SYNTHESIS AND EVALUATION OF SURFACTANTS FROM SELECTED VEGETABLE OILS FOR ENHANCED HEAVY- OIL RECOVERY

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES IN PARTIAL FULFILMENT FOR THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY (Ph.D) IN PETROLEUM ENGINEERING IN THE DEPARTMENT OF PETROLEUM ENGINEERING, COLLEGE OF ENGINEERING, COVENANT UNIVERSITY, OTA

JUNE, 2021

ACCEPTANCE

This is to confirm that this thesis is accepted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Petroleum Engineering in the Department of Petroleum Engineering, College of Engineering, Covenant University, Ota, Nigeria.

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DECLARATION

I, **ABRAHAM, DAMILOLA VICTORIA (14PCN01229)** declare that this research was carried out by me under the supervision of Prof. Oyinkepreye D. Orodu of the Department of Petroleum Engineering and Prof. Vincent E. Efeovbokhan of the Department of Chemical Engineering, College of Engineering, Covenant University, Ota, Nigeria. I attest that this thesis has not been presented either wholly or partially for the award of any degree elsewhere. All sources of data and scholarly information used in this thesis are duly acknowledged

ABRAHAM, DAMILOLA VICTORIA **.....……**

Signature and Date

CERTIFICATION

We certify that the thesis titled "**Synthesis and Evaluation of Surfactants from Selected Vegetable Oils for Enhanced Heavy- Oil Recovery**" is an original work carried out by **ABRAHAM, DAMILOLA VICTORIA (14PCN01229)** in the Department of Petroleum Engineering, College of Engineering, Covenant University, Ota, Ogun State, Nigeria under the supervision of Prof. Oyinkepreye D. Orodu and Prof. Vincent E. Efeovbokhan. We have examined and found the work acceptable as part of the requirements for the award of a degree of Doctor of Philosophy (Ph.D) in Petroleum Engineering.

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Prof. Akan B. Williams .....

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DEDICATION

This research is committed to God for His sufficient grace over me. I also dedicate my thesis to my family. A distinct sense of appreciation to my caring husband, Engr. Abiodun Abraham whose words of motivation and perseverance ring in my ears. He has encouraged me when I was discouraged and most significantly, he has been 100% positive in my capability to get this done. I dedicate this work to my daughter Folasore for your peace, patience and calmness in the course of this journey, you made it so swift to combine motherhood with academics.

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LIST OF ABBREVIATIONS

AOCS	American Oil Chemists' Society
AOS	Alpha Olefin Sulfonate
AS	Alkaline/Surfactant
ASP	Alkaline/Surfactant/Polymer
ASTM	American Society for Testing and Materials
API	American Petroleum Institute
cc/min	cubic centimetre/minute
CEOR	Chemical Enhanced Oil Recovery
CMC	critical micelle concentration
CO	Castor Oil
CSS	Cyclic steam stimulation
EOR	Enhanced Oil Recovery
FAMES	Fatty Acid Methyl Esters Sulfonates
FFA	Free Fatty Acid
FU	Flow Unit
HCL	Hydrochloric acid
HPLC	High Performance Liquid Chromatography
IFT	Interfacial Tension
JO	Jatropha Oil
KOH	Potassium Hydroxide
ME	Microemulsion
Na_2CO_3	Sodium Carbonate
MES	Methyl Ester Sulfonate
NaCl	Sodium Chloride
NARICT	National Research Institute for Chemical Technology
OFITE	OFI Testing Equipment

OOIP	Original Oil in Place
O/W	Oil/Water
RPT	Reservoir Permeability Tester
pH	potential of Hydrogen
PKO	Palm Kernel Oil
PO	Palm Oil
ppm	parts per million
PV	Pore Volume
PVT	Pressure, Volume, and Temperature
RPT	Reservoir Permeability Tester
SAGD	Steam-assisted gravity drainage
SP	Surfactant/Polymer
TAN	Total Acid Number

LIST OF SYMBOLS

Symbols

k	Permeability, mD
ø	Porosity

Units

cP	Viscosity
Psi	Pressure
s	Seconds
ppm	Concentration
mN/m	Interfacial Tension
mD	Permeability
g	Mass
ml	Volume
^{o}C (or ^{o}F)	Temperature

ABSTRACT

Due to the high cost of production of surfactants from petrochemical feedstock, vegetable oils are given considerable attention as another source of feedstock. In this work, the synthesis of surfactants from jatropha oil, castor oil, and palm kernel oil for application in chemical enhanced oil recovery was carried out. The vegetable oils were synthesized by Sulphonation reaction to produce surfactants. The synthesized surfactants were evaluated for recovery of heavy crude from heavy crude oil reservoirs and their performance was compared to those of commercial surfactants. This was achieved by studying the effect of the synthesized surfactants in interfacial tension (IFT) reduction, phase behaviour experiments, and core flooding experiments. The physicochemical properties of the vegetable oils evaluated include viscosity, specific gravity, acid value, and saponification value based on the American Oil Chemists' Society (AOCS) methods. The interfacial tension between the crude oil, brine, and surfactants were measured using the Du-Nouy tensiometer. This was achieved by varying brine and surfactant concentrations done at ambient temperature (27^{o}C) and at reservoir temperature (60^{o}C). The results from the IFT experiments showed that at 10000 ppm, the IFT reduced from 19.8 mN/m to 13.5 mN/m, 13.1 mN/m, 13.4 mN/m, 13.6 mN/m, and 13.3 mN/m with the application of Jatropha, Castor, Palm Kernel, Alpha Olefin Sulfonate (AOS) and Methyl Ester Sulfonate (MES) surfactants respectively. Phase behavior analyses were conducted at a fixed ratio of surfactants to oil in the presence of brine. The surfactant/water/oil system formed a middle phase microemulsion in the presence of Sodium Chloride (NaCl). The result showed that the microemulsion (ME) decreased with a decrease in surfactant concentration values. The microemulsion phase changes from Winsor Type I to Winsor Type II via Winsor Type III. The anionic surfactant, AOS showed the ability to form a three-phase microemulsion. The performance of the synthesized surfactants was then evaluated in core flooding experiments. This was done by investigating the effect of various surfactant concentrations on the recovery of the original oil in place. The cores were first flooded with water when no oil was produced, surfactant flooding was initiated. The range of the oil recovery from the waterflooding process was 24 - 39.29 %. Using 10,000 ppm concentration of Jatropha, Castor, Palm Kernel, Alpha Olefin Sulfonate, and Methyl Ester Sulfonate surfactants gave incremental recovery of 19.3, 41.83, 40.40, 7.40, and 34.79 % respectively. With an increase in surfactant concentration to 20,000 ppm, the percentage of the oil recovered increased to 30.77, 46.41, 44.17, 25.68, and 37.93 % respectively. The Castor based surfactant showed the best results in the reduction of interfacial tension and the percentage of original oil in place recovered.

Keywords: Core flooding, Enhanced Oil Recovery, Interfacial Tension, Sulphonation, and Synthesized Surfactants.