

SEPARATION OF SULFUR COMPOUNDS FROM FCC GASOLINE BY PERVAPORATION

MANISH JAIN



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
AUGUST 2016**

©Indian Institute of Technology Delhi (IITD), New Delhi, 2016

SEPARATION OF SULFUR COMPOUNDS FROM FCC GASOLINE BY PERVAPORATION

by

MANISH JAIN

Department of Chemical Engineering

Submitted

**In fulfilment of the requirements of the degree of Doctor of Philosophy
to the**



INDIAN INSTITUTE OF TECHNOLOGY DELHI

AUGUST 2016

CERTIFICATE

I am satisfied that the thesis entitled “**Separation of Sulfur Compounds from FCC Gasoline by Pervaporation**” being submitted by **Mr. Manish Jain** is worthy of the consideration for the award of the degree of **Doctor of Philosophy** and is a record of the original bonafide research work carried out by him under my guidance and supervision, and the results contained in it have not been submitted in part or full to any other university or institute for award of any degree/diploma.

I certify that he has pursued the prescribed course of research.

SHARAD KUMAR GUPTA

Professor

Department of Chemical Engineering

Indian Institute of Technology Delhi

ACKNOWLEDGMENTS

I wish to express my deepest appreciation to **Prof. Sharad K. Gupta** for his valuable guidance, encouragement and support during the course of this work. Without his constant advice, this work would not have been completed.

I would like to thank the members of student research committee, **Prof. Shantanu Roy, Prof. Anupam Shukla,** and **Prof. Gopal P. Agarwal** for their valuable suggestions and encouragement during the completion of this thesis.

The financial assistance provided by Ministry of Human Resources, Indian Government is appreciated.

I would like to express my sincere gratitude to my lab mate **Mr. Dinesh Attarde** for his love, support, understanding and encouragement throughout all phases of this work.

I owe a special debt of gratitude to my parents for their love and moral support.

I am also indebted to **Mr. Kishore Kondamudi, Mr. Pradeep Kumar Budde,** and **Mr. Aashish Nayak** for their help and suggestions.

(Manish Jain)

ABSTRACT

In recent years, pervaporation has been investigated rigorously for separation of thiophene and its derivatives from the fluid catalytic cracker (FCC) gasoline. However, most of the earlier experimental studies on sulfur removal from FCC gasoline were carried out on membrane test cells containing a small patch of membranes. Industrial scale membrane based operations require membrane modules for accommodating larger membrane area. However in membrane modules, different process variables vary enough along the flow channels. Thus, the performance of the module differs from that membrane test cell at a local point.

Spiral wound and hollow fiber modules are most suitable for desulfurization operation due to high packing density, thus, both module geometries are investigated in this study. Furthermore, the focus of the study is on removal of thiophenes compounds, which are most difficult to remove by other traditional processes. This work is focused on development of suitable mathematical models for predicting the performance of the modules for removal of the sulfur containing species, validating the mathematical model with the experimental results, and analysing the effects of changing operating conditions, module dimensions, and feed compositions.

For theoretically predicting the performance of the modules, suitable mathematical models are obtained by making the microscopic material, energy, and momentum balances along the length of the module. These balances are further coupled to the membrane transport model for determining the local fluxes across the membrane. However, for a membrane test cell, only membrane transport model is required.

First, experiments are carried out with a spiral wound module with different model FCC gasoline at a variety of operating conditions. Values of parameters, such as permeance coefficients, boundary layer resistance parameters on the feed side, and friction factor

parameters on permeate side are unknown. The values of these parameters are determined by using a numerical parameter estimation technique. Later following this procedure, the model predictions are compared with the experimental results for validating the mathematical model. The model predictions showed good agreement with the experiment results for different model gasoline.

The mathematical model developed for hollow fiber modules could not be validated due to unavailability of the experimental results. However, tubular pervaporation membrane modules are commercially available. Since tubular and hollow fiber modules have similar geometry, the same mathematical model can be used for the tubular module. Thus, the experiments were conducted on a tubular membrane module with n-heptane/ thiophene binary system for validating the mathematical model for both hollow fiber and tubular modules.

Parameter estimation results with different binary systems show that the mass transport properties of the membrane for thiophene are affected by other hydrocarbon species present in the feed. While the mass transport properties of the membrane for other hydrocarbons are not affected by thiophene, as the concentration of thiophene is quite low in the FCC gasoline.

Results suggest that operating conditions have a profound effect on the performance of the module. In particular, the module performance may be improved with higher permeate pressures and lower feed temperatures.

Effects of the variations of different module dimensions are also analyzed. For spiral wound module, lower module area, and a higher number of leaves improves the module performance. However, the values of L/W are recommended in the range from 1 to 2. Similarly, for hollow fiber modules, lower membrane area, higher shell porosity, lower length

to diameter ratio of the shell, and higher fiber diameter give better results. The performance of co-current and counter-current hollow fiber modules are found to be nearly same.

Results also show that the thiophene (C_4H_4S) removal from different binary mixtures may be sorted out based on the type of hydrocarbon species present in the binary mixtures as linear alkane > alkene > branched alkane > aromatic compounds. Experimental results and model predictions further show that PDMS membranes are also selective for both thiols and sulfides.

Results for a ternary mixture show that the same mathematical model may also be used for predictions of the module performance by assuming the ternary mixture to be equivalent to a binary mixture of two species: first is thiophene, and the second species is a pseudo-species, having the average physical properties of two other hydrocarbons present in the ternary mixture. The same approach may be extended to a multicomponent feed of a real FCC gasoline, containing a variety of hydrocarbons and sulfur-containing compounds. This approach may provide sufficiently accurate predictions with much lesser efforts in comparison to more rigorous, and much more tedious, multicomponent modeling.

Finally, the performance of a pervaporation process was simulated by using a number of spiral wound modules in series. These simulations demonstrated that the pervaporation might successfully remove thiophene from FCC gasoline up to any desired limit.

INDEX

Title	Page No.
CERTIFICATE	II
ACKNOWLEDGEMENTS	III
ABSTRACT	IV
LIST OF FIGURES	XI
LIST OF TABLES	XIV
1 Introduction	1
2 Literature review	5
2.1 Literature related to sulfur removal from FCC gasoline	5
2.1.1 Review of sulfur selective pervaporative membranes	5
2.1.2 Review of effect of operating conditions	6
2.1.3 Review of effect of hydrocarbon species	6
2.1.4 Removal of other sulfur-containing compounds using pervaporation	7
2.2 Review of membrane transport models	26
2.2.1 Solution diffusion model	26
2.2.2 Pore flow model	28
2.2.3 Non equilibrium thermodynamics based model	28
2.3 Review of membrane modules and their modeling	29
2.4 Gaps in the literature	33
2.9 Aim of the presented work	34
3 Modelling and numerical solution techniques	35
3.1 Local mass transport model	35
3.1.1 Mathematical model for boundary layer	36
3.1.2 Membrane mass transport model	37
3.2 Mathematical modelling for spiral wound membrane module	39
3.3 Modelling of tubular/hollow fiber modules	43
3.4 Solution procedure	47
3.4.1 Input parameters	47

3.4.2	Algorithm for the solution of the mathematical models	47
3.4.3	Parameter estimation method	48
3.4.4	Module performance characteristics	49
4	Experimental setup and procedure	51
4.1	Selection of membrane modules and model gasoline compounds	51
4.2	Experimental setup	53
4.3	Experimental procedure	55
5	Parameter estimation and model validation	56
5.1	Model validation for spiral wound module	56
5.2	Parameter estimation for different single component and binary systems	60
5.3	Comparison of the membrane transport parameters of different systems	62
5.3.1	Permeance coefficients of thiophene containing systems	63
5.3.2	Permeance coefficients of thiol and sulfide containing systems	64
5.3.3	Effect of molecular weight on permeance coefficients	64
5.4	Activation energy of permeance and activation energy of pervaporation	65
5.4.1	Comparison of activation energy of pervaporation for thiophene containing systems	68
5.4.2	Comparison of activation energy of pervaporation for different types of sulfur compounds containing systems	68
5.5	Model validation for tubular module	69
5.6	Summary	71
6	Influence of operating conditions, flow variables and module dimensions	72
6.1	Effect of operating conditions	72
6.1.1	Effect of operating conditions on spiral wound module performance	72

6.1.1.1	Effect of the permeate channel outlet pressure and feed channel inlet temperature	72
6.1.1.2	Effect of feed flow rate	76
6.1.1.3	Effect of thiophene concentration in the feed stream	78
6.1.2	Effect of operating conditions on hollow fiber modules performance	79
6.2	Variation of flow variables along the module	80
6.2.1	Variation of flow variables in a spiral wound module	80
6.2.2	Variation of flow variable in a hollow fiber module	82
6.3	Effect of the module dimensions	85
6.3.1	Variation in the spiral wound module dimensions	85
6.3.1.1	Effect of the membrane area	86
6.3.1.2	Effect of the L/W ratio of the membrane leaves	87
6.3.1.3	Effect of the number of leaves	88
6.3.2	Variation in hollow fiber module dimensions	89
6.3.2.1	Effect of the membrane area	90
6.3.2.2	Effect of the shell side porosity	91
6.3.2.3	Effect of L/D_s ratio of the shell	92
6.3.2.4	Effect of radius of the membrane fibres	93
6.4	Comparison of co-current and counter-current hollow fiber modules	94
6.7	Summary	95
7	Comparison of module performance for different model FCC gasoline feeds and scale-up study	96
7.1	Effect of different hydrocarbon species on the module performance	96
7.2	Effect of molecular weight of thiophene on the module performance	99
7.3	Removal of other types of sulfur-containing species from synthetic gasoline	101
7.4	Modeling of multicomponent gasoline by assuming it as the binary system	103
7.4.1	Experimentation, parameter estimation, and model validation	103
7.4.2	Comparison of the permeance coefficients	108
7.4.3	Comparison on the module performances	109

7.5	Scale-up of pervaporation plant for thiophene removal up to the desired limits	110
7.5.1	Details of the setup	110
7.5.2	Predictions for the performance of the plant	111
7.5.3	Comparison of the different membranes for thiophene removal using scale up pervaporation simulations	113
7.6	Summary	115
8	Conclusion	116
	Future R&D prospectus	119
	Nomenclature	120
	References	123
	Appendix	
A	Derivation of mathematical model for variation of operating parameters along the length of a spiral wound module	139
B	Derivation of mathematical model for hollow fiber and tubular membrane modules	145
C	Physical and chemical properties of the different feed components	150
D	Numerical solution approaches	154
E	Experimental and simulation results in graphical format	161
F	Experimental Results	169
	Bio data	176

LIST OF FIGURES

Figure No.	Title	Page No.
1.1	Schematic diagram of the pervaporation process	03
2.1	Mass transport across the membrane according to Solution-diffusion model with boundary layer resistance	26
2.2	Membrane modules	31
3.1	Concentration profile of component i in the boundary layer and in the membrane	35
3.2	Flow pattern in a spiral wound module leaf	40
3.3	Flow pattern in the hollow fiber membrane modules	43
3.4	Alternative tubular membrane module geometry	46
4.1	The schematic diagram of the pervaporation setup	54
6.1	Effect of permeate channel outlet pressure on spiral wound module performance	73
6.2	Effect of feed channel inlet flow rate on spiral wound module performance	76
6.3	Effect of thiophene concentration in feed stream on spiral wound module performance	79
6.4	Feed side flow variables of spiral wound modules as the function of position	81
6.5	Permeate side flow variables of spiral wound module as the function of position	82
6.6	Feed side flow variables of hollow fiber modules as the function of position	83
6.7	Permeate side flow variables of spiral wound module as the function of position	84
6.8	Dimensional parameters of spiral wound module	85
6.9	Effects of membrane area on the performance of Spiral wound module	86
6.10	Effects of L/W ratio on the performance of Spiral wound module	88
6.11	Dimensional parameters of hollow fiber module	89
6.12	Effects of membrane area on the performance of hollow fiber module	90

6.13	Effects of varying shell side porosity on the performance of hollow fiber module	91
6.14	Effects of varying L/D_s ratio of shell on the performance of hollow fiber module	93
6.15	Effects of varying fiber radius on the performance of hollow fiber module	94
7.1	Performance of spiral wound module for thiophene removal from different feed systems	98
7.2	Comparison of the performance of spiral wound module for different molecular weight thiophene removal at various temperatures	100
7.3	Comparison of the performance of spiral wound module for different types of sulfur-containing compounds removal at various temperatures	102
7.4	Variation in permeance coefficients with varying n-heptane concentration in the ternary feed system	108
7.5	Module performance with varying n-heptane concentration in feed for n-heptane/n-octane/thiophene ternary mixtures at 313 K	110
7.6	Arrangement of modules in series	111
7.7	Retentate flow rate vs. Number of modules in series	112
7.8	Number of modules required for reduction of thiophene up to the desired limits	113
A.1	Control volume for a feed channel of a spiral wound module	139
A.2	Control volume for a permeate channel of a spiral wound module	142
B.1	Feed channel control volume for a hollow fiber module	145
B.2	Permeate channel control volume for a hollow fiber module	147
D.1	Discretization of a spiral wound module leaf for numerical solution	156
D.2	Discretization of hollow fiber module in co-current flow condition	157
D.3	Discretization of hollow fiber module in counter-current flow condition	158
D.4	Discretization of tubular membrane module for numerical solution	160
E.1	Effects of permeate channel outlet pressure on tubular module performance	161
E.2	Effects of feed channel inlet flow rate on tubular module performance	161
E.3	Effects of thiophene concentration in feed stream on tubular module performance	162

E.4	Effects of permeate channel outlet pressure on hollow fiber module performance	162
E.5	Effects of feed channel inlet flow rate on tubular module performance	163
E.6	Effects of thiophene concentration in feed stream on tubular module performance	163
E.7	Comparison of module performance for thiophene removal from different binary systems at different permeate channel outlet pressure	164
E.8	Comparison of module performance for thiophene removal from different binary systems at different feed channel inlet flow rate	164
E.9	Comparison of module performance for thiophene removal from different binary systems at different inlet thiophene concentrations	165
E.10	Comparison of module performance for different types of thiophene removal at different permeate channel outlet pressure	165
E.11	Comparison of module performance for different types of thiophene removal at different feed channel inlet flow rate	166
E.12	Comparison of module performance for different types of thiophene removal at different inlet thiophene concentration	166
E.13	Comparison of module performance for removal of different types of sulfur containing compounds at various permeate outlet pressure	167
E.14	Comparison of module performance for removal of different types of sulfur containing compounds at different feed channel inlet flow rates	167
E.15	Comparison of module performance for removal of different types of sulfur containing compounds at different inlet sulfur containing compound concentration	168

LIST OF TABLES

Table No.	Title	Page No.
2.1	Summary of the literature reported on sulfur compounds removal using pervaporation	09
4.1	Spiral wound module dimensions	51
4.2	Different feed systems selected for analysis	52
4.3	Tubular module dimensions	53
5.1	Experimental results and model predictions for pure n-heptane system, used for parameter estimation and model validation	57
5.2	Experimental results and model predictions of n-heptane/thiophene binary system at 313 K, used for parameter estimation and model validation	59
5.3	Experimental Results and model predictions for pure hydrocarbons	60
5.4	Estimated membrane transport parameters	62
5.5	Estimated values of permeance coefficients for different binary systems at 313 K	63
5.6	Calculated values of activation energy of pervaporation and its related pre-exponential factor (at 313 K)	67
5.7	Experimental results and model predictions for pure n-heptane on tubular module	70
5.8	Experimental results and model predictions for n-heptane/thiophene binary system using tubular membrane module	70
6.1	Values of activity coefficient, vapour pressure, fluxes and enrichment factor of thiophene and n-heptane in a local point of the membrane	74
6.2	Average fluxes of both components with different permeate pressures	75
6.3	Membrane permeance of thiophene in membrane and, in boundary layer at a local point, with different feed temperatures and feed flow rates	77
6.4	Input parameters for simulations of hollow fiber module performance	80
7.1	Standard mixing rules for calculating the average properties	104
7.2	Results of n-heptane/n-octane/thiophene ternary system	106
7.3	Comparison of different membrane used in literature	114
C.1	Molecular weight M_w , Values of critical temperature T_c , critical pressure P_c , critical volume V_c , and compressibility factors z	150

C.2	Values of different coefficients used for calculating the density of the pure compound at different temperature	151
C.3	Values of different coefficients for calculating the viscosity of the pure compound at different temperature	152
C.4	Values of different coefficients for calculating the heat capacity of the pure compound at different temperature	152
C.5	Values of different coefficients for calculating the heat of vaporization of the pure compound at different temperature	153
C.6	Values of different coefficients for calculating the vapor pressure of the pure compounds at different temperature	153
F.1	Experimental results (spiral wound module, n-heptane/thiophene)	169
F.2	Experimental results (spiral wound module, other systems)	170
F.3	Experimental results (tubular module, n-heptane/thiophene)	174