REDUCTION OF FOULING IN A CAUSTIC TOWER

1.1

Mr. Sakchai Thawanworakit

A Thesis Submitted in Partial Fulfilment 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 2000

ISBN 974-334-146-3

1 19303076

Thesis Title	:	Reduction of Fouling in a Caustic Tower
By	:	Mr. Sakchai Thawanworakit
Program	:	Petrochemical Technology
Thesis Advisors	:	Prof. Erdogan Gulari
		Prof. Pramote Chaiyavech
		Asst. Prof. Thirasak Rirksomboon
		Dr. Pramoch Rangsunvigit

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

(Prof. Somchai Osuwan) College Director

Thesis Committee:

(Prof. Erdogan Gutari)

Francte Chaiyaved

(Prof. Pramote Chaiyavech)

(Asst. Prof. Thirasak Rirksomboon)

(Dr. Pramoch Rangsunvigit)

N. Yanumit. (Dr. Nantaya Yanumet)

ABSTRACT

4171025063: PETROCHEMICAL TECHNOLOGY PROGRAM

KEYWORD: Caustic Tower/Antipolymerant/ Antifoulant/ Aldol Condensation
Sakchai Thawanworakit: Reduction of Fouling in a Caustic Tower. Thesis Advisors: Prof. Erdogan Gulari, Prof. Pramote Chaiyavech, Asst. Prof. Thirasak Rirksomboon, and Dr. Pramoch Rangsunvigit, 63 pp. ISBN 974-334-146-3

It was found that the aldol condensation of aldehyde can possibly be the cause of the fouling in a caustic tower. A systematic method of following the fouling formation using a colorimeter was applied. The effects of temperature, concentration of aldehyde, and concentration and type of antipolymerants on the aldol condensation were investigated. It was shown that aldol condensation rates increased with increasing temperature. The aldol condensation rate was proportional to the concentration of aldehyde present. Two antipolymerants used in this work were hydroxylamine hydrochloride and hydroxylamine sulfate. Both antipolymerants inhibited the aldol condensation, and their efficiency decreased with increasing temperature. The efficiency of the reduction was found to be proportional to the concentration of antipolymerant. Comparison of the two antipolymerants indicates that hydroxylamine sulfate is more preferable for reducing fouling. Sodium sulfate, which is present in the spent caustic treatment unit, was found to be a promoter for fouling even in small amounts.

บทคัดย่อ

ศักดิ์ชัย ถวัลย์วรกิจ : การลดการอุดดันในหอคอสติก (Reduction of Fouling in a Caustic Tower) อ. ที่ปรึกษา : ศ. เออร์โดกัล กูลาลี, ศ. ปราโมทย์ ไชยเวช, ผศ. ธีรศักดิ์ ฤกษ์ สมบูรณ์ และ ดร. ปราโมช รังสรรค์วิจิตร 63 หน้า ISBN 974-334-146-3

งานวิจัขนี้เกี่ยวข้องกับการศึกษาการถดการอุดตันในหอดอสติกโดยขั้นดุ้นได้ทำการหา สาเหตุของการอุดดันพบว่ามาจากปฏิกิริยาอักดักอบเด็นเซชั่น การติดตามการเกิดปฏิกิริยาอักดัก ดอนเด็นเซชั่นทำโดยใช้เครื่องวัดสี นอกจากนั้นได้ทำการศึกษาผลของอุณหภูมิ ความเข้มข้นของ อัลดัลดีไฮด์ ความเข้มข้นของสารยับยั้งการเกิดโพลีเมอร์และชนิดของสารยับยั้งการเกิดโพลีเมอร์ ต่อปฏิกิริยาอัลดัลดอนเด็นเซชั่น ผลการทดลองซี่ให้เห็นว่าอัตราการเกิดปฏิกิริยาอัลดัลดอนเด็นเซ ชั่นจะเพิ่มขึ้นเมื่ออุณหภูมิสูงขึ้นและอัตราการเกิดปฏิกิริยาอะขึ้นกับความเข้มข้นของอัลดีไฮด์ สาร ยับยั้งการเกิดโพลีเมอร์ที่ใช้การศึกษาได้แก่ ไฮดรอกซีเอมีนไฮโดรครอไรด์และไฮดรอกซีเอมีนซัล เฟต การทดลองแสดงให้เห็นว่าสารยับยั้งการเกิดโพลีเมอร์ทั้งสองตัวสามารถยังยั่งการเกิดปฏิกิริยา อัลดัลดอนเด็นเซชั่นได้และประสิทธิภาพจะลดลงเมื่ออุณหภูมิเพิ่มขึ้น ประสิทธิภาพของการลด การอุดดันจะขึ้นกับความเข้มข้นของสารยับยั้งการเกิดโพลีเมอร์ทั้งสองตัวสามารถยังยั่งการเกิดปฏิกิริยา อัลดัลกอนเด็นเซชั่นได้และประสิทธิภาพจะลดลงเมื่ออุณหภูมิเพิ่มขึ้น ประสิทธิภาพของการลด การอุดดันจะขึ้นกับความเข้มข้นของสารยับยั้งการเกิดโพลีเมอร์และจากการเปรียบเทียบประสิทธิ ภาพของสารยับยั้งการเกิดโพลีเมอร์ทั้งสองตัวพบว่าไฮดรอกซีเอมีนซัลเฟตมีประสิทธิภาพที่ดีกว่า นอกจากนั้นยังพบว่าโซเดียมซัลเฟตซึ่งมีอยู่ในระบบบำบัดคอสติกเป็นดัวเร่งไท้เกิดการอุดดันใน อปกรณ์ที่ใช้ในระบบบำบัดคอสติก

ACKNOWLEDGEMENTS

I would like to gratefully give special thanks to my advisors, Professor Erdogan Gulari and Dr. Pramoch Rangsunvigit for their constructive criticism and valuable suggestions. I am also deeply indebted to my co-advisors. Professor Pramote Chaiyavech and Dr. Thirasak Rirksomboon for their intensive suggestions, valuable guidance and vital help throughout this research work.

I greatly appreciate all the professors who have tendered invaluable knowledge to me at the Petroleum and Petrochemical College, Chulalongkorn University, and Mr. Surachit Huadsarkhar at the chemical engineering department. Mahidol University, who trained and provided me the technical knowledge on the specific instruments required for this research work.

I wish to express my thanks to all of my friends and to the college staff who willingly gave me warm support and encouragement and to the National Petrochemical Public Co., Ltd. for technical support during the period of the study.

Finally, I am deeply indebted to my family for their love, understanding, encouragement, and for being a constant source of inspiration.

TABLE OF CONTENTS

		PAGE
	Title Page	i
	Abstract (in English)	iii
	Abstract (in Thai)	iv
	Acknowledgements	V
	Table of Contents	vi
	List of Tables	viii
	List of Figures	ix
CHAPTER		
I	INTRODUCTION	1
II	LITERATURE SURVEY	3
	2.1 Fouling Mechanism	3
	2.2 Carbonyl Fouling Mechanism	4
	2.3 Reduction of the Fouling in a Caustic Tower	8
III	EXPERIMENTAL SECTION	11
	3.1 Aldol Condensation of Acetaldehyde	11
	3.2 Reduction of the Fouling by Antipolymerants	12
	3.3 Effects of Sodium Sulfate on the Aldol Condensation	12
	3.4 Characterization of the Organic Substance in the Spen	t
	Caustic from the Caustic Tower	13
IV	RESULTS AND DISCUSSION	15
	4.1 Characterization of the Spent Caustic	15

CHAPTER

V

4.2 Aldol Condensation of Acetaldehyde	20
4.3 Reduction of Fouling by Antipolymerants	28
4.3.1 Hydroxylamine Hydrochloride as an	
Antipolymerant	28
4.3.2 Hydroxylamine Sulfate as an Antipolymerant	37
4.3.3 Efficiency of Antipolymerants	45
4.4 Effects of Sodium Sulfate on the Aldol Condensation	49
CONCLUSIONS AND RECOMMENDATIONS	52
5.1 Conclusions	52
5.2 Recommendations	53
REFERENCES	54
APPENDICES	55
CURRICULUM VITAE	63

LIST OF TABLES

TABLE

A-1	Relationship between the absorbance of the yellow color of	
	the aldol product and time at 25°C in 1%wt NaOH solution.	55
A-2	Relationship between the absorbance of the yellow color of	
	the aldol product and time at 35°C in 1%wt NaOH solution.	56
A-3	Relationship between the absorbance of the yellow color of	
	the aldol product and time at 50°C in 1%wt NaOH solution.	56
A-4	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of antipolymerants and	
	time at 25°C in 1%wt NaOH solution with concentration ratio	
	of acetaldehyde to NaOH 1:1.	57
A-5	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of antipolymerants and	
	time at 35°C in 1%wt NaOH solution with concentration ratio	
	of acetaldehyde to NaOH 1:1.	57
A-6	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of antipolymerants and	
	time at 50°C in 1%wt NaOH solution with concentration ratio	
	of acetaldehyde to NaOH 1:1.	58
A-7	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of sodium sulfate and	
	time at 25°C in 1%wt NaOH solution with concentration ratio	
	of acetaldehyde to NaOH 1:1.	58

PAGE

LIST OF FIGURES

.

FIGURE		PAGE
2.1	Caustic tower.	6
4.1		-
	FT-IR spectrum of the spent caustic.	18
4.2	FT-IR spectrum of the yellow oil and the aldol condensation	10
	product.	19
4.3	Relationship between the absorbance of the yellow color of	
	the aldol product and time at 25°C.	21
4.4	Relationship between the absorbance of the yellow color of	
	the aldol product and time at 35°C.	22
4.5	Relationship between the absorbance of the yellow color of	
	the aldol product and time at 50°C.	23
4.6	Relationship between the absorbance of yellow color of	
	the aldol product and time at the 1:1 acetaldehyde to sodium	
	hydroxide concentration.	24
4.7	Relationship between the absorbance of the yellow color of	
	the aldol product and time at the 0.75:1 acetaldehyde to sodium	
	hydroxide concentration.	25
4.8	Relationship between the absorbance of the yellow color of	
	the aldol product and time at the 0.5:1acetaldehyde to sodium	
	hydroxide concentration.	26
4.9	Relationship between the absorbance of the yellow color of	
	the aldol product and time at the 0.25:1 acetaldehyde to sodium	l
	hydroxide concentration.	27
4.10	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine	

FIGURE

	hydrochloride and time at 25°C.	29
4.11	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine	
	hydrochloride and time at 35°C.	30
4.12	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine	
	hydrochloride and time at 50°C.	31
4.13	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine	
	hydrochloride and time at the 1:1 hydroxylamine hydrochloride	
	to acetaldehyde concentration.	32
4.14	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine	
	hydrochloride and time at the 0.5:1 hydroxylamine hydrochloride	2
	to acetaldehyde concentration.	33
4.15	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine	
	hydrochloride and time at the 0.25:1 hydroxylamine hydrochlorid	le
	to acetaldehyde concentration.	34
4.16	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine	
	hydrochloride and time at the 0.1:1 hydroxylamine hydrochloride	2
	to acetaldehyde concentration.	35
4.17	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine sulfate	
	and time at 25°C.	39

4.18	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine sulfate	
	and time at 35°C.	40
4.19	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine sulfate	
	and time at 50°C.	41
4.20	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine sulfate	
	and time at the 1:1 hydroxylamine sulfate to acetaldehyde	
	concentration.	42
4.21	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine sulfate	
	and time at the 0.5:1 hydroxylamine sulfate to acetaldehyde	
	concentration.	43
4.22	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of hydroxylamine sulfate	
	and time at the 0.25:1 hydroxylamine sulfate to acetaldehyde	
	concentration.	44
4.23	Comparison of the antipolymerant efficiency at 25°C.	46
4.24	Comparison of the antipolymerant efficiency at 35°C.	47
4.25	Comparison of the antipolymerant efficiency at 50°C.	48
4.26	Relationship between the absorbance of the yellow color of	
	the aldol product from the addition of sodium sulfate	
	and time at 25°C.	51
B-1	Reduction efficiency of the antipolymerants at 25°C.	59
B-2	Reduction efficiency of the antipolymerants at 35°C.	59

PAGE

FIGURE

B-3	Reduction efficiency of the antipolymerants at 50°C.	60
C-1	Relationship between the absorbance of the yellow color of	
	the aldol product and temperature(K) in 1%wt NaOH solution	
	at 15 minutes.	61
C-2	Relationship between the absorbance of the yellow color of	
	the aldol product and temperature(K) in 1%wt NaOH solution	
	at 20 minutes.	62