STUDIES ON SHEAR AND GRAVITY INDUCED COALESCENCE IN OIL - WATER EMULSIONS

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by

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THESIS CERTIFICATE

This is to certify that the thesis entitled **'Studies on Shear and Gravity Induced Coalescence in Oil - Water Emulsions'** submitted by **Ms. Meenakshi Mazumdar** to the Indian Institute of Technology-Delhi for the award of degree of **Doctor of Philosophy (PhD)** is a bona fide record of research work carried out by her under my supervision. The contents of this thesis have not been submitted to any other institutes or university for the award of any degree or diploma.

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-Meenakshi Mazumdar

ABSTRACT

Emulsions are ubiquitously found in numerous applications of engineering interest. A frequently encountered class of emulsions that are of more contemporary interest in the upstream petroleum industry are highly stable concentrated oil-water (O/W) emulsions of crude. Owing to the stability of such emulsions, traditional gravity separators used for effecting separation of oil and water phases are now superseded by newer technologies. Due to the processing of large volumes of such emulsions, it is often argued that shear induced coalescence is one of the economically viable and attractive options for destabilization. However, the role of shear in the separation of concentrated emulsions, where a population of drops interacts, is still not known. Thus, the motivation of the present work was to investigate shear and gravity induced coalescence in stable emulsions.

The first part of the present study deals with a situation where gravity is the primary driver of separation. Here, the effect of volume fraction and surfactant concentration on the evolving drop size distribution was investigated. With the aid of spatial and temporal variations in drop size distribution measurements at the early stages of destabilization, some novel phenomena were explored. It is reported that, for the higher volume fraction of dispersed phase, even though the rate of coalescence increased, the actual separation of distinct oil phase was delayed.

Another major contribution of the current work lies on studies of shear-driven coalescence. This study revealed that the drop size distribution of dispersed phase (resembling moderately heavy crude) exhibit the kinetics of coalescence as a function of shear rate, volume fraction, and viscosity ratio of dispersed to the continuous phase. When the viscosity ratio was less than unity, shearing yielded bimodal distributions at low volume fractions. However, for higher volume

fractions, drop size distributions show multimodal nature. On the contrary, when this viscosity ratio was greater than unity, a reduced rate of coalescence was observed. Nevertheless, it was shown that there exists a range of shear rates within which the rate of coalescence enhanced.

A theoretical prediction of the time evolution of drop size distributions for shear-driven coalescence was implemented through Population Balance Modeling. When dispersed phase volume fraction was low, an existing diameter based coalescence efficiency equation could emulate the bimodal distributions as observed in experiments. However, its predictions deviated at higher volume fractions. In order to explain a possible multiple drop interaction at the higher volume fractions, a Multi Drop Coalescence (MDC) model was proposed. Upon its integration with the Population Balance Equation, the MDC model was extensively validated for a wide range of reported experimental data in the open literature. Further, it was also employed to determine transient drop size distribution as measured in the present study and was shown to be valid for emulsion systems with both low as well as the high volume fraction of the dispersed phase.

Finally, the inferences from above studies were extended to report destabilization of Kuwaiti crude oil-water emulsions. This effort explored the behavior of such emulsions both in the presence as well as in the absence of surfactant, under the influence of shear. Furthermore, the transient drop size distributions were predicted through the MDC model.

In conclusion, the observations of all the above-mentioned studies have been integrated to propose a guideline on the nature of destabilization of crude oil-water emulsions. The work reported herein will form a foundation for further research in this field and would aid in designing of efficient industrial scale coalescers using the minimalist approach.

सार

इंजीनियरिंग हित के कई अनुप्रयोगों में इमल्शन को सर्वव्यापी पाया जाता है। अपस्ट्रीम पेट्रोलियम उद्योग में अधिक समकालीन ब्याज की एक सामंजस्यीय सामग्रियों का अक्सर सामना करना पड़ता है जो अत्यधिक स्थिर केंद्रित तेल-पानी (ओ / डब्ल्यू) कच्चे तेल के इमल्शन हैं। इस तरह के इमल्शन की स्थिरता के कारण, पारंपरिक गुरुत्वाकर्षण विभाजक जो कि तेल और पानी के चरणों को अलग करने के लिए इस्तेमाल किया जाता है, अब नई प्रौद्योगिकियों से आगे निकल जाता है। इस तरह के इमल्शन के बड़े संस्करणों के प्रसंस्करण के कारण, यह अक्सर तर्क दिया जाता है कि कतरनी प्रेरित सहसंस्था अस्थिरता के लिए आर्थिक रूप से व्यवहार्य और आकर्षक विकल्पों में से एक है। हालांकि, केंद्रित इमल्शन के पृथक्करण में कतरनी की भूमिका, जहां बूंदों की आबादी आदान-प्रदान करती है, अभी भी ज्ञात नहीं है। इस प्रकार, वर्तमान काम की प्रेरणा स्थिर इमल्शन में कतरनी और गुरुत्वाकर्षण प्रेरित सहयोजन की जांच करना था।

वर्तमान अध्ययन का पहला भाग ऐसी स्थिति से संबंधित है जहां गुरुत्वाकर्षण अलग होने का प्राथमिक ड्राइवर है। यहां, उभरते ड्रॉप आकार के वितरण पर वॉल्यूम अंश और सर्फटेक एकाग्रता का प्रभाव जांच लिया गया था। अस्थिरता के प्रारंभिक चरणों में ड्रॉप आकार वितरण माप में स्थानिक और अस्थायी रूपांतरों की सहायता से, कुछ उपन्यास घटनाओं का पता लगाया गया। यह बताया गया है कि फैले हुए चरण के उच्च मात्रा के अंश के लिए, हालांकि सहसंवेदन की दर में वृद्धि हुई है, अलग तेल चरण की वास्तविक जुदाई में देरी हुई थी।

वर्तमान काम का एक और बड़ा योगदान कतरनी-संचालित संगति के अध्ययन पर है। इस अध्ययन से पता चला है कि फैलाने वाले चरण के ड्रॉप आकार के वितरण (मामूली भारी कच्चे तेल की तरह) कतरनी दर, मात्रा अंश, और निरंतर चरण में छितरी हुई चिपचिपाहट अनुपात के एक समारोह के रूप में संलयन के कैनेटीक्स प्रदर्शित करते हैं। जब चिपचिपापन अनुपात एकता से कम था, तो कतरनी कम मात्रा के अंशों पर द्विमूल्य वितरण उत्पन्न करती थी। हालांकि, उच्च मात्रा

भिन्न के लिए, ड्रॉप आकार के वितरण मल्टीमॉडल प्रकृति दिखाते हैं। इसके विपरीत, जब यह चिपचिपापन अनुपात एकता से अधिक था, तो एक अल्पसंख्यकता की दर को देखा गया। फिर भी, यह दिखाया गया था कि कतरनी दर की एक सीमा होती है जिसके भीतर संलयन की दर बढ़ा दी जाती है।

जनसंख्या संतुलन मॉडलिंग के माध्यम से कतरनी-संचालित संगति के लिए ड्रॉप आकार के वितरण के समय के विकास का एक सैद्धांतिक भविष्यवाणी लागू किया गया था। जब फैलाव के चरण खंड अंश कम था, तो एक मौजूदा व्यास आधारित सहसंयोजन दक्षता समीकरण प्रयोगों में मनाए अनुसार द्विआधारी वितरण का अनुकरण कर सकता है। हालांकि, इसकी भविष्यवाणियां उच्च मात्रा के अंशों में भटकती हैं उच्च मात्रा भिन्नों पर संभव बहु ड्रॉप इंटरैक्शन की व्याख्या के लिए, एक मल्टी ड्रॉप कोलेजेंस (एमडीसी) मॉडल का प्रस्ताव किया गया था। जनसंख्या संतुलन समीकरण के साथ इसके एकीकरण पर, खुले साहित्य में रिपोर्ट किए गए प्रयोगात्मक आंकड़ों की एक विस्तृत श्रृंखला के लिए एमडीसी मॉडल को व्यापक रूप से मान्य किया गया था। इसके अलावा, यह वर्तमान अध्ययन में मापा गया क्षणिक ड्रॉप आकार वितरण को निर्धारित करने के लिए भी कार्यरत था और छितित अवस्था के उच्च मात्रा के अंश के साथ-साथ कम और दोनों के साथ पायस प्रणाली के लिए वैध दिखाया गया था।

आखिरकार, उपरोक्त अध्ययनों के निष्कर्षों को कुवैती के कच्चे तेल के पानी के पानी के अम्लीकरण की रिपोर्ट करने के लिए विस्तारित किया गया। इस प्रयास ने कतरनी के प्रभाव में उपस्थिति में और साथ ही सर्फेक्टेंट की अनुपस्थिति में ऐसे इमल्शन के व्यवहार का पता लगाया। इसके अलावा, एमडीसी मॉडल के माध्यम से क्षणिक ड्रॉप आकार वितरण का अनुमान लगाया गया था।

निष्कर्ष में, सभी उपर्युक्त अध्ययनों की टिप्पणियों को कच्चे तेल के पानी के अवसंरचना के अस्थिरता की प्रकृति पर एक दिशानिर्देश देने के लिए एकीकृत किया गया है। यहां रिपोर्ट किए गए काम इस क्षेत्र में आगे के शोध के लिए एक नींव बनाएगा और न्यूनतम औद्योगिक दृष्टिकोण का उपयोग करके कुशल औद्योगिक पैमाने के कोलेस्सर्स को डिजाइन करने में सहायता करेगा।

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NOMENCLATURE

n	Number density distribution, m^{-6} (μm^{-6})
U, V	Volumes of colliding drop, m^3 (μm^3)
f_c	Coalescence frequency ($m^3\ s^{-1}$)
M	Number of grid points
N(i)	Number density of the i^{th} grid point, m^{-3} (μm^{-3})
$f_v(D)$	volume distribution of drop sizes, m^{-1} (μm^{-1})
$<D>$	Volume average diameter, m (μm)
$<D_0>$	Initial volume average diameter, m (μm)
N_t	Total number concentration of drops at time t, m^{-3} (μm^{-3})
N_0	Total number concentration of drops at t=0, m^{-3} (μm^{-3})
a_0	Model Parameter (Eq. 4.23)
t	time, s (h)
k	coalescence coefficient when W is constant, s^{-1}
W	Stability ratio, (-)
J_{ij}	Collision rate per unit volume between drops i and j, $m^{-3}\ s^{-1}$ ($\mu m^{-3}\ s^{-1}$)
J^0_{ij}	Smoluchowski's collision rate per unit volume between drops i and j, $m^{-3}\ s^{-1}$ ($\mu m^{-3}\ s^{-1}$)
t_s	time interval, s
t_d	drainage time, s (ms)
h_{crit}	critical thickness of thin film, m (nm)
h_0	thickness of draining thin film at t=0, m (nm)
F	viscous force, N
K	coalescence coefficient when W is not constant, s^{-1}
C_0	constant in the equation of K, (-)
q_{ij}	ratio of size of colliding drops, (-)
r	radius of drop, m
m	Model Parameter (Eq. 4.23)
$m1$	Model Parameter (Eq. 4.23)
r_c	Model Parameter (Eq. 4.23)
r_{c1}	Model Parameter (Eq. 4.23)

Greek letters

$\dot{\gamma}$	Shear rate, s^{-1}
ϕ	Volume fraction of dispersed phase
μ_d	Viscosity of dispersed phase, mPas
μ_c	Viscosity of continuous phase, mPas
α_{ij}	Coalescence efficiency, (-)
α_0	Coalescence efficiency constant, (-)
μ_i	mean of i^{th} Gaussian distribution, m (µm)
σ	interfacial tension, mN/m
β	Coalescence kernel, $m^3\ s^{-1}$ ($\mu m^3\ s^{-1}$)

Abbreviations

DP	Dispersed Phase
CP	Continuous Phase
VAD	Volume Average Diameter, m (µm)
DSD	Drop Size Distribution
NIS	Nikon Imaging System
AR	Advanced Research
RPM	Revolutions Per Minute
PBE	Population Balance Equation
PBM	Population Balance Model
MDC	Multi-Drop Coalescence