.01	0
1.489	61.28	14.30	1.98	22.44	0
1.489	55.94	20.33	2.19	21.54	0
1.489	57.82	16.49	2.08	23.61	0
1.489	58.36	17.00	2.05	22.59	0
1.641	57.10	19.04	1.82	22.04	0
1.641	53.88	22.70	1.87	21.55	0
1.641	57.43	19.26	1.73	21.59	0
2.327	51.17	26.42	1.14	21.27	0
2.327	46.08	31.16	1.22	21.55	0
2.327	52.73	23.52	1.15	22.60	0

FBMR Temperature (°C)		
0.01 m	452	
0.32 m	480	
0.52 m	494	
0.78 m	513	
1.08 m	531	
1.29 m	553	
1.59 m	562	
Bed Average	522.2	
2.26 m	488	

Time Averaged Conditions			
P (kPa abs)	724		
P _m (kPa abs)	NA		
Feed C_7H_{16} (g/h)	139		
Feed Water (g/h)	702		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	NA	
Permeate 6	NA	

Experiment: Heptane.3a					
Stream Location (m) Sample Gas Dry Composition (%)				on (%)	
Stream Location (m)	H_2	CH ₄	CO	CO ₂	C7H16
0.219	38.84	39.03	0.32	21.81	0
0.219	37.91	38.70	0.32	23.07	0
0.219	36.52	41.79	0.31	21.39	0
0.371	41.15	34.96	0.42	23.47	0
0.371	39.08	37.66	0.43	22.83	0
0.371	37.80	38.76	0.43	23.01	0
0.473	35.81	41.77	0.43	21.99	0
0.473	35.46	42.09	0.42	22.02	0
0.473	37.06	40.23	0.41	22.31	0
0.727	44.28	32.23	0.95	22.54	0
0.727	44.47	32.65	0.86	22.02	0
0.727	42.60	35.14	0.88	21.37	0
0.981	52.00	24.06	1.67	22.27	0
0.981	48.89	27.72	1.68	21.71	0
0.981	51.06	24.49	1.67	22.78	0
1.235	52.38	23.37	1.54	22.71	0
1.235	53.85	21.85	1.50	22.80	0
1.235	50.74	25.99	1.54	21.72	0
1.235	49.92	27.26	1.57	21.25	0
1.235	49.73	26.91	1.52	21.84	0
1.235	52.19	23.89	1.48	22.43	0
1.235	45.43	31.09	1.61	21.87	0
1.489	54.82	20.55	2.37	22.25	0
1.489	57.54	17.59	2.33	22.53	0
1.489	56.91	18.40	2.33	22.36	0
1.489	53.12	22.27	2.55	22.06	0
1.489	55.04	20.47	2.47	22.01	0
1.641	53.22	23.16	2.03	21.59	0
1.641	53.65	22.79	2.12	21.44	0
1.641	53.31	23.38	2.14	21.17	0
2.327	49.21	27.33	1.43	22.03	0
2.327	49.92	26.06	1.36	22.67	0
2.327	47.08	30.27	1.43	21.22	0

FBMR Temperature (°C)		
0.01 m	442	
0.32 m	478	
0.52 m	493	
0.78 m	513	
1.08 m	528	
1.29 m	549	
1.59 m	560	
Bed Average	520.2	
2.26 m	465	

Time Averaged Conditions			
P (kPa abs)	726		
P _m (kPa abs)	NA		
Feed C_7H_{16} (g/h)	94		
Feed Water (g/h)	710		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	NA	
Permeate 6	NA	

Experiment: Heptane.3b					
Stream Location (m) Sample Gas Dry Composition (%)				tion (%)	
Stream Elecation (m)	H ₂	CH ₄	CO	CO ₂	C_7H_{16}
0.219	45.53	31.71	0.32	22.44	0.00
0.219	42.93	34.36	0.35	22.36	0.00
0.219	47.06	30.21	0.34	22.39	0.00
0.371	45.80	30.88	0.45	22.87	0.00
0.371	44.64	32.27	0.46	22.63	0.00
0.371	47.54	29.56	0.46	22.45	0.00
0.473	43.16	34.29	0.35	22.20	0.00
0.473	42.27	35.04	0.35	22.33	0.00
0.473	43.08	34.58	0.37	21.98	0.00
0.727	52.08	24.59	0.78	22.55	0.00
0.727	53.83	22.51	0.80	22.86	0.00
0.727	53.55	23.26	0.78	22.41	0.00
0.981	58.41	17.67	1.50	22.43	0.00
0.981	56.37	19.61	1.52	22.50	0.00
0.981	56.90	18.65	1.54	22.90	0.00
1.235	56.55	20.68	1.31	21.47	0.00
1.235	58.51	19.64	1.25	20.61	0.00
1.235	53.58	23.87	1.28	21.27	0.00
1.235	53.65	22.25	1.27	22.83	0.00
1.235	55.98	20.42	1.29	22.30	0.00
1.235	52.57	25.39	1.33	20.71	0.00
1.235	56.34	19.77	1.33	22.56	0.00
1.235	56.13	19.79	1.28	22.79	0.00
1.235	57.28	18.77	1.27	22.68	0.00
1.489	60.88	15.28	1.95	21.90	0.00
1.489	59.97	14.70	2.01	23.32	0.00
1.489	59.60	16.01	1.96	22.42	0.00
1.489	59.93	16.57	2.07	21.44	0.00
1.489	59.85	14.71	2.05	23.38	0.00
1.489	61.64	12.65	1.93	23.78	0.00
1.641	55.84	20.48	1.89	21.79	0.00
1.641	53.42	22.23	1.90	22.44	0.00
1.641	56.11	19.77	1.94	22.18	0.00
2.327	52.88	25.03	1.02	21.07	0.00
2.327	51.93	24.73	1.06	22.28	0.00
2.327	55.27	19.61	1.06	24.05	0.00

FBMR Temperature (°C)		
0.01 m	414	
0.32 m	452	
0.52 m	460	
0.78 m	491	
1.08 m	485	
1.29 m	492	
1.59 m	497	
Bed Average	480	
2.26 m	451	

Time Averaged Conditions			
P (kPa abs)	585		
P _m (kPa abs)	101		
Feed C_7H_{16} (g/h)	119		
Feed Water (g/h)	753		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	0.012	
Permeate 6	NA	

Experiment: Heptane.4a					
Streem Location (m)	eam Location (m) Sample Gas Dry Composition (%)				
Stream Elocation (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	50.20	26.86	0.20	21.44	1.29
0.219	46.35	30.91	0.21	21.19	1.34
0.219	45.14	31.74	0.21	21.52	1.39
0.371	50.69	23.87	0.40	22.97	2.05
0.371	52.22	22.71	0.41	22.63	2.00
0.371	54.83	18.80	0.28	23.66	2.41
0.727	46.69	30.46	0.61	22.20	0.00
0.727	47.22	29.43	0.62	22.66	0.01
0.727	48.50	28.44	0.61	22.39	0.00
0.981	52.61	23.28	0.92	22.64	0.53
0.981	49.74	26.71	0.99	22.37	0.14
0.981	52.10	24.15	0.98	22.68	0.01
1.133	46.35	30.89	0.98	21.76	0.02
1.133	51.38	25.00	0.87	22.75	0.00
1.133	50.76	25.37	0.89	22.93	0.05
1.235	47.89	30.00	0.66	21.42	0.00
1.235	47.76	29.17	0.63	22.38	0.00
1.235	46.65	30.67	0.63	22.00	0.00
1.235	48.34	28.69	0.78	22.08	0.00
1.235	46.85	30.01	0.68	22.45	0.02
1.235	48.79	28.51	0.68	21.99	0.01
1.235	48.64	27.42	0.69	23.21	0.01
1.387	49.81	26.79	0.73	22.55	0.05
1.387	47.02	29.97	0.78	22.16	0.00
1.387	47.78	29.09	0.76	22.28	0.00
1.489	51.88	25.35	0.94	21.78	0.00
1.489	50.94	25.64	1.01	22.35	0.00
1.489	51.52	25.01	1.01	22.37	0.00
1.489	52.65	24.08	0.99	22.19	0.00
1.641	50.58	26.14	0.73	22.54	0.00
1.641	48.88	27.71	0.74	22.66	0.01
1.641	47.48	29.52	0.75	22.24	0.00
2.327	48.57	28.10	0.77	22.55	0.01
2.327	53.22	22.66	0.73	23.39	0.00
2.327	48.89	27.64	0.77	22.70	0.00

FBMR Temperature (°C)		
0.01 m	417	
0.32 m	448	
0.52 m	458	
0.78 m	494	
1.08 m	489	
1.29 m	493	
1.59 m	500	
Bed Average	480	
2.26 m	460	

Time Averaged Conditions		
P (kPa abs)	587	
P _m (kPa abs)	36	
Feed C_7H_{16} (g/h)	119	
Feed Water (g/h)	753	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	1.009	
Permeate 6	NA	

Experiment: Heptane.4b					
Stream Leasting (m) Sample Gas Dry Composition (%)					
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C ₇ H ₁₆
0.219	46.75	29.83	0.21	21.82	1.38
0.219	43.15	33.75	0.20	21.64	1.25
0.219	42.79	34.00	0.24	21.79	1.17
0.371	54.08	20.35	0.38	22.91	0.05
0.371	52.08	22.63	0.39	22.64	0.03
0.371	50.78	23.25	0.42	23.22	0.10
0.727	49.63	26.83	0.68	22.83	0.00
0.727	46.44	30.20	0.71	22.61	0.00
0.727	46.13	30.90	0.69	22.21	0.00
1.133	49.14	27.64	0.92	22.29	0.01
1.133	48.51	28.22	0.91	22.36	0.00
1.133	50.04	25.77	0.96	23.23	0.00
1.235	47.55	27.55	0.74	24.13	0.00
1.235	47.44	28.28	0.73	23.53	0.00
1.235	47.26	28.42	0.71	23.58	0.00
1.387	44.50	26.75	0.88	27.84	0.02
1.387	46.53	25.21	0.85	27.38	0.01
1.387	48.13	23.94	0.81	27.10	0.00
1.387	42.70	28.64	0.91	26.93	0.81
1.387	45.29	26.28	0.92	27.49	0.02
1.489	50.66	22.97	1.05	25.25	0.02
1.489	51.72	22.00	1.16	25.06	0.00
1.489	50.21	23.72	1.20	24.84	0.00
1.489	43.53	30.63	0.79	25.02	0.01
1.641	47.91	25.05	0.81	26.21	0.01
1.641	48.37	25.08	0.80	25.75	0.00
1.641	46.03	27.05	0.82	26.10	0.00
2.327	46.93	26.09	1.00	25.97	0.01
2.327	46.10	26.19	1.04	26.66	0.01
2.327	51.29	21.61	0.92	26.18	0.00

FBMR Temperature (°C)		
0.01 m	421	
0.32 m	447	
0.52 m	458	
0.78 m	494	
1.08 m	487	
1.29 m	495	
1.59 m	500	
Bed Average	480	
2.26 m	468	

Time Averaged Conditions		
P (kPa abs)	722	
P _m (kPa abs)	101	
Feed C ₇ H ₁₆ (g/h)	119	
Feed Water (g/h)	753	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	0.169	
Permeate 6	NA	

Experiment: Heptane.4c					
Streem Location (m)	Stream Location (m) Sample Gas Dry Composition (%)				tion (%)
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	40.19	37.22	0.18	21.31	0.99
0.219	40.63	36.62	0.15	21.65	0.93
0.219	41.80	35.36	0.15	21.84	0.85
0.371	56.05	17.90	0.20	23.88	1.96
0.371	50.86	24.22	0.32	22.74	1.76
0.371	48.88	26.42	0.30	22.59	1.71
0.371	49.31	26.32	0.33	22.30	1.73
0.727	45.46	31.49	0.61	22.35	0.00
0.727	45.33	31.96	0.58	22.02	0.00
0.727	45.84	30.74	0.57	22.70	0.00
0.981	48.44	28.14	0.91	22.46	0.00
0.981	49.00	27.47	0.90	22.56	0.00
0.981	49.51	26.74	0.89	22.80	0.00
1.133	48.91	27.36	0.85	22.80	0.02
1.133	49.57	26.91	0.85	22.61	0.00
1.133	48.61	28.07	0.83	22.43	0.00
1.235	45.76	30.80	0.67	22.62	0.15
1.235	46.17	30.48	0.65	22.67	0.01
1.235	47.89	28.70	0.64	22.72	0.00
1.387	47.59	29.37	0.74	22.29	0.00
1.387	46.90	29.17	0.73	23.16	0.00
1.387	46.58	29.31	0.71	23.36	0.00
1.387	45.56	30.99	0.74	22.61	0.00
1.387	44.42	31.80	0.74	22.98	0.00
1.387	45.91	30.32	0.73	22.96	0.00
1.387	52.84	20.20	0.70	26.13	0.01
1.387	46.87	29.26	0.73	23.03	0.00
1.387	46.48	29.51	0.74	23.17	0.00
1.489	49.80	26.21	1.02	22.90	0.00
1.489	50.33	25.62	1.02	22.92	0.00
1.489	50.23	25.35	1.01	23.22	0.00
1.641	46.03	30.02	0.68	23.17	0.00
1.641	46.28	30.01	0.65	23.03	0.00
1.641	45.88	30.16	0.77	23.04	0.00
2.327	47.25	28.80	0.79	23.13	0.00
2.327	47.31	28.64	0.79	23.24	0.00
2.327	47.33	28.58	0.78	23.29	0.00

FBMR Temperature (°C)		
0.01 m	425	
0.32 m	451	
0.52 m	460	
0.78 m	496	
1.08 m	489	
1.29 m	494	
1.59 m	501	
Bed Average	482	
2.26 m	471	

Time Averaged Conditions		
P (kPa abs)	718	
P _m (kPa abs)	26	
Feed C_7H_{16} (g/h)	119	
Feed Water (g/h)	753	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	NA	
Permeate 2	NA	
Permeate 3	NA	
Permeate 4	NA	
Permeate 5	1.423	
Permeate 6	NA	

Experiment: Heptane.4d					
Stream Location (m)	(m) Sample Gas Dry Composition (%)				
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	40.93	36.54	0.18	21.31	1.02
0.219	41.43	35.98	0.17	21.63	0.77
0.371	48.86	26.07	0.34	22.73	1.99
0.371	50.48	24.66	0.32	22.61	1.92
0.727	44.70	32.72	0.61	21.89	0.00
0.727	45.43	32.04	0.59	21.82	0.00
1.133	48.77	27.46	0.90	22.79	0.00
1.133	48.74	27.23	0.90	23.07	0.00
1.133	48.18	28.77	0.84	22.16	0.00
1.235	45.04	30.03	0.67	24.16	0.01
1.235	46.59	28.21	0.66	24.43	0.00
1.387	42.34	26.56	0.78	30.25	0.01
1.387	41.12	27.31	0.87	30.64	0.00
1.387	42.89	27.00	0.78	29.24	0.00
1.387	42.41	25.50	0.80	31.08	0.01
1.387	42.41	26.17	0.79	30.55	0.00
1.387	43.20	27.40	0.82	28.39	0.00
1.387	43.71	25.98	0.81	29.41	0.00
1.489	48.84	24.10	1.10	25.86	0.00
1.489	48.17	24.04	1.13	26.43	0.00
1.489	48.56	24.39	1.15	25.82	0.00
1.641	43.91	27.54	0.79	27.67	0.01
1.641	43.34	28.38	0.77	27.39	0.00
1.641	44.46	27.22	0.76	27.49	0.00
2.327	44.91	25.93	0.97	28.16	0.00
2.327	45.25	25.16	0.97	28.59	0.00
FBMR Temperature (°C)					
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0.01 m	387				
0.32 m	476				
0.52 m	451				
0.78 m	472				
1.08 m	468				
1.29 m	478				
1.59 m	506				
Bed Average	475				
2.26 m	464				

Time Averaged Conditions			
P (kPa abs)	605		
P _m (kPa abs)	25		
Feed C_7H_{16} (g/h)	105.8		
Feed Water (g/h)	666.8		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.426	
Permeate 2	0.617	
Permeate 3	0.410	
Permeate 4	0.252	
Permeate 5	0.562	
Permeate 6	0.816	

Experiment: Heptane.5a					
Stream Location (m) Sample Gas Dry Composition (%)					tion (%)
Stream Location (III)	H_2	CH ₄	CO	CO ₂	C7H16
0.219	46.45	28.63	0.48	23.84	0.60
0.219	45.94	28.98	0.47	23.97	0.63
0.219	47.49	27.58	0.45	23.85	0.63
0.371	36.21	28.24	0.60	34.95	0.00
0.371	36.12	27.40	0.61	35.87	0.00
0.473	26.90	27.45	0.34	45.31	0.00
0.473	26.90	27.59	0.37	45.14	0.00
0.625	25.06	16.26	0.54	58.14	0.00
0.625	24.73	15.87	0.56	58.84	0.00
0.727	37.56	30.41	0.50	31.54	0.00
0.727	37.66	30.28	0.53	31.54	0.00
0.879	33.52	28.62	0.54	37.32	0.00
0.879	34.60	27.01	0.53	37.85	0.00
0.981	33.41	23.60	0.69	42.30	0.00
0.981	33.38	23.73	0.66	42.23	0.00
1.133	31.82	18.18	0.81	49.19	0.00
1.133	31.33	18.40	0.82	49.44	0.00
1.235	36.33	24.22	0.68	38.77	0.00
1.235	35.89	25.33	0.67	38.10	0.00
1.387	34.84	21.68	0.84	42.64	0.00
1.387	34.42	22.00	0.79	42.78	0.00
1.489	35.13	18.97	0.99	44.92	0.00
1.489	34.11	19.76	1.01	45.12	0.00
1.489	33.81	19.60	1.04	45.55	0.00
1.489	34.60	19.07	1.01	45.32	0.00
1.489	35.08	18.46	1.04	45.41	0.00
1.489	34.61	18.06	1.04	46.29	0.00
1.641	29.58	23.67	0.81	45.94	0.00
1.641	30.84	22.64	0.81	45.72	0.00
2.327	36.94	17.56	1.18	44.32	0.00
2.327	37.33	17.31	1.17	44.19	0.00
2.327	37.86	16.80	1.18	44.16	0.00

FBMR Temperature (°C)		
0.01 m	402.0	
0.32 m	495.6	
0.52 m	472.9	
0.78 m	495.6	
1.08 m	493.3	
1.29 m	502.9	
1.59 m	535.9	
Bed Average	499.4	
2.26 m	470.5	

Time Averaged Conditions			
P (kPa abs)	601		
P _m (kPa abs)	25		
Feed C ₇ H ₁₆ (g/h)	102.4		
Feed Water (g/h)	645.2		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.525	
Permeate 2	0.667	
Permeate 3	0.508	
Permeate 4	0.293	
Permeate 5	0.623	
Permeate 6	0.966	

Experiment: Heptane.5b					
Stream Logation (m)	Stream Location (m) Sample Gas Dry Composition (%)				tion (%)
Stream Location (m)	H ₂	CH ₄	СО	CO ₂	C7H16
0.219	43.04	31.14	0.57	25.24	0.01
0.219	41.31	33.18	0.55	24.94	0.01
0.219	41.47	32.77	0.60	25.15	0.01
0.371	38.02	23.15	0.81	38.02	0.00
0.371	37.41	23.38	0.81	38.39	0.00
0.473	26.77	19.46	0.50	53.27	0.00
0.473	27.67	18.08	0.50	53.75	0.00
0.625	23.47	9.89	0.73	65.91	0.00
0.625	23.70	9.68	0.71	65.91	0.00
0.727	39.46	28.01	0.91	31.62	0.00
0.727	40.71	25.68	0.93	32.68	0.00
0.879	36.56	23.07	0.86	39.51	0.00
0.879	35.84	22.90	0.88	40.38	0.00
0.981	35.78	17.57	1.04	45.61	0.00
0.981	36.02	17.86	1.04	45.07	0.00
1.133	32.13	11.68	1.19	55.00	0.00
1.133	31.76	12.06	1.24	54.94	0.00
1.235	38.32	19.12	1.03	41.53	0.00
1.235	38.51	20.06	1.03	40.40	0.00
1.387	35.72	17.02	1.18	46.08	0.00
1.387	35.86	16.77	1.15	46.21	0.00
1.489	35.42	12.84	1.60	50.14	0.00
1.489	35.98	12.20	1.50	50.32	0.00
1.489	37.00	14.38	1.47	47.16	0.00
1.489	37.34	13.05	1.52	48.09	0.00
1.641	31.44	16.92	1.30	50.34	0.00
1.641	31.79	17.19	1.33	49.69	0.00
1.641	31.70	16.20	1.32	50.78	0.00
2.327	37.63	13.08	1.56	47.74	0.00
2.327	37.05	12.97	1.58	48.39	0.00

FBMR Temperature (°C)			
0.01 m	415.7		
0.32 m	518.5		
0.52 m	500.3		
0.78 m	520.0		
1.08 m	515.2		
1.29 m	525.0		
1.59 m	562.0		
Bed Average	523.5		
2.26 m	481.3		

Time Averaged Conditions		
P (kPa abs)	602	
P _m (kPa abs)	25	
Feed C_7H_{16} (g/h)	99.2	
Feed Water (g/h)	625.0	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	1.782	
Permeate 2	0.700	
Permeate 3	0.710	
Permeate 4	0.500	
Permeate 5	0.690	
Permeate 6	1.065	

Experiment: Heptane.5c					
Stream Location (m)	Sample Gas Dry Composition (%)				
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	44.67	28.60	0.69	26.04	0.006219
0.219	41.27	30.36	0.71	27.66	0
0.371	40.09	14.98	1.24	43.69	0
0.371	39.73	17.01	1.24	42.02	0
0.473	27.84	12.77	0.71	58.68	0
0.473	24.71	16.04	0.75	58.50	0
0.625	22.93	5.48	0.95	70.64	0
0.625	21.44	5.59	0.95	72.01	0
0.727	41.23	25.23	1.17	32.37	0
0.727	42.22	22.62	1.16	34.01	0
0.727	43.25	18.47	1.21	37.07	0
0.879	41.21	19.11	1.27	38.41	0
0.981	39.12	14.42	1.40	45.07	0
0.981	37.67	14.21	1.49	46.63	0
1.133	39.60	10.92	1.57	47.92	0
1.133	37.96	10.17	1.65	50.22	0
1.235	38.05	16.64	1.45	43.86	0
1.235	39.42	13.60	1.38	45.59	0
1.235	39.32	15.95	1.43	43.30	0
1.387	37.93	8.62	1.58	51.87	0
1.387	35.96	11.59	1.69	50.76	0
1.489	36.91	8.03	1.95	53.11	0
1.489	36.45	7.53	1.99	54.03	0
1.489	36.41	7.43	1.99	54.17	0
1.489	36.53	7.78	2.02	53.67	0
1.489	36.83	7.10	2.00	54.07	0
1.489	36.82	6.72	1.97	54.50	0
1.489	35.98	7.15	2.06	54.81	0
1.489	35.73	7.29	2.10	54.88	0
1.489	35.80	6.94	2.03	55.23	0
1.489	36.70	6.12	2.04	55.13	0
1.489	36.20	6.84	2.14	54.82	0
1.641	35.06	9.00	1.75	54.18	0
1.641	32.47	11.64	1.91	53.98	0
2.327	35.14	6.98	1.70	56.18	0
2.327	34.54	8.04	1.70	55.72	0
2.327	34.89	7.99	1.72	55.40	0

FBMR Temperature (°C)		
0.01 m	394.8	
0.32 m	503.0	
0.52 m	471.6	
0.78 m	495.9	
1.08 m	489.6	
1.29 m	499.9	
1.59 m	535.9	
Bed Average	499.3	
2.26 m	453.0	

Time Averaged Conditions			
P (kPa abs)	403		
P _m (kPa abs)	25		
Feed C ₇ H ₁₆ (g/h)	68.3		
Feed Water (g/h)	430.1		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.273	
Permeate 2	0.505	
Permeate 3	0.390	
Permeate 4	0.207	
Permeate 5	0.447	
Permeate 6	0.693	

Experiment: Heptane.6a					
Stucom Location (m)	Stream Location (m) Sample Gas Dry Composition (%)				tion (%)
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	45.31	28.72	0.73	25.25	0.00
0.219	44.13	30.08	0.71	25.08	0.00
0.219	42.68	31.69	0.68	24.96	0.00
0.371	39.14	19.45	0.98	40.43	0.00
0.371	39.16	20.83	0.99	39.02	0.00
0.473	28.87	16.21	0.59	54.33	0.00
0.473	29.16	15.85	0.62	54.38	0.00
0.625	26.82	8.90	0.81	63.46	0.00
0.625	26.97	9.12	0.80	63.11	0.00
0.727	42.78	22.90	0.90	33.43	0.00
0.727	42.46	23.51	1.01	33.01	0.00
0.879	38.29	19.35	0.93	41.44	0.00
0.879	38.42	20.48	0.95	40.15	0.00
0.981	37.52	16.36	1.08	45.04	0.00
0.981	37.49	16.18	1.10	45.23	0.00
1.133	35.25	12.13	1.27	51.35	0.00
1.133	35.09	12.11	1.28	51.52	0.00
1.235	39.75	17.19	1.09	41.97	0.00
1.235	40.67	17.03	1.09	41.20	0.00
1.387	36.88	13.92	1.29	47.91	0.00
1.387	36.60	13.98	1.24	48.17	0.00
1.489	38.12	11.41	1.89	48.57	0.00
1.489	38.64	10.50	1.82	49.03	0.00
1.489	37.85	11.00	1.71	49.44	0.00
1.489	37.76	10.70	1.75	49.79	0.00
1.641	31.88	13.98	1.45	52.68	0.00
1.641	31.39	13.40	1.47	53.74	0.00
2.327	37.94	9.64	1.61	50.81	0.00
2.327	37.48	10.48	1.69	50.36	0.00

FBMR Temperature (°C)		
0.01 m	392.3	
0.32 m	496.8	
0.52 m	470.4	
0.78 m	490.2	
1.08 m	493.4	
1.29 m	504.3	
1.59 m	534.3	
Bed Average	498.2	
2.26 m	482.5	

Time Averaged Conditions			
P (kPa abs)	802		
P_{m} (kPa abs)	25		
Feed C_7H_{16} (g/h)	136.5		
Feed Water (g/h)	860.3		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.908	
Permeate 2	0.923	
Permeate 3	0.613	
Permeate 4	0.398	
Permeate 5	0.812	
Permeate 6	1.229	

Experiment: Heptane.6b					
Stream Location (m)	Sample Gas Dry Composition (%)				
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	40.21	33.19	0.51	25.92	0.16
0.219	40.73	32.65	0.48	25.99	0.16
0.219	40.69	32.93	0.47	25.76	0.15
0.371	35.36	25.22	0.80	38.62	0.00
0.371	35.70	24.31	0.76	39.24	0.00
0.473	28.80	30.43	0.36	40.41	0.00
0.473	29.23	31.01	0.34	39.42	0.00
0.625	24.18	11.29	0.68	63.85	0.00
0.625	24.06	11.82	0.67	63.45	0.00
0.625	23.80	11.02	0.66	64.51	0.00
0.727	37.45	28.78	0.65	33.11	0.00
0.727	36.82	29.24	0.64	33.30	0.00
0.879	34.16	25.35	0.74	39.75	0.00
0.879	34.45	24.27	0.74	40.54	0.00
0.981	34.39	18.93	0.94	45.74	0.00
0.981	34.47	19.84	0.97	44.72	0.00
1.133	30.95	12.83	1.15	55.07	0.00
1.133	30.38	12.43	1.15	56.04	0.00
1.235	37.05	21.61	0.95	40.39	0.00
1.235	36.99	21.51	0.93	40.57	0.00
1.387	34.89	18.38	1.02	45.72	0.00
1.387	34.78	18.02	1.02	46.17	0.00
1.489	35.90	16.35	1.40	46.35	0.00
1.489	34.62	13.72	1.41	50.26	0.00
1.489	35.02	13.61	1.42	49.95	0.00
1.489	34.53	13.43	1.42	50.62	0.00
1.489	36.19	15.61	1.37	46.83	0.00
1.489	36.18	15.20	1.39	47.23	0.00
1.641	31.37	19.84	1.14	47.65	0.00
1.641	31.09	19.36	1.15	48.40	0.00
2.327	36.92	15.09	1.36	46.63	0.00
2.327	36.43	14.88	1.34	47.36	0.00

FBMR Temperature (°C)		
0.01 m	380	
0.32 m	492	
0.52 m	454	
0.78 m	466	
1.08 m	463	
1.29 m	474	
1.59 m	500	
Bed Average	475	
2.26 m	461	

Time Averaged Conditions			
P (kPa abs)	605		
P _m (kPa abs)	101		
Feed C_7H_{16} (g/h)	105.8		
Feed Water (g/h)	666.8		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	0.006	
Permeate 2	0.005	
Permeate 3	0.008	
Permeate 4	0.008	
Permeate 5	0.013	
Permeate 6	0.017	

Experiment: Heptane.7a					
Stream Location (m)	Sample Gas Dry Composition (%)				
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	48.45	28.40	0.49	21.91	0.75
0.219	49.34	27.30	0.49	22.10	0.77
0.219	48.25	28.73	0.49	21.77	0.75
0.371	45.19	32.02	0.54	22.26	0.00
0.371	44.43	32.89	0.54	22.14	0.00
0.371	44.18	32.89	0.54	22.39	0.00
0.473	35.74	40.79	0.22	23.26	0.00
0.473	34.97	40.99	0.23	23.81	0.00
0.473	35.63	40.99	0.21	23.17	0.00
0.625	38.05	37.48	0.29	24.18	0.00
0.625	38.20	37.57	0.28	23.94	0.00
0.727	42.25	35.27	0.39	22.10	0.00
0.727	41.91	35.35	0.41	22.34	0.00
0.727	41.38	36.16	0.40	22.05	0.00
0.879	40.34	37.04	0.33	22.29	0.00
0.879	39.91	37.75	0.38	21.96	0.00
0.981	42.46	33.59	0.43	23.51	0.01
0.981	41.85	34.63	0.44	23.08	0.00
0.981	42.00	34.36	0.43	23.22	0.00
1.133	42.64	33.79	0.48	23.09	0.00
1.133	42.57	34.18	0.48	22.76	0.00
1.235	43.09	34.16	0.44	22.31	0.00
1.235	42.61	34.76	0.44	22.19	0.00
1.387	43.90	33.10	0.50	22,50	0.00
1.387	43.91	33.04	0.49	22,55	0.00
1.489	46.25	30.87	0.82	22.06	0.00
1.489	45.55	32.00	0.79	21.66	0.00
1.489	46.26	30.28	0.75	22.70	0.00
1.489	47.14	29.50	0.70	22.66	0.00
1.489	46.72	29.81	0.72	22.76	0.00
1.489	46.07	30.63	0.69	22.62	0.00
1.489	46.09	30.54	0.66	22.70	0.00
1.489	46.39	29.97	0.67	22.97	0.00
1.489	46.05	30.60	0.65	22.70	0.00
1.489	45.84	30.92	0.67	22.57	0.00
1.641	45.71	30.98	0.67	22.63	0.00
1.641	45.73	31.00	0.66	22.61	0.00
2.327	47.20	29.51	0.71	22.59	0.00
2.327	47.36	29.23	0.70	22.71	0.00

FBMR Temperature (°C)		
0.01 m	383	
0.32 m	482	
0.52 m	455	
0.78 m	469	
1.08 m	467	
1.29 m	477	
1.59 m	505	
Bed Average	476	
2.26 m	461	

Time Averaged Conditions			
P (kPa abs)	605		
P _m (kPa abs)	50		
Feed C ₇ H ₁₆ (g/h)	105.8		
Feed Water (g/h)	666.8		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	0.856	
Permeate 2	0.296	
Permeate 3	0.198	
Permeate 4	0.120	
Permeate 5	0.331	
Permeate 6	0.485	

Experiment: Heptane.7b					
Stream Location (m)	Sample Gas Dry Composition (%)				
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	45.91	29.82	0.52	22.99	0.77
0.219	46.91	29.02	0.46	22.85	0.76
0.219	48.60	27.02	0.47	23.16	0.76
0.371	39.89	29.44	0.59	30.08	0.00
0.371	40.22	28.69	0.60	30.49	0.00
0.473	30.74	32.70	0.32	36.25	0.00
0.473	30.17	33.87	0.30	35.67	0.00
0.625	31.23	27.22	0.47	41.09	0.00
0.625	30.69	26.53	0.46	42.31	0.00
0.727	39.72	32.45	0.49	27.34	0.00
0.727	38.44	34.98	0.49	26.10	0.00
0.879	36.90	32.70	0.48	29.93	0.00
0.879	36.49	32.44	0.46	30.60	0.00
0.981	38.26	29.31	0.58	31.86	0.00
0.981	37.83	28.93	0.59	32.65	0.00
1.133	37.11	26.64	0.72	35.53	0.00
1.133	36.98	26.18	0.70	36.14	0.00
1.235	39.04	29.99	0.58	30.39	0.00
1.235	39.22	29.15	0.60	31.03	0.00
1.387	38.70	27.93	0.66	32.71	0.00
1.387	38.41	28.78	0.65	32.15	0.00
1.489	40.86	24.19	0.91	34.05	0.00
1.489	40.17	24.79	0.90	34.14	0.00
1.489	40.16	24.81	0.89	34.15	0.00
1.489	39.49	25.44	0.89	34.18	0.00
1.489	39.79	24.88	0.89	34.44	0.00
1.641	37.44	27.69	0.85	34.02	0.00
1.641	37.81	27.49	0.84	33.86	0.00
2.327	41.58	23.24	0.96	34.21	0.00
2.327	41.52	23.35	0.99	34.15	0.00
2.327	41.58	23.54	0.97	33.92	0.00

FBMR Temperature (°C)		
0.01 m	395	
0.32 m	495	
0.52 m	471	
0.78 m	492	
1.08 m	493	
1.29 m	504	
1.59 m	537	
Bed Average	499	
2.26 m	467	

Time Averaged Conditions			
P (kPa abs)	605		
P _m (kPa abs)	25		
Feed C_7H_{16} (g/h)	127.1		
Feed Water (g/h)	640.7		
Feed H ₂ (slpm)	0		

Permeate H ₂ (slpm)		
Permeate 1	1.775	
Permeate 2	0.857	
Permeate 3	0.525	
Permeate 4	0.321	
Permeate 5	0.716	
Permeate 6	1.040	

Experiment: Heptane.8a					
Stream Location (m)	Sample Gas Dry Composition (%)				
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	41.85	31.06	0.73	25.43	0.93
0.219	45.17	27.88	0.67	25.35	0.95
0.371	35.41	26.55	0.87	37.17	0.00
0.371	36.04	25.32	0.85	37.80	0.00
0.473	27.87	29.31	0.45	42.37	0.00
0.473	27.35	30.37	0.44	41.83	0.00
0.625	22.57	13.49	0.79	63.15	0.00
0.625	22.47	14.07	0.81	62.65	0.00
0.727	35.21	32.97	0.74	31.08	0.00
0.727	35.15	31.48	0.76	32.61	0.00
0.879	32.04	27.55	0.79	39.62	0.00
0.981	32.26	20.81	1.08	45.84	0.01
0.981	32.82	20.35	1.06	45.76	0.01
1.133	28.75	15.89	1.31	54.05	0.00
1.235	33.83	24.95	1.12	40.09	0.00
1.235	34.45	21.82	1.08	42.65	0.00
1.387	32.51	21.03	1.23	45.23	0.00
1.489	35.16	15.81	1.66	47.37	0.00
1.489	34.17	16.80	1.73	47.31	0.00
1.489	34.82	15.06	1.69	48.43	0.00
1.489	33.20	15.51	1.72	49.57	0.00
1.489	34.18	18.70	1.65	45.47	0.00
1.489	33.88	17.52	1.66	46.94	0.00
1.641	29.38	20.59	1.41	48.62	0.00
2.327	34.74	16.79	1.69	46.79	0.00
2.327	34.75	16.55	1.68	47.02	0.00

FBMR Temperature (°C)		
0.01 m	394	
0.32 m	497	
0.52 m	473	
0.78 m	493	
1.08 m	490	
1.29 m	502	
1.59 m	539	
Bed Average	499	
2.26 m	467	

Time Averaged Conditions		
P (kPa abs)	606	
P _m (kPa abs)	25	
Feed C_7H_{16} (g/h)	85.7	
Feed Water (g/h)	648.2	
Feed H ₂ (slpm)	0	

Permeate H ₂ (slpm)		
Permeate 1	1.555	
Permeate 2	0.666	
Permeate 3	0.474	
Permeate 4	0.266	
Permeate 5	0.564	
Permeate 6	0.873	

Experiment: Heptane.8b					
Stream Location (m) Sample Gas Dry Composition (%)				tion (%)	
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16
0.219	43.88	28.82	0.56	26.49	0.25
0.219	43.32	29.36	0.56	26.48	0.28
0.371	37.84	21.90	0.86	39.40	0.00
0.371	39.15	18.74	0.84	41.27	0.00
0.371	36.91	22.18	0.86	40.05	0.00
0.473	34.34	18.95	0.41	46.30	0.00
0.473	30.47	21.44	0.43	47.66	0.00
0.625	29.80	5.04	0.60	64.55	0.00
0.625	28.07	8.33	0.70	62.89	0.00
0.727	41.58	22.93	0.73	34.77	0.00
0.727	41.39	23.96	0.69	33.96	0.00
0.879	36.98	19.54	0.73	42.74	0.00
0.879	37.42	20.45	0.71	41.42	0.00
0.981	37.18	15.14	0.90	46.78	0.00
0.981	37.07	16.01	0.89	46.03	0.00
0.981	37.56	15.00	0.92	46.52	0.00
1.133	34.48	9.65	1.01	54.86	0.00
1.133	35.21	10.34	1.03	53.42	0.00
1.235	40.41	16.18	0.91	42.51	0.00
1.235	40.14	16.18	0.91	42.77	0.00
1.387	36.80	14.28	1.03	47.88	0.00
1.387	36.85	12.57	0.99	49.59	0.00
1.489	38.52	9.50	1.34	50.64	0.00
1.489	38.28	10.07	1.45	50.20	0.00
1.489	37.39	9.47	1.42	51.72	0.00
1.489	36.88	9.18	1.41	52.53	0.00
1.489	39.17	9.45	1.36	50.03	0.00
1.489	38.29	10.84	1.49	49.38	0.00
1.489	38.11	10.53	1.47	49.88	0.00
1.641	28.65	14.69	1.09	55.57	0.00
1.641	28.76	13.70	1.11	56.42	0.00
2.327	37.26	10.41	1.22	51.10	0.00
2.327	37.53	9.36	1.21	51.91	0.00
2.327	38.50	10.99	1.23	49.29	0.00

FBMR Temperature (°C)				
0.01 m	431			
0.32 m	480			
0.52 m	483			
0.78 m	503			
1.08 m	503			
1.29 m	512			
1.59 m	518			
Bed Average	500			
2.26 m	484			

Time Averaged Conditions				
P (kPa abs)	602			
P _m (kPa abs)	25			
Feed C_7H_{16} (g/h)	136.5			
Feed Water (g/h)	860.3			
Feed H ₂ (slpm)	0			

Permeate H ₂ (slpm)				
Permeate 1	1.535			
Permeate 2	1.566			
Permeate 3	0.525			
Permeate 4	0.392			
Permeate 5	0.700			
Permeate 6	1.287			

Experiment: Heptane.9						
Stream Location (m)	Sample Gas Dry Composition (%)					
Stream Location (m)	H ₂	CH ₄	CO	CO ₂	C7H16	
0.219	38.07	27.20	0.59	34.13	0.00	
0.219	37.67	26.83	0.61	34.89	0.00	
0.371	43.71	24.03	0.74	31.49	0.03	
0.371	41.84	26.16	0.79	31.16	0.05	
0.371	40.25	29.14	0.78	29.78	0.05	
0.473	37.11	32.34	0.43	30.12	0.00	
0.473	33.83	36.64	0.41	29.12	0.00	
0.625	37.59	29.78	0.62	32.00	0.00	
0.625	38.23	28.51	0.62	32.64	0.00	
0.625	37.85	28.01	0.63	33.50	0.00	
0.727	39.26	22.27	0.96	37.50	0.00	
0.727	38.94	22.85	0.95	37.26	0.00	
0.879	34.24	16.86	1.02	47.88	0.00	
0.879	35.20	15.45	1.02	48.33	0.00	
0.981	40.20	16.81	1.22	41.77	0.00	
0.981	40.28	17.49	1.22	41.01	0.00	
1.133	35.80	9.88	1.46	52.86	0.00	
1.133	35.37	10.66	1.50	52.48	0.00	
1.235	40.56	16.94	1.23	41.27	0.00	
1.235	40.73	16.44	1.21	41.63	0.00	
1.387	39.86	14.62	1.43	44.10	0.00	
1.387	39.59	14.14	1.40	44.87	0.00	
1.489	38.91	10.66	1.74	48.70	0.00	
1.489	39.03	9.90	1.71	49.35	0.00	
1.489	39.10	10.25	1.76	48.88	0.00	
1.489	39.02	9.67	1.74	49.57	0.00	
1.489	38.49	10.46	1.77	49.28	0.00	
1.489	39.13	10.59	1.82	48.47	0.00	
1.489	38.77	10.33	1.80	49.10	0.00	
1.489	39.54	9.48	1.78	49.20	0.00	
1.641	38.92	11.99	1.44	47.65	0.00	
1.641	37.35	12.29	1.61	48.75	0.00	
1.641	38.19	12.08	1.59	48.15	0.00	
2.327	40.14	11.74	1.56	46.55	0.00	
2.327	40.07	11.18	1.55	47.21	0.00	
2.327	40.24	11.68	1.56	46.52	0.00	