

**YELLOW OIL FORMATION AT ACID GAS REMOVAL UNIT
IN AN ETHYLENE PLANT**

Ms. Hathaikarn Choosuwan

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma
and Case Western Reserve University

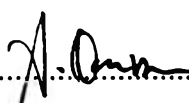
1997

ISBN 974-636-175-9

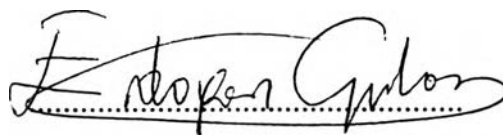
I 2109326x


Thesis Title : Yellow Oil Formation at Acid Gas Removal Unit
in An Ethylene Plant
By : Ms. Hathaikarn Choosuwan
Program : Polymer Science
Thesis Advisors : Prof. Erdogan Gulari
Dr. Nantaya Yanumet
Dr. Pramote Chaiyavech


Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfillment of the requirements for the Master's Degree of Science.


..... Director of the College
(Prof. Somchai Osuwan)

Thesis Committee


(Prof. Erdogan Gulari)


.....
(Dr. Nantaya Yanumet)


.....
(Assoc. Prof. Anuvat Sirivat)

ABSTRACT

952005 : POLYMER SCIENCE PROGRAM

KEY WORDS : YELLOW OIL / FOULING / CARBONYL

POLYMERIZATION / ALDOL CONDENSATION /

HATHAIKARN CHOOSUWAN : YELLOW OIL FORMATION

AT ACID GAS REMOVAL UNIT IN AN ETHYLENE PLANT.

THESIS ADVISORS : PROF. ERDOGAN GULARI, DR.

NANTAYA YANUMET, AND DR. PRAMOTE CHAIYAVECH

41 pp. ISBN 974-636-175-9

In the acid gas removal unit, a serious problem that reduces ethylene plant efficiency is fouling. Acid gas removal system is a unit of an ethylene plant that olefin producers use to carry out caustic scrubbing to remove acid gases from the cracked gas stream. This process produces carbonyl polymers commonly called yellow oil. An olefin producer in Thailand also encounters this problem. In this thesis we investigated the conditions leading to the formation of yellow oil and attempted to characterize it chemically. Finally hydroxylamine hydrochloride is employed to prevent the formation of the yellow oil.

บทคัดย่อ

หทัยกานต์ ชูสุวรรณ : การเกิดน้ำมันเหลืองที่หน่วยขจัดแก๊ซกรดในกระบวนการผลิตเอทิลีน (Yellow Oil Formation at Acid Gas Removal Unit in an Ethylene Plant) อ. ที่ปรึกษา : ศาสตราจารย์ เออโดแกน กุลารี่ ดร. นันทยา ยานูเมศ และ ดร. ปราโมทย์ ไชยเวช 41 หน้า ISBN 974-636-175-9

ในหน่วยขจัดแก๊ซกรด ปัญหาสำคัญที่ลดประสิทธิภาพการทำงานคือ การเกิดสิ่งอุดตัน หน่วยขจัดแก๊ซกรดเป็นหน่วยหนึ่งในกระบวนการผลิตเอทิลีน มีหน้าที่ขจัดแก๊ซกรดออกจากแก๊ซเอทิลีน ซึ่งกระบวนการนี้ได้เกิดพอลิเมอร์คาร์บอนิลเรียกว่าน้ำมันเหลือง ผู้ผลิตเอทิลีนในประเทศไทยได้ประสบปัญหานี้เช่นกัน ในงานวิจัยนี้ได้ค้นคว้าถึงสถานะที่ทำให้เกิดการก่อตัวของน้ำมันเหลืองและได้นำน้ำมันเหลืองมาวิเคราะห์ทางเคมี ในที่สุดได้มีการนำสารไฮดรอกซิลลามีนไฮโดรคลอไรด์มาทดลองเป็นตัวช่วยขยับปฏิบัติการเกิดน้ำมันเหลือง

ACKNOWLEDGMENTS

The author would like to express deepest gratitude to her advisors, Prof. Erdogan Gulari and Dr. Nantaya Yanumet for their constant enthusiasm and support throughout this study. Their invaluable guidance has been essential for the completion of this thesis.

She greatly appreciates all professors who have taught her and helped her gain the knowledge needed in this work. She is also greatly indebted to the faculty members and all the staff of the College who contributed in various degrees to the success of her thesis.

She would like to thank National Petrochemical Public Company for providing the financial support for her work and the Petroleum and Petrochemical College for providing her the scholarship for the two-year Master Degree program.

She also wishes to thank all the staff at NPC for helping her to start work during the first three months at Rayong and Erol Seker who helped with some experiments during her stay at the University of Michigan in March 1997.

Finally, she is indebted to her father, mother, brother, sister, and friends whose love, concern, encouragement and understanding played the greatest role in her success.

TABLE OF CONTENTS

CHAPTER		PAGE
	Title Page	i
	Abstract	iii
	Acknowledgments	v
	Table of Contents	vi
	List of Tables	viii
	List of Figures	ix
I	INTRODUCTION	
	1.1 An Overview of an Ethylene Plant	1
	1.2 Yellow Oil Formation in the Caustic Tower Operation	4
	1.3 Carbonyl Fouling Mechanisms	7
	1.4 Literature Reviews	8
	1.5 Objectives	10
II	EXPERIMENTAL SECTION	
	2.1 Materials	11
	2.2 Instrumentation and Characterization Techniques	
	2.2.1 Fourier Transform Infrared (FTIR) Spectroscopy	12
	2.2.2 Gel Permeation Chromatography	13
	2.2.3 Elemental Analysis	13
	2.3 Procedures	
	2.3.1 The Aldol Condensation of Acetaldehyde	15
	2.3.2 Carbonyl Stabilization Reaction	16

CHAPTER	PAGE
III RESULTS AND DISCUSSION	
3.1 Gross Observations	17
3.2 Characterization of the Yellow Oil and Aldol Condensation Products	
3.2.1 Elemental Analysis	17
3.2.2 Fourier Transform Infrared Spectroscopy	21
3.2.3 Size Exclusion Chromatography (SEC)	27
3.3 Carbonyl Polymerization and Stabilization	
3.3.1 Carbonyl Stabilization by Using Hydroxylamine as Stabilizer	30
3.3.2 Time Study of Aldol Condensation Reaction by UV-visible Spectroscopy	32
IV CONCLUSIONS	38
REFERENCES	39
CURRICULUM VITAE	41

LIST OF TABLES

TABLE		PAGE
3.1	Elemental analysis data of yellow oil and products from aldol condensation reaction	18
3.2	The conversion of elemental data into an empirical formula of the yellow oil sample	19
3.3	Band assignments of yellow oil spectrum	21
3.4	The carbonyl stabilization by using hydroxylamine as stabilizer in 100 ml aldol condensation solution (varies weight of stabilizer)	31

LIST OF FIGURES

FIGURE	PAGE
1.1 The simplified olefin block flow diagram	3
1.2 Flow diagram of caustic scrubber system	6
1.3 The aldol condensation reaction of carbonyl compound	7
3.1 The aldol condensation of acetaldehyde under basic condition	20
3.2 Spectrum of yellow oil (solid) prepared by KBr pellet technique	24
3.3 Comparison between spectrum of yellow oil and spectrum of aldol condensation product (reaction time 3 h.)	25
3.4 Spectra of aldol condensation products in various times	26
3.5 The molecular weight distribution of yellow oil	27
3.6 The molecular weight distributions of yellow oil sample and sample from aldol condensation, reaction time 24 h.	28
3.7 The changing of molecular weight distributions of products from aldol condensation at various times	29
3.8 The chemical reaction between acetaldehyde and hydroxylamine	30
3.9 UV spectrum of aldol condensation product, reaction time 5 min.	33
3.10 UV spectrum of aldol condensation product, reaction time 10 min.	33
3.11 UV spectrum of aldol condensation product, reaction time 30 min.	34
3.12 UV spectrum of aldol condensation product, reaction time 1 h.	34
3.13 UV spectrum of aldol condensation product, reaction time 2 h.	35
3.14 UV spectrum of aldol condensation product, reaction time 4 h.	35
3.15 UV spectrum of aldol condensation product, reaction time 6 h.	36
3.16 UV spectrum of aldol condensation product, reaction time 8 h.	36

FIGURE**PAGE**

3.17 UV spectrum of aldol condensation product, reaction time 10 h. 37