THE EFFECT OF PRECIPITANT ON APHALTENE AGGREGATION AND DEPOSTION

5

Wattana Chaisoontornyotin

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, Case Western Reserve University, and Institut Français du Pétrole

2013

T. 2.837289X

The Effect of Precipitant on Asphaltene Aggregation and
Deposition
Wattana Chaisoontornyotin
Petrochemical Technology
Prof. H. Scott Fogler
Asst. Prof. Pomthong Malakul

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

College Dean

(Asst. Prof. Pomthong Malakul)

Thesis Committee:

H.Scott Fog

(Prof. H. Scott Fogler)

me

(Asst. Prof. Pomthong Malakul)

umath Chinaly

(Prof. Sumaeth Chavadej)

Verrapet Testayale

(Dr. Veerapat Tantayakom)

ABSTRACT

5471030063: Petrochemical Technology Program Wattana Chaisoontornyotin: The Effect of Precipitant on Asphaltene Aggregation and Deposition. Thesis Advisors: Prof. H. Scott Fogler and Asst. Prof. Pomthong Malakul 50 pp. Keywords: Asphaltene/ Precipitant/ Aggregation/ Deposition

Asphaltenes are fraction of crude oil that cause serious problems in the petroleum industry. The goal of this study is to compare trends in asphaltene aggregation and deposition. More specifically, to relate the asphaltene aggregation particle-particle collision efficiency to the deposition rate by varying the precipitant carbon number and concentration. Establishing a relationship between the aggregation and deposition behavior of asphaltenes will provide valuable insight into both processes. The amount of asphaltenes that are destabilized with different precipitants and at various concentrations was obtained from centrifugation experiments, and the collision efficiency for asphaltene aggregation was calculated using a geometric population balance model. The results revealed that for a fixed volume fraction of precipitant, the asphaltene-asphaltene collision efficiency decreased with higher carbon number precipitants. Decreasing the precipitant concentration resulted in lower collision efficiency. A correlation between collision efficiency and mixture solubility parameter was established for the oil used and different precipitants. In order to investigate asphaltene deposition behavior using different precipitants, the deposition rate was measured using capillary flow. The consistency of the capillary deposition apparatus has been improved by considering the initial inner diameter of the capillary. Scanning electron microscopy (SEM) images of the asphaltene deposits were obtained and used to assess the mixing of oil and precipitant.

บทคัดย่อ

วรรธนะ ชัยสุนทรโยธิน : ผลของสารตกตะกอนต่อการรวมตัวและการเกาะติดของ แอลฟัลทีน (The Effect of Precipitant on Asphaltene Aggregation and Deposition) อาจารย์ที่ปรึกษา: ศาสตราจารย์ ดร. เอช สก๊อตต ฟอกเลอร์ และผู้ช่วยศาตราจารย์ ดร. ปมทอง มาลากุล ณ อยุธยา 50 หน้า

แอลฟัลทีนคือส่วนประกอบในน้ำมันดิบที่ก่อให้เกิดปัญหาสำคัญในอุตสาหกรรม จดประสงค์ของงานวิจัยนี้คือ ทำการเปรียบเทียบแนวโน้มของการรวมตัวและการ ปิโตรเลียม เกาะติดของแอลฟัลทีนและเชื่อมโยง collision efficiency ระหว่างอนุภาคในการรวมตัวของแอล ฟัลทีนกับอัตราการเกาะติดของแอลฟัลทีนโดยทำการเปลี่ยนจำนวนการ์บอนและความเข้มข้นของ สารตกตะกอน ทั้งนี้ ปริมาณแอลฟัลทีนซึ่งถูกทำให้ไม่เสถียรโคยใช้สารตกตะกอนและความ เข้มข้นต่างๆสามารถหาได้จากการทดลองโดยใช้การเหวี่ยง ส่วน collision efficiency ของการ รวมตัวของแอลฟัลทีนนั้นสามารถคำนวณได้จากการใช้โมเคลgeometric population balance ผล จากการทคลองแสคงให้เห็นว่าที่ความเข้นข้นคงที่ collision efficiency ระหว่างแอลฟัลทีนลคลง ตามการเพิ่มจำนวนการ์บอนของสารตกตะกอน ส่วนการลดความเข้มข้นของสารตกตะกอนส่งผล ให้ collision efficiency มีค่าลุคลง ความสัมพันธ์ระหว่าง collision efficiency และ solubility parameter ของของผสมสำหรับน้ำมันที่ใช้และสารตกตะกอนต่างๆถูกสร้างขึ้นสำหรับน้ำมันและ สารตกตะกอนต่างๆ ที่ใช้ นอกจากนี้ พฤติกรรมการเกาะติดของแอลฟัลทีนโดยใช้สารตกตะกอน ต่างๆ ได้ถูกศึกษาโดยวัดอัตราการเกาะติดด้วยอุปกรณ์การไหลในแคปปิลารี่ และทำการปรับปรุง ้ความสอดคล้องของการวัดการเกาะติดในแคปปิลารี่ โดยการคำนึงถึงขนาดเส้นผ่านศูนย์กลาง ภาพของแอลฟัลทีนที่เกาะติดที่ถ่ายโดยใช้กล้องจุลทรรศน์อิเลคตรอนถูก ภายในของแคปปิลารื่ นำมาใช้ในการประเมินการผสมของน้ำมันและสารตกตะกอน

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my advisor, Prof. H. Scott Fogler for giving me a great opportunity and a memorable experience to do research at the University of Michigan. I also would like to thank my co-advisor, Asst. Prof. Pomthong Malakul for being helpful in my thesis and giving advices to me. Moreover, I am very grateful to have Prof. Sumaeth Chavadej and Dr. Veerapat Tantayakom as my thesis committee.

I would also like to thank the group members, Michael Hoepfner, Nasim Haji Akbari Balou, Claudio Vilas Boas Favero, and Nina Gasbarro, for numerous helpful suggestions and valuable discussion. In addition, I would like to thank Phitsanu Teeraphapkul for helping in performing onset experiments.

The author would like to thank the sponsors of the University of Michigan Industrial Affiliates Program for financial support. Program members include the following: Chevron, ConocoPhillips, MSi Kenny, NALCO, BP, Shell, Statoil and Total. I am also grateful for the scholarship and funding of the thesis work provided by the Petroleum and Petrochemical College; and the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand

I would like to acknowledge and thank the University of Michigan staffs: Laura Bracken, Susan Hamlin, Michael Africa, Shelley Fellers, and Pablo Lavalle who provided technical support, departmental and visiting scholar business.

I would like to give special thanks to Thanawat Thanthong for many helpful discussions and Thammaporn Somkhan for contributed to proofread many of my manuscript.

Finally, I would like to give a personal thank to my family for their support and encouragement. Thank you very much.

TABLE OF CONTENTS

Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	x

PAGE

CHAPTER

Ι	INTRODUCTION	1
II	LITERATURE REVIEW	3
	2.1 Crude Oil and Asphaltenes	3
	2.2 Asphaltene Precipitation	3
	2.3 Population Balance Model	8
	2.4 Asphaltene Deposition	10
III	EXPERIMENTAL	15
	3.1 Materials	15
	3.1.1 Crude Oil	15
	3.1.2 Precipitants	15
	3.1.3 Toluene	16
	3.2 Equipment	16
	3.2.1 Nikon Eclipse E600 optical microscope	16
	3.2.2 Sorvall Legend X1R Centrifuge	16
	3.2.3 Hardvard apparatus 22 Syringe pump	16

	3.2.4 Scale Calibration	17
	3.2.5 Eppendorf Micro Centrifuge 5418	17
	3.2.6 Branson 1510 Sonicator	17
	3.2.7 Fisher Scientific Isotemp Incubator	17
	3.2.8 Sensotec A-5/882-15 pressure transducer	17
	3.2.9 Cole-Parmer Polystat Heated Circulating Baths	17
	3.2.10 Teledyne ISCO Model 500D Syringe pump	17
	3.2.11 Stainless steel capillary	18
	3.3 Software	18
	3.3.1 WinTV2000	18
	3.3.2 NI Datalogger	18
	3.3.3 MatLab	18
	3.4 Methodology	18
	3.4.1 Crude Oil Pre-Treatment	18
	3.4.2 Centrifugation Experiment	18
	3.4.3 Onset Experiment	19
	3.4.4 Asphaltene Deposition	20
	3.4.5 Measuring Diameter of Capillary	20
IV	RESULTS AND DISCUSSION	21
	4.1 Amount of Precipitated Asphaltenes	21
	4.2 Collision Efficiency	24
	4.3 A Correlation between Collision Efficiency and Solubility	
	Parameter	27
	4.4 Asphaltene Deposition	32
v	CONCLUSIONS AND RECOMMENDATIONS	41
	REFERENCES	42

CHAPTER	PAGE
APPENDIX	45
Appendix A Population Balance Model Fit	48
Appendix B Onset Time of Oil A	48
CURRICULUM VITAE	50

LIST OF TABLES

TABLE		PAGE
3.1.1.1	SARA composition of Oil A	15

	1	
3.1.1.2	Physical properties of Oil A	15
3.1.2.1	Physical properties of Precipitants	16
4.3.1	Refractive index and solubility parameter of Oil A and	29
	precipitants at 60°C	
4.3.2	Solubility parameter at 60°C from Akbarzadeh's work in	29
	2005 and the relation between the RI and solubility	
	parameter for paraffinic and aromatic hydrocarbons at 60°C.	
4.3.3	Solution solubility parameter at 60°C for various volume %	30
	precipitants in Oil A	
4.4.1	Capillary Diameters	38

LIST OF FIGURES

FIGU	FIGURE	
2.2.1	The amount of precipitated asphaltenes as a function of	
	precipitant.	4
2.2.2	Micrographs showing asphaltene precipitation for a crude-	
	heptane mixture containing 50 vol. % heptane and 50 vol. %	
	K-1 crude oil as a function of time.	5
2.2.3	The amount of precipitated asphaltene as a function of time	
	at 50 vol. % heptane for K-1 crude oil.	5
2.2.4	Yield of precipitated asphaltene at various precipitants and	
	precipitant concentrations as a function of carbon number of	
	precipitant.	6
2.2.5	Master curve for relation between detection time and the	
	difference between solubility parameter of asphaltene and	
	solution squared at 20°C.	7
2.3.1	Experimental and simulated evolution of the separated	
	aggregates using for 50 vol. % heptane.	8
2.3.2	The collision efficiency of K1 crude oil as a function of	
	heptane concentration from previous work.	9
2.4.1	The capillary deposition apparatus set up.	11
2.4.2	The CFD simulations of the mixing section indicated that	
	crude oil and heptane are completely mixed before they	
	reach the outlet.	11
2.4.3	The pressure drop profile with varying heptane	
	concentrations.	12
2.4.4	Normalized deposition pressure drop for heptane in Oil A,	
	scaled by viscosity and the concentration of insoluble	
	asphaltenes in the capillary and time is shifted by the	
	deposition induction time, t _d .	13

2.4.5	SEM images from the capillary inlet (left) and outlet (right)	
	with 0.02 inch ID and 5 cm length capillary at 30 vol. $\%$	
	heptane for 3 runs	14
3.4.2.1	Schematic of a centrifugation experiment.	19
4.1.1	Amount of precipitated asphaltenes for Oil A at 60°C for 35	
	vol. % heptane, octane, nonane, and decane.	22
4.1.2	Amount of precipitated asphaltenes for Oil A at 60°C for 30	
	vol. % heptane.	22
4.1.3	Amount of precipitated asphaltenes for Oil A at 60°C for 40	
	vol. % decane.	23
4.1.4	Amount of precipitated asphaltenes at equilibrium for 35	
	vol. % heptane, octane, nonane, and decane as a function of	
	carbon number of precipitants at 60°C.	23
4.2.1	Amount of asphaltene precipitated as a function of time at	
	minimum SSE between the simulated and experimental	
	results for Oil A at 60°C and 35 vol. % heptane.	24
4.2.2	Amount of asphaltene precipitated as a function of time for	
	Oil A at 60°C for 35 vol. % heptane.	25
4.2.3	Amount of asphaltene precipitated as a function of time at	
	minimum SSE between the simulated results using all, the	
	first portion, and the second portion of the data and	
	experimental results for Oil A at 60°C and 35 vol. %	
	heptane.	26
4.2.4	The collision efficiency at minimum SSE with min-max	
	error bar for Oil A at 60°C for different precipitants and	
	different precipitant concentrations.	27
4.3.1	Detection time for Oil A at 60°C for 35 vol. % heptane,	
	octane, nonane, and decane.	31

4.3.2	Asphaltene solubility parameter for Oil A at 60°C for	
	heptane, octane, nonane, and decane.	31
4.3.3	The correlation between collision efficiency and solubility	
	parameter for Oil A at 60°C.	32
4.4.1	Pressure drop trajectory for Oil A at 60°C for 35 and 30	
	vol. % heptane.	33
4.4.2	Pressure drop trajectory of the previous and current results	
	for Oil A at 60°C for 35 and 30 vol. % heptane.	33
4.4.3	Capillary diameters of 35 and 30 vol. % heptane of previous	
	results and current results.	34
4.4.4	The pressure drop trajectory for Oil A at 60°C for 35 and 30	
	vol. % heptane normalized by using radius of capillary.	35
4.4.5	The normalized pressure drop trajectory for Oil A at 60°C	
	for 35 and 30 vol. % heptane.	35
4.4.6	The pressure drop trajectory for Oil A at 60°C for 35 vol. %	
	decane.	36
4.4.7	SEM images of the deposit at capillary inlet of 35 vol. $\%$	
	decane in Oil A. Image a. is an unused capillary inlet and	
	images b. and c. are used capillary inlet.	37
4.4.8	The normalized pressure drop trajectory for Oil A at 60°C	
	for 35 vol. % octane.	37
4.4.9	The normalized pressure drop trajectory for Oil A at 60°C	
	for 35 vol. % hexane.	38
4.4.10	SEM images of the deposition capillary inlet of 35 vol. %	
	octane (1a. and 1b.) and hexane (2a. and 2b.) in Oil A.	39
4.4.11	The normalized pressure drop trajectory for Oil A at 60°C	
	for various precipitants and precipitant concentrations.	40

4.4.12	The average of normalized pressure drop trajectory for Oil A	
	at 60°C for various precipitants and precipitant	
	concentrations without the induction time.	40
Al	Amount of asphaltene precipitated as a function of time at	
	minimum SSE between the simulated results using all, the	
	first portion, and the second portion data and experimental	
	results for Oil A at 60°C and 30 vol. % heptane.	45
A2	Amount of asphaltene precipitated as a function of time at	
	minimum SSE between the simulated results using all, the	
	first portion, and the second portion data and experimental	
	results for Oil A at 60°C and 35 vol. % octane.	46
A3	Amount of asphaltene precipitated as a function of time at	
	minimum SSE between the simulated results using all, the	
	first portion, and the second portion data and experimental	
	results for Oil A at 60°C and 35 vol. % nonane.	46
A4	Amount of asphaltene precipitated as a function of time at	
	minimum SSE between the simulated results using all, the	
	first portion, and the second portion data and experimental	
	results for Oil A at 60°C and 35 vol. % decane.	47
A5	Amount of asphaltene precipitated as a function of time at	
	minimum SSE between the simulated results using all, the	
	first portion, and the second portion data and experimental	
	results for Oil A at 60°C and 40 vol. % decane.	47
B1	Optical Microscopy for Oil A at 60°C for 35 vol. % heptane	48
B2	Optical Microscopy for Oil A at 60°C for 35 vol. % octane	48
B3	Optical Microscopy for Oil A at 60°C for 35 vol. % nonane	49
B4	Optical Microscopy for Oil A at 60°C for 35 vol. % decane	49

PAGE