STUDY OF OPERATING CONDITIONS ON FABRICATION OF A KAOLIN HOLLOW FIBRE MEMBRANE

ZYKAMILIA BINTI KAMIN

SCHOOL OF ENGINEERING AND INFORMATION TECHNOLOGY
UNIVERSITI MALAYSIA SABAH
2011

STUDY OF OPERATING CONDITIONS ON FABRICATION OF A KAOLIN HOLLOW FIBRE MEMBRANE

ZYKAMILIA BINTI KAMIN

THESIS SUBMITTED IN FULFILLMENT FOR THE DEGREE OF MASTER OF ENGINEERING

SCHOOL OF ENGINEERING AND
INFORMATION TECHNOLOGY
UNIVERSITI MALAYSIA SABAH
2011

DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, excerpts, equations, summaries and references, which have been duly acknowledged.

2 August 2011

Zykamilia binti Kamin
PK20078209

CERTIFICATION

NAME	:	**ZYKAMILIA BINTI KAMIN**
MATRIC NO.	:	**PK20078209**
TITLE	:	**STUDY OF OPERATING CONDITIONS ON FABRICATION OF A KAOLIN HOLLOW FIBRE MEMBRANE**
DEGREE	:	**MASTER OF ENGINEERING (CHEMICAL ENGINEERING)**
VIVA DATE	:	**11 MARCH 2011**

DECLARED BY

1. SUPERVISOR

Assoc. Prof. Dr. Rosalam Hj. Sarbatly Signature

ACKNOWLEDGEMENT

Alhamdulillah, I am grateful towards ALLAH SWT for giving me strength and ability to complete this study.

I am sincerely thankful to Associate Professor Dr. Rosalam Hj. Sarbatly for all his guidance, invaluable expert advices and review on my research throughout the duration of this study and preparation of this thesis. My sincere appreciation also goes to Professor Dr. Duduku Krishnaiah and Professor Dr. Awang Bono for their invaluable advice and guidance.

I wish to thank Associate Professor Dr. Abdul Hamid Ahmad, the Director for the Institute for Tropical Biology and Conservation, Associate Professor Dr. Mahmud Sudin the dean of the School of International Tropical Forestry, Professor Dr. Saleem Mustafa the Director of Borneo Marine Research Institute, University of Malaysia Sabah (UMS), Professor Zainal Arifin Ahmad of School of Materials and Mineral Resources Engineering, University of Science Malaysia and the School of Engineering and Information Technology, UMS for providing the facilities for the convenient of my research work.

I also want to thank the Ministry of Science, Technology and Innovation (MOSTI) for funding this project through the Science Fund Grant (Gant No. 03-01-10-SF0023) and to the University of Malaysia Sabah (UMS) for the financial aid through the UMS scholarship.

I am greatly indebted to my beloved parents, for their encouragement, support and sacrifices throughout my study and I appreciate it very much. To my sister and brothers, a big thanks for their support and encouragement. To my friends in Membrane Technology Research Group UMS, thank you for your support.

Last but not least, I wish to express my sincere thanks to all those who have one way or another helped me in making this study a success. May Allah bless you all.

Zykamilia Kamin
2 August 2011

ABSTRACT

STUDY OF OPERATING CONDITIONS ON FABRICATION OF A KAOLIN HOLLOW FIBRE MEMBRANE

A high surface to volume ratio and harsh environments stability of a ceramic hollow fibre membrane attracts its current use. Currently, it is produced using expensive advanced ceramics (Al_2O_3, Ti_2O, ZrO_2 etc.). In this research, the inexpensive kaolin was proposed as hollow fibre membrane material. However, available spinning condition for hollow fibre membrane (HFM) preparation of the existing materials is not suitable for kaolin. Therefore this study reveals the fundamental knowledge to prepare kaolin HFM. Morphology study is important as an indicator for ceramic HFM applications either in separation or deposition of catalyst. In this study, various suspensions were prepared containing kaolin, polyethersulfone (PESf) and n-methyl-2-pyrrolidone (NMP) as ceramic powder, polymer binder and solvent respectively, spun at 0, 3 and 6 cm air gaps and later sintered between 1100 and 1600 °C. The results showed that suspensions viscosity between 1.280 x 10^3 and 3.310 x 10^5 cp were obtained. Fibres with regular cross-section were achieved at 3 and 6 cm air gaps. Subsequently, an increased in spinneret dimension required for a higher air gap to form a continuously nascent fibre. By scanning electron microscopy, asymmetric fibres were obtained; with outer finger-like voids and inner finger-like voids dominated the fibre cross-section at a low viscosity and a low air gap respectively. At increasing viscosity and air gap heights, the voids growth were inhibited by their respective contrast voids, due to the increased of kaolin particles amount at distributed particle size coupled with the gravitational effect and a retention time for particles orientation. Sponge region were seen to dominate the fibre cross-section in the most viscous (ratio of kaolin/PESf 3.5 (S6)) fibres spun at 6 cm (the longest air gap). After sintering, fibres asymmetric structures were retained; however, the S6 fibre outer finger-like voids sintered at 1600 °C were eliminated. The kaolin fibre morphology showed versatile structures depending on the process condition used.

ABSTRAK

Membran gentian berongga seramik (MGBS) digunakan disebabkan nisbah permukaan berbanding isipadu yang tinggi dan stabil dalam persekitaran yang ektrim. Pada masa kini, kajian tertumpu kepada penghasilan MGBS dengan menggunakan bahan seramik termaju (Al_2O_3, Ti_2O, ZrO_2 dll) yang tidak ekonomik. Oleh kerana itu, kaolin, sejenis bahan yang lebih ekonomik dicadangkan dalam kajian ini. Namun, keadaan pemintalan sedia ada yang digunakna untuk memintal bahan seramik termaju atau polimer untuk penghasilan membran gentian berongga didapati tidak sesuai untuk kaolin. Oleh itu, kajian ini mendedahkan pengetahuan asas dalam peyediaan MGBS berasaskan kaolin. Kajian morfologi adalah penting sebagai indikasi untuk melihat kesesuaian membran untuk diaplikasikan samada dalam pemisahan atau pemendapan pemangkin. Dalam kajian ini, pelbagai kelikatan suspensi disediakan yang mengandungi kaolin dan polietersulfon (PESf) sebagai polimer dan n-metil-2-pirolidon (NMP) sebagai pelarut. Suspensi ini kemudian dipintal pada jarak udara 0, 3 dan 6 sm dan kemudian disinter pada suhu di antara 1100 dan 1600 °C . Keputusan menunjukkan kelikatan suspensi berada dalam julat 1.280 x 10^3 dan 3.310 x 10^5 cp. Struktur keratan rentas yang sekata dihasilkan pada jarak udara lebih daripada 0 sm. Didapati dimensi spinneret yang lebih besar memerlukan jarak udara yang lebih tinggi bagi menghasilkan pintalan berterusan nasen gentian berongga. Melalui 'scanning mikroskop elektron' (SEM), stuktur asimetrik diperolehi untuk semua jenis gentian; dengan jejari luar dan jejari dalam mendominasi keratan rentas gentian pada suspensi yang berkelikatan rendah dan dipintal pada jarak udara rendah. Dengan kenaikan pada kelikatan suspensi dan jarak udara, pertumbuhan jejari ini direncatkan oleh jejari kontras masing-masing, kerana peningkatan jumlah partikel kaolin pada saiz yang berbeza dan digabungkan dengan kesan graviti dan bertambahnya masa retensi untuk partikel tersebut berorientas. Stuktur seperti span didapati mendominasi keratan kentas gentian pada gentian terlikat (nisbah kaolin/PESf 3.5 (S6)) dipintal pada jarak tertinggi (6 sm). Setelah disinter, serat struktur asimetrik pada semua gentian masih kekal, tetapi stuktur seperti jejari pada bahagian luar gentian S6 yang disinter pada suhu tertinggi (1600 °C) telah hilang. Secara keseluruhannya, morfologi serat kaolin menunjukkan struktur yang pelbagai yang bergantung kepada keadaan proses operasi yang digunakan.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CR	Centre region
DLVO	Derjaguin and Landau, Verwey and Overbeek
DMAc	Dimethylacetamide
EDM	Electrical discharge machining
FCC	Face-centered cubic
FESEM	Field emission scanning electron microscopy
FIV	Flow induced vibration
IL	Ignition loss
IR	Inner region
NMP	N-methyl-2-pyrrolidone
OD/ID	Outside diameter/inside diameter
OR	Outside region
PESf	Polyethersulfone
PES	Polyethersulfone
PVP	Polyvinylpyrrolidone
SEM	Scanning electron microscopy

LIST OF NOMENCLATURES

A	Area, m^2
C	Coefficient in the particle-particle pair interaction
c	Particle concentration, mol m^{-3}
J_1	Flux of diffused non-solvent, mol m^{-2} s^{-1}
J_2	Flux of diffused solvent, mol m^{-2} s^{-1}
k	Constant
N	Number of edges
N_c	Critical pore coordination number
Q	Cation
t	Time, s
V_b	Volume of the bed, m^{-3}
V_p	Volume of particles constituting a bed, m^{-3}
X	Anion
ρ_1 and ρ_2	Number of atoms per unit volume in two interacting bodies, m^{-3}
η_{sp}	Specific viscosity
ρ	Particle's density, kg m^{-3}
ε	Volumetric porosity
π	Circle's circumference divided by its diameter

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Overview

A membrane is a semipermeable barrier which permits the passage of one or more selected components of a gas and/or liquid mixtures though its wall. The passage is possible under certain driving forces which include pressure, concentration gradient or voltage differences across the membrane.

Application of membrane technology in an industrial process attracts users because it is more economical compared to other separation technology. These technologies include crystallization, absorption, adsorption, solvent extraction or cryogenics. Membranes are also being used due to the rise of energy costs in recent decades. They are also has the advantage in the ability to control the permeation rate of a chemical species, in which it is absent in other separation processes.

In the 1960s, the membrane market in the United States was worth under US$20 million. However, in 2003, Business Communications Company Inc. of Connecticut reported that its worth has increase to US$6.5 billion and is still growing at 6 % annually (Membrane market put at US$4.5 billion, 2003). These developments covered in six principal industrial process areas markets: microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas separation and pervaporation.

Continuous effort is being made to develop membranes with superior qualities that involves closely within a membrane production. In doing so, several key issues needed to be addressed particularly in the production technique to produce a durable membrane or membrane support for harsh environments, high permeability and high separation area with an economical production cost.

Recently, membrane technology development shows that ceramic membranes in hollow fibre configuration can become a potential solver for these issues. However, a ceramic hollow fibre membrane commonly suffers from problems such as brittleness that due to the defects occurred during the membrane production. These defects will become worsen in the proceeding stages which are the spinning process and the sintering process (Liu and Li, 2005). Another limitation of ceramic hollow fibre is the sintering process which is expensive, which adding to the production cost.

Interestingly, the economic issues of a ceramic hollow fibre membrane production could also be approached from material wise. Previous researchers have been using expensive advanced ceramics such as Al_2O_3, SiO_2 and TiO_2 to produce ceramic hollow fibre membranes. Recently, a motivation to use a more economic material arises when kaolin in aqueous suspension system proven can be used to produce a tubular membrane.

In contrast, a hollow fibre membrane is usually produced in a polymeric (non aqueous) suspension system. Following the motivation to study the kaolin/polymer spinning suspension, a fabrication system needs to be developed. Current data available for spinning conditions are only suitable for advanced ceramics/polymeric suspensions. These data are also sometimes not publicly available and are often considered a trade secret. Since the spinning system comprises a series of parameters that need to be controlled, a spinning condition needs to be established to tailor the production of a defect free kaolin hollow fibre.

Therefore it is important to understand the relationship among key steps in kaolin hollow fibre production which are suspension preparation, spinning process and sintering processes to produce a defect free low cost kaolin hollow fibre membrane. Accordingly, this study will look in depth into the hollow fibre production stages. The production stages important aspects will be covered to provide an understanding on kaolin hollow fibre membrane production. Through this contribution the kaolin hollow fibre membranes would find their niche in chemical reaction/separation, not replacing existing membranes, but rather contributing an added dimension to current capabilities.

1.2 Problem Statement

While literature on the polymeric hollow fibre membrane production is easily available, little information is found on the ceramic hollow fibre membrane production. Only a few published reports are accessible on preparing ceramic membranes in hollow fibre configuration; although the membrane is commercially available. This is due to the strictly commercial secret. The same situation applied to kaolin membrane production which is being produced mostly in flat sheet configuration. Therefore, the purpose of this study is to provide fundamental knowledge to prepare kaolin hollow fibre membrane by understanding the relationship between the production stages (spinning dope composition, spinning process and sintering process) and the fibre morphology structure. The results of this study should contribute to the knowledge of kaolin membrane fabrication. In achieving these goals, several objectives are outlined.

1.3 Research Objectives

The objective of this research is to produce kaolin hollow fibre membranes. Detail objectives include: with the following objectives:

a. To characterize the kaolin particle size and composition
b. To characterize the spinning suspension formulations viscosity at different kaolin/ Polyethersulfone ratios.
c. To study the operating conditions of the spinning process of air gaps and spinneret openings on the morphology structure of membrane precursors.
d. To investigate the effect of sintering temperatures on the morphology structure of sintered fibres.

1.4 Scope of Study

The research methodology of this study involves three main tasks which are suspensions preparation, spinning process and sintering process. Spinning suspension is usually characterized for its cloud point and viscosity measurement; however this study only focused on the viscosity study since cloud point is only vital in polymeric suspension system (Yeow *et al.*, 2005; Mansourizadeh *et al.*, 2010).

In spinning process, parameters such as suspension extrusion rate, bore fluid rate, tearing rate, air gap height and spinneret dimension are important (Mulder, 2000; Aroon *et al.*, 2010) to determine morphology and separation properties; but this study only focused on air gap (Liu *et al.*, 1992; Khayet, 2003; Tasselli *et al.*, 2005) and spinneret dimension (Chung *et al.*, 2000; Peng and Chung 2008) because these are among the most important parameters that influence the final morphology of nascent fibres.

In particular, the study of the effect spinneret dimension on ceramic suspension was never been done. In the sintering process, parameters such as sintering time, sintering temperature, shrinkage, cooling and heating rate influences the final product; however, in this study only the sintering temperature will be considered because it is the important effect that influence morphology structure transformation (Liu and Li, 2005; Mosadeghkhah *et al.*, 2007; Dong *et al.*, 2009) during sintering. The precursors and sintered fibres, are usually characterized for its permeability, pore size, porosity, and mechanical strength; nevertheless this study only focuses on the fibre morphology structure because it is among vital indicator to determine the membrane suitable application (Liu and Li, 2005; Wei *et al.*,2008; Kingsbury and Li, 2009). Therefore, the experimental work has been designed accordingly and shown in Figure 1.1.

1.5 Thesis Organization

Chapter 1 starts with a background overview of ceramic hollow fibre membrane. This chapter covers the membrane market and membrane applications, critical problems, objectives, and study scopes.

Chapter 2 presents the literature survey of ceramic hollow fibre technology and development. The chapter also explains extensively regarding the spinning formulation spinning process and sintering process used in this research.

Chapter 3 presents the formulation of ceramic suspension by varying the ceramic powder composition based on the literature recommended quantity.

The spinning process and sintering process method that is conducted to obtain the hollow fibre precursors and products are outlined. The suspension viscosity and microstructure characterization methods are also presented.

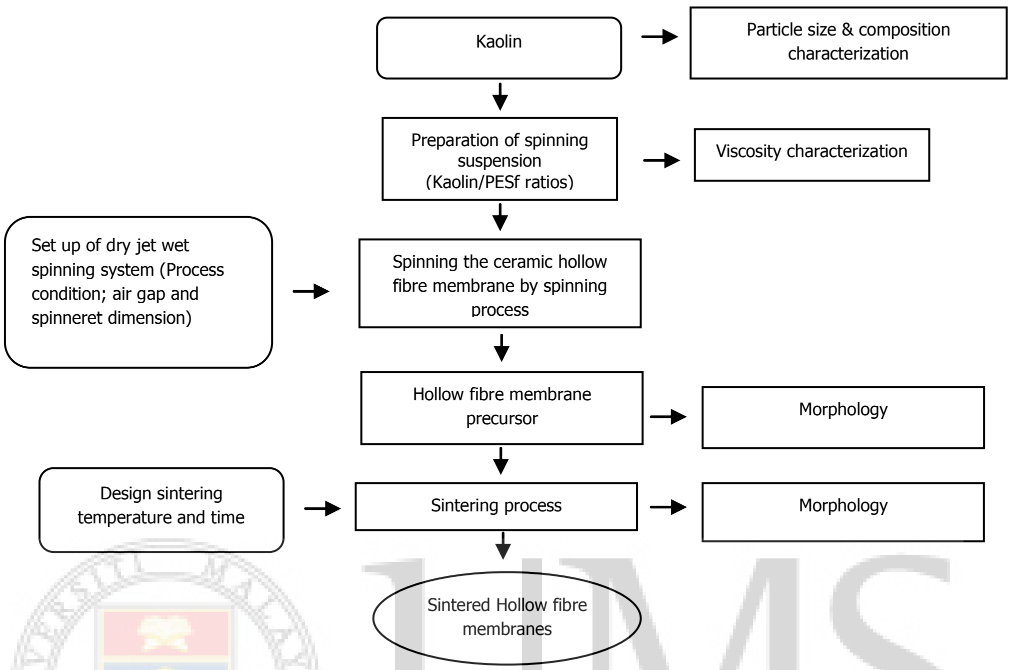

Figure 1.1: Experimental design of this study.

Chapter 4 presents the data obtained for viscosity and microstructure of the ceramic hollow fibre composition followed by discussion on the effect of viscosity, air gaps and sintering temperature to the microstructure of the ceramic hollow fibre.

Finally, Chapter 5 concludes the effect of various mixture components on the viscosity of the hollow fibre suspension. This chapter also concludes the effect of spinning parameters such as air gap, spinneret dimension and sintering temperature on the microstructure of the hollow fibre precursors and sintered fibres. Recommendation for future works are also included.