TANNIN FROM LOCAL *RHIZOPHORA MUCRONATA* BARKS AS DEFLOCCULANT IN DRILLING FLUIDS

NUR ASMA SASABILA BINTI LATEFI

A thesis submitted in fulfillment of the
Requirements for the award of the degree of
Master of Petroleum Engineering

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

JUNE 2018

"My dearest daddy, mum, family, lecturers and friends"

This is for all of you.

ACKNOWLEGDEMENT

First of all, i would like to express deepest gratitude to the Almighty and most Gracious Allah SWT for the blessing and opportunity for me to finish master proposal.

I would love to express my sincere thanks and great gratitude to my parents for their never ending support through out the entire project, my supervisor Assoc Prof Abdul Razak Ismail for guiding me throughout this entire process and for his brilliant advices, patience and ideas, former colleagues for all the knowledge, materials and equipment about drilling fluids tests and also staffs from Bioenergy Department, FRIM for the knowledge and all the respective engineers in SCOMI GRTC.

I would like to also thank my fellow friends for helping especially regarding the drilling fluids problems and fellow classmates for helping me out through out the whole research. Even simple deeds are a blessed, thank you for the help and cooperation.

ABSTRACT

Optimization of drilling fluids is required to make sure the drilling fluids performance is at its best. There are few elements in drilling fluids that can be optimized and one of it is dispersant. Dispersant in general substances added to the suspension to improve separation and also prevent it from settling and clumping. In drilling fluids or mud, dispersant were better referred as deflocculant. The major purpose of using deflocculant is to reduce viscosity of drilling fluids and prevent colloid to occur or any sorts of suspension in mud. One possible dispersant or thinner for drilling fluids identified is tannin from bark waste. In this report, the source of tannin is from the bark of *Rhizophora Mucronata* taken from Kuala Sepetang, Perak. The best extraction solvents are methanol and water at 100°C with total extraction time of 3 hours. There are 72.86% of condensed tannin and 0.1085% of hydrolysable tannin in *Rhizophora Mucronata*. Based on the experimental results performance, tannin extracts from *Rhizophora Mucronata* barks work best at temperature ranging from 225°F to 275°F with not more than 8 grams concentration. The plastic viscosity and yield point for tannin show similar results to the industrial tannin at these temperature and gram concentration. Therefore, for this master project it can be concluded that tannin from *Rhizophora Mucronata* is feasible to be used as deflocculant for drilling fluids as its performance is on par with industrial deflocculant.

ABSTRAK

Penambahbaikan bagi bendalir penggerudian diperlukan bagi memastikan prestasi bendalir penggerudian sentiasa terbaik. Terdapat beberapa elemen didalam bendalir penggerudian yang menjalani penambahbaikan, antaranya ialah penyahsebaran. Penyahsebaran merupakan bahan yang ditambah ke campuran bendalir penggerudian bagi meningkatkan lagi proses pemisahan dan juga menghalang berlakunya mendapan dan gumpalan. Dalam konteks bendalir penggerudian, bahan ini lebih dikenali sebagai penyahgumpalan. Tujuan utama penggunaan penyahgumpalan ini adalah untuk mengurangkan kelikatan bendalir penggerudian dan juga menghalang penggumpalan untuk berlaku di dalam campuran bendalir penggerudian. Dalam kajian ini, sumber yang digunakan adalah dari spesis *Rhizophora Mucronata* daripada Kuala Sepetang. Metanol dan air telah dikenalpasti sebagai pelarut yang paling efektif dengan suhu 100°C selama 3 jam. Terdapat 72.86% adalah tannin pekat manakala 0.1085% adalah tannin terhidrolisis di dalam spesies *Rhizophora Mucronata*. Berdasarkan hasil ujian, ia dapat dikenalpasti bahawa tannin dari *Rhizophora Mucronata* dapat berfungsi sebagai penyahgumpalan bagi bendalir penggerudian dengan suhu bermula dari 225°F hingga 275°F dan had berat sebanyak 8 grams. Kelikatan plastik dan tahap alah menunjukkan prestasi yang sama dengan penyahgumpalan yang digunakan dalan industri pada suhu dan kepekatan grams tersebut. Oleh itu, bagi projek ini tannin dari *Rhizophora Mucronata* dikenal pasti standing dengan penyahgumpalan yang digunakan dalam industri.

TABLE OF CONTENT

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
	LIST OF ABBREVIATIONS	xii
	LIST OF SYMBOLS	xiii
	LIST OF APPENDICES	xiv
1	**INTRODUCTION**	**1**
	1.1 Research Background	1
	1.2 Problem statement	2
	1.3 Project Objectives	3
	1.4 Scope of study	3
	1.5 Significance of study	4
2	**LITERATURE REVIEW**	**5**

	2.1 Drilling Fluid	5
	2.2 Function of Drilling Fluid	6
	2.3 Type of Drilling Fluid	6
	2.4 Flocculation in water base drilling fluid	7
	2.5 Drilling Fluid Tests	12
	2.6 Tannin Extraction from Plant Source	15
	2.7 Tannin from *Rhizophora Mucronata* barks Chemical Characterisation	18
	2.8 Tannin from *Rhizophora Mucronata* barks as Deflocculant	20
3	**METHODOLOGY**	**22**
	3.1 Extraction of Tannin from *Rhizophora Mucronata* barks	22
	3.2 Characterisation of Tannin	24
	3.2.1 Condensed Tannin	24
	3.2.2 Hydrolysable Tannin	25
	3.3 Drilling Fluid Field Tests	27
4	**RESULTS AND ANALYSIS**	**30**
	4.1 Extraction of Tannin (Lab Scale)	30
	4.2 Analysis of Tannin Characterisation	32
	4.2.1 Condensed Tannin	32
	4.2.2 Hydrolysable Tannin	33
	4.3 Tannin Performance in Drilling Fluid	34
	4.3.1 Mud properties with 2g Additives at 225°F (Base Case)	34
	4.4 Optimisation of Tannin from *Rhizophora Mucronata* as Deflocculant in Drilling Fluid	38
	4.4.1 Temperature Effects on Tannin Performance	38
	4.4.2 Concentration Effects on Tannin Performance	41

5 CONCLUSIONS AND RECCOMENDATIONS 44

5.1 Conclusions 44

5.2 Recommendations 46

REFERENCES 47

APPENDICES A 52

APPENDICES B 54

APPENDICES C 60

LIST OF TABLES

TABLE NO	TITLE	PAGE
3.1	Mud formulation	27
4.1	Extraction for four different solvents	29
4.2	The condensed tannin (CT)	31
4.3	The hydrolysable tannin (HT)	32
4.4	Mud properties BHR at 225°F	34
4.5	Mud properties AHR at 225°F	35

TABLE OF FIGURES

FIGURE NO	TITLE	PAGE
2.1	High mud weight drilling fluid	9
2.2	Soxhlet extractor setup	16
2.3	Supercritical fluid extraction (SFE)	17
2.4	Pressurized water extraction (PWE) process flow.	18
2.5	*Rhizophora Mucronata* barks	19
2.6	Tannin extracts in powdered form	20
3.1	Grinded *Rhizophora Mucronata* barks	22
3.2	Laboratory Soxhlet Extraction Setup	23
3.3	Tannin extracted after 3 hours	24
3.4	Commercial tannin (desco)	28
3.5	After hot-rolled mud	29
4.1	PV and YP AHR with 2g concentration at 225°F	36
4.2	Gel strength with 2g concentration at 225°F	37
4.3	Temperature effects to the plastic viscosity PV	38
4.4	Temperature effects to the yield point YP	39
4.5	Temperature effects to the gel strength 10 min	40
4.6	Concentration effects to the plastic viscosity PV at 225°F	41
4.7	Concentration effects to the yield point YP at 225°F	42
4.8	Concentration effects to the gel strength 10 min	43

LIST OF ABBREVIATIONS

AHR	-	After hot-rolled
BHR	-	Before hot-rolled
CT	-	Condensed tannin
HCL	-	Hydrochloric acid
HT	-	Hydrolysable tannin
PV	-	Plastic viscosity
PWE	-	Pressurised water extraction
RBF	-	Round bottom flask
RPM	-	Revolution per minute
SI	-	Stiasy index
SE	-	Soxhlet extraction
SFE	-	Supercritical fluid extraction
YP	-	Yield point

LIST OF SYMBOLS

$\boldsymbol{\theta_{300}}$	-	Dial reading at 300rpm
$\boldsymbol{\theta_{600}}$	-	Dial reading at 600rpm

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Sample calculation	52
B	Methodology procedures	54
C	Additional experimental results	60

CHAPTER 1

INTRODUCTION

1.1 Research Background

This research is mainly focusing on the evaluation of natural and organic tannin extracts obtained from natural source *Rhizophora Mucronata* barks as deflocculant in drilling fluids and comparison with the commercially used deflocculant (desco deflocculant) available in oil and gas industry. The extractions of tannins were carried out using the Soxhlet standard procedures using four different solvents, which are acetone, toluene, water and methanol with 100% concentration respectively. Based on the experiment results, it is found that the most suitable solvens are methanol and water. Tannins extracts from *Rhizophora Mucronata* barks were then categorized as condensed tannins (CT) and Hydrolysable Tannins (HT). Further elaboration on the extraction process and analysis of CT and HT can be found in this research. Tannin extracted then brought to test for its effects on drilling fluids. The extracted tannins is identified to work as efficient as desco deflocculant in terms of treating the flocculation problem based on the viscosity, plastic viscosity (PV), yield point (YP) and gel strength. Details on the findings can be found through this research. Further research should be done to commercially use tannin extracts from *Rhizophora Mucronata* as industrial deflocculant.

1.2 Problem Statement

There are vast challenges that is related to the drilling fluid. Among the major problems are loss of circulation, stuck pipe, barite sag, shale instability and many more. These problems are related to one another thus making the designing of the drilling-fluid system vital. There are so many factors affecting the driling fluid systems, one of it is flocculation. Flocculation is a situation where formation of particle associations in a suspension creating a gel-like system of drilling fluid. Flocculation problem is often encountered during the discharging of the drilling fluids both during short-term and long-term transport processes during the pumping process. Short term transport includes the initial mixing and passive diffusion of drilling mud plumes (jets) and the initial sedimentation of mud solids. The long-term transport includes the re-suspension, dispersion, and deposition of drilling mud particles over longer periods of time.

Flocculation is not favorable in the industry depending on the situation and cases as it alters the properties of the drilling fluids. Among the properties affected are plastic viscosity, yield point, gel strengths and funnel viscosity as well as increase the fluid loss. Flocculation problems also structurally alters the clay particles in the fluid, which can increase the resistance to flow as they are more structured. Gel-like drilling mud can cause stuck pipe, increase in viscosity thus requires more pump power as well as potentially causing surging. Therefore, flocculation problems must be avoided or fix. One of the way to cater flocculation is by adding the deflocculant additive into the drilling fluid.

There are few types of deflocculant use in the oil and gas industry currently in Malaysia. However, for industrial use deflocculant are mostly imported and being treated by chemicals in order for it to work on desired situation thus it is not environmental friendly. Furthermore, so far there is no locally produced deflocculant in Malaysia and no deflocculant made from the bark waste. Thus, the oil and gas industry in Malaysia is in need of having an environmental friendly deflocculant and locally produced deflocculant would be beneficial in terms of economic growth for our country.

1.3 Project Objective

This research is focusing on the evaluation of the natural tannin extracts obtained from *Rhizophora Mucronata* barks as deflocculant in drilling fluids and comparison with the commercial deflocculant. The main objectives are to:

1. To study the performance of tannin extracts from *Rhizophora Mucronata* barks as deflocculant on drilling fluid at different temperatures.
2. To compare the performance of tannin extracts from *Rhizophora Mucronata* barks to the commercial deflocculant (desco).

1.4 Scope of Study

This study will be govern by these following scope of study.

1. The extraction solvents of tannins from *Bakau Minyak* barks by using soxhlet extraction method and the characterization into condensed tannin (CT) and hydrolyzable tannin (HT).
2. The performance of tannins extracted from *Rhizophora Murconata* barks in drilling fluids and comparison to the commercial deflocculant in industry at different temperature of 225°F, 250°F and 275°F.
3. The amount of tannin added (ranging 2 g to 15 g) to the drilling fluid to find the optimum amount of tannin.

1.5 Significance of The Study

This study open up the possibilities of a new environmental friendly deflocculant to be discovered made from Malaysia's local mangrove bark source that is tannin extracts from *Rhizophora Mucronata* barks. This hopefully will lessen the demands of current commercially used tannins, which is mostly imported from China. This will also flaunt a new business opportunity for the local especially those involved in mangrove and charcoal business. However, a full through out research should be done to achieve such goals.

REFERENCES

Afidah Abdul Rahim (2005). *Physico-chemical characterization of man- grove tannins as corrosion inhibitors*. PhD Thesis, Universiti Sains Malaysia.

Amarc, H. D. (2011). *Life-cycle impact assessment of oil drilling mud system in Algerian arid.* Department of Environment and Heritage Protection , 1-4.

American Petroleum Institute. 1997. *Recommended Practice Standard Procedure for Field Testing Water- Based Drilling Fluids, API Recommended Practice 13B*–1 2nd Ed., Washinton, D. C.: American Petroleum Institute, 5-6 and 49-50.

API 13B-1 ANSI/API 13B-1/ISO 10414-1, *Recommended Practice for field testing water-based drilling fluid*, 3ra ed. 2003, 1–44.

Arapitsas, P. (2012). *Hydrolyzable tannin analysis in food.* Food Chemistry, 135(3), 1708-1717. doi:10.1016/j.foodchem.2012.05.09.

Braghiroli, F., Fierro, V., Pizzi, A., Rode, K., Radke, W., Delmotte, L,Celzard, A. (2013). *Reaction of condensed tannins with ammonia* Elsevier B.V. doi:10.1016/j.indcrop.2012.11.024.

Caenn, R., Darley, H., & Gray, G. R. (2011). *Composition and properties of drilling and completion fluids*. US: Gulf Publishing Company.

Caenn, R. C. (1996). Drilling fluids: State of the art. *Original Research Article Journal of Petroleum Science and Engineering* , 221-230.

Committee, A. (2004). *Drilling fluids processing handbook* Elsevier Science & Technology Books.

Darley, H (1957), *A Test for Degree of Dispersio in Drilling Muds*, Shell Development CO,Houstan Texas, Vol 210, 4481.

Darley, H. and Gray, G.R., *Composition and Properties of Drilling and Completion Fluids*, 5th ed, Gulf Publishing Company, Houston (1988).

Elgailani Isam Eldin Hussein and Christina Yacoub Ishak, 2016, *Methods foe Ectraction and Characterisation of Tannins from Some Acacia Species of Sudan*, Pak.J.Anal. Environ.Chem. Vol 17, No 1(2016) 43-49

Falcão, L., Araújo, M.E.M., 2011. Tannins characterisation in new and historical vegetable tanned leather fibres by spot tests. J. Cult. Herit. 12, 149–156.

Gayen, S., & Ghosh, U. (2013). *Purification and characterization of tannin acyl hydrolase produced by mixed solid state fermentation of wheat bran and marigold flower by Penicillium notatum* NCIM 923. BioMed Research International, 2013, 1-6. doi:10.1155/2013/596380

Guo, L. D. (2013). *Study of the Rheological Properties of Various Oil-Based Drilling Fluids.* Universiti Teknologi PETRONAS , 1-30.

Growcock, F., & Harvey,T. (2005). *Drilling fluids-chapter 2.* (pp. 15-68) Elsevier Inc. doi:10.1016/B978-075067775-2/50003-2

Hagerman, A.E., 1988. *Extraction of tannin from fresh and preserved leaves*. J. Chem. Ecol. 14, 453-461. Hagerman, A.E., 2001. Web site: http://miavx1.muohio.edu/ hagermae/ Hagerman, A.E., Butler, L.G., 1989. Choosing appropriate methods and standards for assaying tannin. J. Chem. Ecol. 15, 1795-1810.

Hagerman (2002). *Condesed Tannin Structural Chemistry.*

Hamza, H. A., Stanonik, D. J., Kessick, M. A. (1996). *Flocculation of lime-treated oil sands tailings*. Fuel, 75(3), 280-284. doi:10.1016/0016-2361(95)00222-7

Handa, S., Khanuja Sigh., Smith, P., Longo., Gennaro, Dev Dutt Rakesh. (2008). *Extraction Technologies for Medicinal and Aromatics Plants: General*

Methods of Extraction of Medicinal Plants. Hot Continuous Extraction (Soxhlet). 22-30.

ISO10416:2008, *Petroleum and natural gas industries-Drilling fluids-Laboratory testing,* 2008.

Know Energy Solutions. (n.d.). Retrieved from *Properties of Drilling Fluid:* http://www.knowenergysolutions.com/conventional-energy/oil-and gas/drilling/mud- engineering/properties-of-drilling-fluid/

L.Chupin, C. Motillon, F.Charrier-El Bouhtoury, A. Pizz, B.Charrier. (2013) 897-903. *Characterisation of maritime pine (Pinus pinaster) bark tannins extracted under different conditions by spectroscopic methods, FTIR and HPLC.*

Lummus, J. L. and Azar, J. J. 1986. Drilling fluids. *Drilling fluids optimization: a practical field approach*. Tulsa, Oklahoma, EE.UU: Penn. Well Publishing Company,

M. A. Pérez and R. A. Colina, Pdvsa Intevep, *Rheological Behaviour of Water-Based Drilling Fluids Contaminated with Gypsum ($CaSO_4$) Using Unmodified Dividivi Tannins (Caesalpinia coriaria) as Deflocculant Agent*. SPE-177032-MS

M. Enamul Hossain. Abdulaziz Abdullah Al-Majed. *Fundamentals of Sustainable Drilling Engineering*, John Wiley & Sons 2015.

Mahto, V., & Sharma, V. P. (2004). *Rheological study of a water based oil well drilling fluid.* Journal of Petroleum Science and Engineering, 45(1), 123-128. doi:10.1016/j.petrol.2004.03.008

Martínez, B., Rincón, F., & Ibáñez, M. V. (2000). *Optimization of tannin extraction from infant foods.* Journal of Agricultural and Food Chemistry, 48(6), 2097-2100. doi:10.1021/jf991267o

Markom, M., Hasan, M., Daud, W. R. W., Singh, H., & Jahim, J. M. (2007). *Extraction of hydrolysable tannins from phyllanthus niruri linn.: Effects of solvents and extraction methods.* Separation and Purification Technology, 52(3), 487-496. doi:10.1016/j.seppur.2006.06.003

Neff, J. M. (2005). PERF. *Retrieved from Composition, Environmental Fates, and Biological Effects of Water Based Drilling Muds and Cuttings Discharged to the Marine Environment: A Synthesis and Annotated Bibliography*: http://www.perf.org/images/Archive_Drilling_Mud.pdf

Negm, N. A., Tawfik, S. M., Abdou, M. I., Badr, E. A., & Ghuiba, F. M. (2015). *Evaluation of some nonionic surfactants derived from tannic acid as additives for water-based mud.* Journal of Surfactants and Detergents, 18(2), 309-319. doi:10.1007/s11743-014-1627-9

Odenbaugh, M. L. and Ellman, R. C. 1967. *Leonardite and other materials as drilling fluid dispersants and viscosity control agents*, Report of investigation 7043, 1-22, United States department of the interior. *Bureau of Mines,*

Plaza, M & Turner, C, 2015, *Pressurized hot water extraction of bioactives,* Department of Chemistry, Center for Analysis and Synthesis (CAS), Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

Ping, L., Pizzi, A., Guo, Z. D., & Brosse, N. (2011). *Condensed tannins extraction from grape pomace: Characterization and utilization as wood adhesives for woodparticleboard*.IndustrialCrops&Products,34(1),90914.doi:10.1016/j.indcrop.2011.02.009

Politte, M. (1985). Invert Oil and Mud Rheology as a Function of Temperature and Pressure. SPE/IADC Drilling Conference, New Orleans, Louisiana .

Rodrigues, J. (2006). New Multifunctional Polymeric Additives for Water-Based Muds.

Safi,B., Zarouri, S., Chabane-Chaouache, R., Saidi, M., & Benmounah, A. (2015*). Physico-chemical and rheological characterization of water-based mud in the presence of polymers.* Journal of Petroleum Exploration and Production Technology, doi:10.1007/s13202-015-0182-x

Schlumberger. (2007). Retrieved 03 22, 2017, from Drilling Mud: Monitoring and Managing it: http://www.slb.com/~/media/Files/resources/oilfield_review/ors 89/ jul89/4_drilling_mud.pdf

Schlumberger Oilfield Glossary. (n.d.). Retrieved 03 22, 2017 Retrieved from Oilmud Emulsifier:http://www.glossary.oilfield.slb.com/en/Terms.aspx?LookIn=term% 20nam e&filter=oil-mud%20emulsifier

Sukardjo, S. (1987). *Natural regeneration status of commercial mangrove species (Rhizophora Mucronata and Bruguiera gymnorrhirra) in the mangrove forest of Tanjung Bungin, Banyuasan District, South Sumatera*. Forest Ecology and Management, 20, 233–252.

Van Dyke, K. (2000). Drilling Fluids (1st ed.). PETEX, Austin, Texas .

Wilson, M. A., & Hatcher, P. G. (1988). *Detection of tannins in modern and fossil barks in plant residues by high resolution solid-state: Nuclear magnetic resonance*. Organic Geochemistry, 12, 539–546.

Young, S.& Ramses,G. (2006). *High-performance water-based mud improves results: Five component system matches invert emulsion mud.* Euromoney Trading Limited.

Yoshida, T., Hatano, T., Okuda, T., (1989) *Chromatography of Tannins. IV. Separation of labile oligomeric hydrolysable tannins and related polyphenols by centrifugal partition chromatography.* J. Chromatogr. 467, 139_147.