UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF ESTER-BASED DRILLING FLUIDS FOR WELLBORE ENHANCEMENT

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DEVELOPMENT OF ESTER-BASED DRILLING FLUIDS FOR WELLBORE ENHANCEMENT

By

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DEVELOPMENT OF ESTER-BASED DRILLING FLUIDS FOR WELLBORE ENHANCEMENT

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Institute : Advance Technology

Ester-based drilling fluid has been accepted as an alternative to mineral oils in drilling applications and currently being usedin oil or gas wells exploration around the world. However, the ester has many deficiencies such as high kinematic viscosity andpoorthermal and oxidative stabilities whichlimit its ability to carry and transfer drilled solids under high pressure and high temperature wells. Thus, the main aim of the study is to overcome these limitations by developing the high performance ester-based drilling fluids for deep and ultra-deep wells that operate under high pressure and high temperature conditions. The low pressure technology was applied in the synthesis of the ester to minimize ester hydrolysis and thermal instability issues during the drilling operation. The rapid ester synthesis involved the reaction between2-ethylhexanol and vegetable oil-based methyl esters C_{8-12} in the presence of sodium methoxide as the catalyst. In order to obtain the optimum synthesis conditions, a response surface methodology (RSM) was appraised based on the central composite design. The product with 77 wt. % 2-EH C_{12} ester content wasobtainedfrom both RSMmodel and experimental data. The 2-EH C_{12} ester exhibited properties similar to the commercial ester, i.e. kinematic viscosity of 5.2 mm^2/sec at 40°C and 1.5 mm^2/sec at 100°C, specific gravity of 0.854, 170°C flash point, and -7°C pour point. While the properties of 2-EH $C_{8/10}$ ester base oil were 3.2 and 1.2 mm^2/sec of kinematic viscosity at 40 and 100°C respectively, 80°C flash point, and -15°C of pour point.

Various conventional, micro and nano-ester-based drilling formulations were prepared and characterized based on the API Recommended Practice 13B-2. Calcium carbonate ($CaCO_3$) of 5 µm particles, commercial graphene (powder and platelets) and carbon nanosphere (produced in house) nanoparticles have been used as the rheology enhancer and fluid loss agent in geothermal drilling fluid formulation.The performances of 2-EH ester-based drilling fluids were assessed under different hot rolling temperatures (121, 135, 149, 177, 212 and 232^{o}C) for 16 hours. The improvement in both thermal and hydrolytic stability of the synthesized 2-EH C_{8-12} esters may be due to the unique transesterification method using methyl ester route as opposed to the conventional fatty acids route.Furthermore,the addition of only 0.1wt% of graphene (powder type) to the

formulation enhanced further the ester-based drilling fluid performances. The stability of the fluid to plug 10 µm of formation size was evidenced when only 8 ml of filtration and 775 mDarcy of permeability was obtained using (533.4/50.8 × 25.4/101.6) mm ceramic disc.

In this study, simulation of conventional and nano-ester-based drilling fluids in eccentric, dual phase flow through horizontal well was performed with the help of three dimensional CFD, Fluent package. The simulation was successful and demonstrated the capabilityof 2-EH ester based drilling fluid to carry and transfer cutting particles of 3, 4.45 and 7 mm sizes in a highly eccentric annular flow of 0.8 eccentricities. The critical fluid velocity that demonstrated the fluid ability to carryand transport cuttings without cuttings bed was at 2.86 m/s. These results confirmed that 2-ethylhexyl ester-based drilling fluids have the potential to be commercialized and used in deep and ultra-deep wells without sagging, pipe sticking, and wellbore instability issues.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMBANGUNAN CECAIR PENGGERUDIAN BERASASKAN ESTER UNTUK PENAMBAHBAIKAN LUBANG TELAGA

Oleh

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Lumpur penggerudian berasaskan ester telah diterima pakai sebagai alternatif kepada lumpur penggerudian berasaskan minyak galian di dalam proses penggerudian dan pada masa ini sedang digunakan untuk menggerudi telaga minyak dan gas di seluruh dunia. Akan tetapi, minyak berasaskan ester ini mempunyai keupayaan yang terhad untuk membawa dan memindahkan pepejal hasil penggerudian, menstabilkan lubang telaga dan menggali telaga lebih jangkauan. Beberapa pendekatan telah dipertimbangkan untuk mengatasi kekurangan minyak ester ini. Maka, tujuan utama bagi kajian ini adalah untuk mengatasi had limitasi ini dengan menghasilkan lumpur penggerudian berasaskan ester yang berprestasi tinggi bagi penggerudian telaga dalam dan sangat dalam. Teknologi bertekanan rendah telah digunakan didalam proses sintesis ester untuk meminimumkan ester yang terhidrolisis dan isu ketidakstabilan terma semasa operasi penggerudian. Sintesis ester secara pantas melibatkan 2-etilheksanol dan C_{8-12} metil ester dari minyak sayuran dengan sodium metoksida sebagai pemangkin. Untuk mendapatkan keadaan optimum bagi proses sintesis, kaedah permukaan respons (RSM) telah digunakan dan dinilai berdasarkan reka bentuk komposit pusat. Produk yang terhasil mengandungi 77wt% ester 2-EH C_{12} daripada model RSM dan data-data eksperimen. Ester 2-EH C_{12} mempunyai ciri-ciri yang sama seperti ester komersial berasaskan minyak galian, iaitu, kelikatan kinematic 5.2 mm^2/sec pada 40^oC dan 1.5 mm^2/sec pada 100^oC, graviti spesifik : 0.854, takat kilat pada 170^oC dan takat tuang pada -7^oC. Manakala, ester 2-EH $C_{8/10}$ mempunyai kelikatan kinematic 3.2, 1.2 mm^2/sec pada 40 ans 100^oC, takat kilat pada 80^oC dan takat tuang pada -15^oC.

Formulasi lumpur penggerudian mikro konvensional dan lumpur penggerudian nano berasaskan ester telah disediakan dan dicirikan mengikut piawaianAPI Recommended Practice 13B-2. Partikel Kalsium karbonat ($CaCO_3$) bersaiz 5 μm, serbuk dan emping grafin serta partikel nano karbon nanosfera telah digunakan sebagai pemangkin reologi dan agen penghalang kehilangan cecair di dalam formulasi lumpur penggerudian geotermal. Prestasi lumpur penggerudian berasaskan ester 2EH dinilai pada suhu penggolek panas yang berbeza (121, 135, 149, 177, 212 dan 232^oC) selama 16 jam. Peningkatan di

dalam kedua dua kestabilan terma dan hidrolitik bagi ester 2EH C_{8-12} ini mungkin disebabkan oleh kaedah transesterifikasi yang unik dan berlainan daripada cara konvensional untuk mengsintesis asid lemak. Selain itu, hanya 0.1 wt% serbuk nanografin meningkatkan lagi prestasi lumpur penggerudian berasaskan ester ini sebagai alternatife kepada lumpur penggerudian berasaskan minyak galian. Ia boleh memalam 10 μm saiz formasi dengan 8 ml penapisan dan 775 mDarcy kebolehtelapan dengan menggunakan cakera seramik bersaiz (533.4/50.8 × 25.4/101.6) mm

Dalam kajian ini, usaha telah dijalankan untuk mensimulasikan lumpur penggerudian mikro dan nano berasaskan ester di dalam telaga aliran dwi fasa mendatar yang unik dengan bantuan pakej Fluent tiga dimensi (CFD). Keputusan yang diperolehi telah berjaya dan menunjukkan bahawa lumpur berasaskan ester 2EH mempunyai keupayaan untuk membawa dan memindahkan partikel keratan bersaiz 3, 4.45 dan 7 mm di dalam aliran annulus yang sangat asentrik pada 0.8 asentrik. Purata halaju cecair yang diperlukan untuk membawa dan mengangkut cebisan batu tanah tanpa pengumpulannya di dasar telaga adalah pada 2.86 m/s. Keputusan-keputusan berikut mengesahkan bahawa lumpur penggerudian berasaskan ester 2EH mempunyai potensi untuk dikomersialkan dan digunakan pada telaga dalam dan telaga sangat dalam tanpa menyebabkan kemerosotan prestasi, masalah paip tersekat dan ketidakstabilan dasar telaga.

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I certify that a Thesis Examination Committee has met on 17 November 2015 to conduct the final examination of Lina Ismail Jassim on her thesis entitled "Development of Ester-Based Drilling Fluids for Wellbore Enhancement" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

A	after hot rolling
API	American Petroleum Institute
APPA	Automated permeability plugging apparatus
B	before hot rolling
bo	Constant
bi	linear model coefficient
bii	quadratic model coefficient
C	calibration constant
CCD	Central Composite Design
CDV	Critical deposition velocity
CF	Coefficient of friction
CFD	Computational fluid dynamic
Cl	coefficient of lubricity
CNT	Carbon nanotube
CMC	Carboxymethylcellulose
CMHEC	carboxymethyl-hydroxyethylcellulose
CRV	Critical re-suspension velocity
DF	Drilling fluid
EBF	Ester based fluid
EE3	Ethylhexyl Ester 3
2-EH	Ethylhexanol
EOR	Enhancement Oil Recovery
EPA	Environmental Protection Agency
ES	electrical stability, volt
EXD	energy dispersive x-ray spectrometry
F	Force vector, N
F-value	Test for comparing model variance with residual (error) variance
FFA	free fatty acid, %
FESEM	Field Emission Scanning Electron Microscopy
FID	flame ionization detector
FL	Fluid loss
FP	flash point, C
GBFs	Gas based fluids
GC	Gas Chromatography
GIT	Grid Independency Test

HTHP	High Temperature High Pressure
IEF	Invert emulsion drilling fluid
IO	Internal olefin
K	Flow consistency index, Pa s
K_{pq}	interphase momentum exchange coefficient
LAO	Linear alpha olefin
LP	Linear paraffin
m	mass, g
ME	methyl ester
MW	Molecular weight
n	Flow behaviour index, dimensionless
N	normality of KOH solution, %
NCS	Nano carbon sphere
NGO	Non-Government Organization
NP	Nanoparticles
OBFs	Oil based fluids
OWR	Oil to water ratio
Δ	Pressure differential, Pa
PAO	poly-alpha olefin
Pour P	Pour point, C
PP	Pressure Penetration
PPT	Plugging Permeability Test
Prob	Probability of seeing the observed F value
PV	Plastic viscosity, cP
Q	Flow rate, m3/s
ROP	Rate of penetration
RSM	Response Surface Methodology
S_q	Source expression, Kg/s
SBF	Synthetic based fluid
SG	Specific gravity, g/cm3
SPS	Sulphonated polystyrene
SWF	Shallow water flow
tav	Time avarage, sec
	thickness of mud cake, mm
TEM	Transmission electron microscopy
UBD	Underbalanced drilling

UCM	Upper Convective Maxwell
V	Volume, m3
WP	Water Content, %
w	weight, g
WBFs	Water based fluids
xi and xj	Independent factors
y	Content of 2-EH ester, (wt.%)
YP	Yield point, psi

CHAPTER 1

INTRODUCTION

This chapter covers the background of drilling operation and general information about drilling fluids, problem statement that is currently in oil and gas industry, objectives, contribution, and scope of this research, as well as the whole thesis organization.

1.1 Background

Drilling, well completion, and production are the three main processes involved in activating a well after the identification of oil or gas reserves. In terms of cost, the drilling process represents 80% of the total well establishment cost. There are various types of wells, including vertical, inclined, horizontal to sub-sea, and deep-sea wellbores (Fink, 2012a). The drilling fluid is crucial in drilling operations as its main task is to achieve the well drilling objectives effectively. The drilling fluid can be in liquid form or foam, depending on the combination of air and liquid. When the operation occurs in deep or ultra-deep wells, the drilling fluids used are commonly called drilling muds. Almost all drilling fluids and particularly drilling muds are comprised of a wide range of chemicals which provide the different physical properties required by the drilling fluids (Shah et al., 2010). In addition, for specific wellbore requirements, specialized drilling fluids are usually required (Fink, 2012a).

The American Petroleum Institute states “a drilling fluid is defined as a circulating fluid, used in rotary drilling to perform any or all of the various functions required in drilling operations” (Fink, 2012a). Drilling fluids are traditionally a blend of chemicals and natural compounds, which is pumped through the drill pipe after being released from the bit nozzles. It can transport rock cuttings from subterranean well holes to the surface through an annular space between the drill pipe and the wall of the hole (Nasiri et al., 2009). Drilling fluids are specially formulated to control conditions and alleviate problems that can occur during the well drilling. They are also used to cool and lubricate the drill bit, clean the base of the drill hole, and facilitate the cutting of holes surfaces. Drilling fluids are classified as oil-based fluid (OBF), water-based fluid (WBF), synthetic-based drilling fluid (SBF), invert emulsion fluid (IEF), and air or foam fluids (Shah et al., 2010). The most prevalent types used to drill oil wells are WBF and OBF types. In general, the formulation of a drilling fluid consists of a base fluid as the continuous phase, and a number of additives. These additives vary in type and amount, depending on the conditions of a well. The composition is matched to the well physical requirements so that efficient carrying of the rock cuttings to the surface takes place. Since the function of drilling fluid is not just to cool and lubricate the drilling bit, but also to control the stability of the well bore, the drilling fluid forms a thin, low permeability filter cake along the well bore to prevent fluids (oil, gas, and water) from penetrating through permeable rocks (Ryen et al., 2011a).Thus, a correctly-selected drilling fluid composition is necessary to affect the rheological behavior and ensure the success of the well drilling.

1.2 Problem statement

Concerns on the effects of some petroleum based products on the environment, specifically the toxicity and the long term of biodegradability of OBFs residues. Daan and other researchers (1993) found that contaminated cuttings with diesel and mineral oils took 8 years to degrade. Therefore, the legislations imposed by international environmental protection agencies, which ban the use of mineral and diesel oils in several parts of the world.

These legislations motivate researchers to synthesize, develop, and use products that have zero impact on the environment. Synthetic products provide an opportunity for ecologically-sound components in drilling operations, providing enhanced lubricity, thermal and chemical stability, and wellbore integrity. Synthetic products generally can be tailor-made to suit special applications and not normally available in nature.

Ethers, esters, olefin, paraffin, and linear alpha olefin, are synthetic hydrocarbons. Of these, esters represent the best alternatives to mineral oil-based drilling fluids due to its non-toxicity, biodegradability, and availability (Ghalambor et al., 2008; Kim et al., 2001; Dosunmu & Joshua, 2010; and Fadairo & Falode, 2012). However, ester has two main deficiencies, which are its high viscosity which limits the rock cutting carrying abilities, and thermal instability. In the latter case, under high temperature condition (above 121^{o}C), hydrolysis of ester together with acidity condition, and excess alkalinity causing saponification reaction with water to create calcium soaps. Excessive presence of these soaps has adverse effect on drilling fluid rheology and wellbore stability.

A review of the literature indicated that there are two main approaches used to improve ester performance. These are modification of the chemical structure and use of additives. Modification of the ester chemical structure: The esterification reaction takes places between the fatty acids and low molecular alcohol. Thus, manipulating the chemical structure involves changing the carbon chain length, branch, or linear characteristics, and the degree of saturation. These methods affect the physical properties of viscosity, flash point, and pour point. Ester-based drilling fluids usually exhibit thermal stability up to only (121°C). In term of temperature, the drilling fluid should be stable up to 250°C to be suitable for industrial drilling. Hence, various patents have been filed in the development of stable products (Mueller et al., 1992, 1993, 1995, and 1999).

The second approach is the manipulation of additives used in the formulation. Water solution can be added to ester base oil to perform invert emulsion fluid. This class of fluid is recognized to reduce ester-based drilling fluid viscosity and drilling fluids costs (Mueller et al., 1992). Lime and oleophilic amine compounds can be used to avoid reactions with the free carboxylic acid, formed by hydrolysis (Mueller et al., 1995). To stabilize invert ester based drilling fluid, negative alkalinity can be achieved by adding protonated amine as an emulsifying agent. This is to reduce the hydrolysis reaction, and improve the thermal stability of the ester up to (149^{o}C) (Patel, 1999). The blend of ester-based drilling fluids and mineral oils together with visco-plex 6-954 was also proposed to improve the ester based fluid performance but only up to (177^{o}C) (Nasiri et al., 2009).

Ultra-high temperatures, high pressure (HTHP) conditions, symbolize another challenge to drilling formulation during well drilling. These include how temperature and pressure conditions can change the drilling fluid rheology and increase the challenges to wellbore instability. Thus, require drilling fluid with special formulations. Although a real field test is the best trial option for new fluid system, simulation using computational fluid dynamic software would also give important information about the fluid. Hence, to investigate the performance of new fluid in certain well conditions and to avoid unexpected behavior of fluid, simulation model has become even more significant tool and used to evaluate the new fluid behavior.

1.3 Contribution of the research

The purpose of the research is to identify ways in which drilling operations can be enhanced to overcome the environmental issues and other performance issues that affect the ester-based drilling fluids in deep and ultra-deep wells. Ester base oils are chosen due to its lubricity, higher thermal and chemical stability, and its inherent properties such as non-toxicity, non-flammability, high biodegradability, and high-strength properties that can later improve the performance of drilling fluids. Other performance criteria also include low pour point, long service life, and compatibility with presently-used base fluids. The low pressure technology was applied in the synthesis of the ester to minimize ester hydrolysis and thermal instability issues faced by commercial ester-based fluids during the drilling operation. The improvement in both thermal and hydrolytic stability is due to the unique transesterification method using methyl ester route as opposed to the conventional fatty acids route. Furthermore, ester-based fluid is a green product, thus it will assist companies to promote a healthy environment and provide a good return on the investment.

1.4 Research objectives

The followings are the research objectives of the study.

1. To synthesize base oils for ester-based drilling fluids from C_{8-12} methyl ester and 2-ethylhexanol (2-EH) via the low pressure transesterification process, and determine the optimum synthesis conditions of 2-EH ester content using response surface methodology.

2. To prepare novel drilling fluid formulations from newly synthesized ester base oils using conventional, advanced, ultra-advanced additives and to characterize the fluids based on theAPI Recommended Practice 13B-2, 2012.

3. To investigate the effect of adding micro and nano particles in ester-based drilling fluids for ultra-high temperature application.

4. To simulate the ability of newly synthesized ester-based drilling fluids to carry and transport drilled cuttings using three-dimensional computational fluid dynamics.

1.5 Scope of research

1.5.1 Synthesis of ester-based oil as continuous phase in IEF

The synthesis of a new 2-ethylhexyl ester was conducted using renewable $C_{8/10}$ and C_{12} methyl ester groups and 2-ethylhexanol in the presence of sodium methoxide as alkaline catalyst. Low pressure technology was applied to transesterify two types of ester base oils. Response surface methodology (RSM) based on central composite design (CCD) was applied to optimize the synthesis conditions of the reactions. Four factors were considered for optimization study, which were: reaction temperature (60-100^{o}C), time of reaction (5-30 minutes), catalyst concentration (0.2-1wt. %) and 2-EH to oil molar ratio (3:1) while the pressure of reaction was fixed at 20 mbar.

1.5.2 Preparation of novel formulations from synthesis base oils

In this study, the drilling fluid is an inverse emulsion fluid, generated by the use of 2-EH ester oils as the continuous phase mixed with brine solution as internal or discontinuous phase, then conventional, advance or ultra-advance type of additives were added. These additives have been used to formulate different drilling fluid formulations to adjust the variety of wellbore conditions. Therefore, aging temperatures that have been used were (121, 135, 149, 177, 200, and 232^{o}C). Then fluid characterizations were conducted based on American Petroleum Institute procedures (API Recommended Practice 13B-2, 2012).

1.5.3 Preparation of micro and nano-ester based drilling formulations

Micro–ester based drilling formulations were prepared using an invert emulsion system with ultra-advance additives and calcium carbonate ($CaCO_3$) of 5 μm as a bridging material, which was dynamically aged at 200^{o}C. Nano-ester based formulations were formed using an invert emulsion system and the combination of advance and ultra-advance types of additives as well as nano particles additives of 0.1 wt.% of three types (commercial powder and platelets of graphene, and in house CNS) were added and subsequently combined with the drilling fluid. Then following American Petroleum Institute procedures (API Recommended Practice 13B-2, 2012), the characterization of the fluids were conducted. Furthermore, TEM, and Raman spectroscopy were used to analyze the response of mud cake in the presence of nano particle additives and verify the potential of the additives to be used as rheology modifier and fluid loss agents under 232^{o}C.

1.5.4 Simulated drilling fluid flow in an annular space

A simulation model based on three-dimensional computational fluid dynamics (CFD) with FLUENT ® software was implemented to study the effects of Herschel-Bulkley fluids rheology (conventional formulation and nano- fluid formulation) and the rotation of the drill pipe on the axial velocity profile, cuttings concentration, instantaneous and tangential velocities. The computational tool was also used to simulate the effect of fluid flow rates (30, and 50 Ls) on the wellbore cleaning ability.

1.6 Organization of thesis

The thesis consists of five chapters. Chapter One is an introduction to the background and significance of the study, and also comprises the objectives and scope of the research. Chapter Two provides an extensive review and analysis of previous research relevant to the present study. It also covers a review of the literature on various aspects of drilling fluids, including their synthesis, application, evaluation, and a simulation of environmentally-friendly drilling conditions. Chapter Three presents the general materials and methods used in our study, which starts with the right selection of methyl ester group and alcohol, and the optimization of transesterification reaction in order to obtain a high yield of ethylhexyl ester. Its physical and chemical properties and suitability as the base-oil in synthetic-based drilling fluid is evaluated. Furthermore, high performance drilling formulations were designed and their properties were tested following the American Petroleum Institute procedures (API Recommended Practice 13B-2, 2012). The simulation model was set up using CFD with FLUENT ® software, to simulate the cutting transport ability of two types of newly formulated fluid. Chapter Four presents the results in relation to the formulated objectives, which include a statistical analysis of the optimization method using RSM, fluid formulation and characterization, and simulation of the effect of drill pipe rotation and position on the results of two-phase flow inside the annuli. Finally, Chapter Five presents the conclusion of this research and recommendations for future studies.

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