DEVELOPMENT OF MULTIFUNCTIONAL ADDITIVES FOR ENGINE OIL/FUELS AND ZIEGLER NATTA CATALYSTS FOR POLYPROPYLENE SYNTHESIS

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APRIL 2024

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by

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Submitted

In fulfilment of the requirements of the degree of Doctor of Philosophy

to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

APRIL 2024

Dedicated to My Heavenly Parents

CERTIFICATE

This is to certify that the thesis entitled “**DEVELOPMENT OF MULTIFUNCTIONAL ADDITIVES FOR ENGINE OIL/FUELS AND ZIEGLER NATTA CATALYSTS FOR POLYPROPYLENE SYNTHESIS**” being submitted by Ms. Sameeksha Raizada to the Department of Chemistry, Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy is a record of bonafide research work carried out by her.

She has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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ACKNOWLEDGEMENTS

By the divine providence of Almighty GOD, my heavenly mother, my beloved sister, Jigyasa Raizada, and my father (now heavenly), this is when my ship docks, and I have the chance to sincerely thank everyone who helped me with my research and has been a part of my enthralling journey. I did my best to compile a list of all those who made significant contributions at this point, and I apologize for any omissions. Aside from my efforts, the support and advice of many others play a significant role in accomplishing this thesis.

I sincerely thank my supervisor, Prof. Ravi Shankar, Department of Chemistry, Indian Institute of Technology Delhi for his thorough direction, priceless recommendations, and persistent encouragement. His prompt counsel, methodical approach, and rigorous scrutiny have provided the foundation for shaping my thesis in a successful direction. I will always be grateful for his leadership, protection, and support. I thank my co-supervisor, Dr. Gurpreet Singh Kapur, for his valuable suggestions, recommendations, priceless insight, and corrections, which have contributed to shaping this thesis. I sincerely thank Prof. Kamal Pant, Prof. S. Nagendran, Prof. Kuntal Manna, and Prof. Leena Nebhani for their valuable insights, suggestions, and mentorship throughout this journey. My special thanks are due to Dr. Sukhdeep Kaur for providing invaluable suggestions and formidable mentorship in conducting the research work. I thank Dr. Gurmeet Singh for always helping remove and resolve any administrative blockages to carry out the research. I thank Dr. Rashmi Rani for discussions wherever I found a doubt about conducting the research on the bench. I thank Dr. Usha Rani for sharing her knowledge in Silane Chemistry, which removed many doubts in my mind.

I extend my gratitude to Dr. Sujit Mondal and Dr. Amardeep Singh from the Analytical Department, Indian Oil, R&D, for understanding the urgency of the NMR and XPS results, respectively, and assisting me in finishing the work on time. I would like to thank my friends and colleagues, Mr. Rahul Meshram, Mr. Hafiz Mayeen, and Mr. Sandeep Singh, for their abundant help in sharing their expertise in determining the lubricity of additive blends in ultra-low sulfur diesel (ULSD) using High-frequency reciprocating rig. I also thank Mr. Dr. Rameshwar Chowdhary and Mr. Saurabh Mishra for the anti-wear and anti-friction studies of the additive *blends in base oil. Special thanks to Dr. Maya Chakradhar and Dr. Fariha Saleem, who are due for the corrosion studies and insightful conversation regarding lubricant science. My heartfelt thanks to my dear lab mates Dr. Ekta Jakhar and Dr. Ragini Jain for their moral support and guidance. In the same vein, I am grateful to Indian Oil Corporation and R&D for sponsoring me for the Ph.D. program at IIT Delhi and the entire Chemistry Dept, IIT Delhi. I thank IIT Delhi for bestowing me the platform to conduct and pursue my doctoral degree.*

गुरुर्ब्रह्मा ग्रुरुर्विष्णुः गुरुर्देवो महेश्वरः।

गुरुः साक्षात् परं ब्रह्म तस्मै श्री गुरवे नमः॥

Sameeksha Raizada
Sameeksha Raizada

ABSTRACT

The thesis is devoted to a systematic study on three important aspects of petrochemical industry, namely, the development of lubricity improvers for ultra-low sulfur diesel (ULSD), multifunctional additives for engine oil formulations, and polymerization of propylene using Ziegler Natta catalyst. The former two aspects are relevant to meet the standard norms and regulations to limit the emission of polluting elements such as S and polar trace components from fossil fuels without compromising fuel efficiency. In this context, the application of poly(isobutylene succinic anhydride) derivatives tethered with functionally substituted discrete siloxanes/polydimethylsiloxanes have been examined for their efficacy as lubricity improvers in ultra-low sulfur diesel as well as multifunctional additives in base oil. Blends with varying concentrations of additives have been studied to evaluate physical parameters such as viscosity index, kinematic viscosity, and density. These blends are found to be useful in improving the anti-wear and anti-friction attributes of ULSD or base oil. A few examples among the multifunctional additives understudy have shown significant dispersion efficiency of the blends on carbon soot in the base oil and exhibit superior activity as compared to the commercial additive. The results are included in Chapters 3 and 4 of the thesis. In Chapter 5, polypropylene with characteristic properties has been synthesized using ZN catalyst with an emphasis on understanding the role of siloxanes/alkoxysilanes as external donors.

सार

थीसिस पेट्रोकेमिकल उद्योग के तीन महत्वपूर्ण पहलुओं पर एक व्यवस्थित अध्ययन के लिए समर्पित है, अर्थात्, अल्ट्रा-लो सल्फर डीजल (यूएलएसडी) के लिए चिकनाई सुधारकों का विकास, इंजन तेल फॉर्मूलेशन के लिए बहुक्रियाशील एडिटिव्स और ज़िग्लर नट्टा उत्प्रेरक का उपयोग करके प्रोपलीन का पोलीमराइजेशन। पहले के दो पहलू ईंधन दक्षता से समझौता किए बिना जीवाश्म ईंधन से एस और ध्रुवीय ट्रेस घटकों जैसे प्रदूषणकारी तत्वों के उत्सर्जन को सीमित करने के लिए मानक मानदंडों और विनियमों को पूरा करने के लिए प्रासंगिक हैं। इस संदर्भ में, कार्यात्मक रूप से प्रतिस्थापित असतत सिलोक्सेन/पॉलीडिमिथाइलोक्सेन के साथ जुड़े पॉलीसोब्यूटिलीन स्यूसिनिक एनहाइड्राइड डेरिवेटिव के अनुप्रयोग की अल्ट्रा-लो सल्फर डीजल में चिकनाई सुधारक के साथ-साथ बेस ऑयल में बहुक्रियाशील एडिटिव्स के रूप में उनकी प्रभावकारिता के लिए जांच की गई है। चिपचिपाहट सूचकांक, गतिक चिपचिपाहट और घनत्व जैसे भौतिक मापदंडों का मूल्यांकन करने के लिए एडिटिव्स की अलग-अलग सांद्रता वाले मिश्रणों का अध्ययन किया गया है। ये मिश्रण यूएलएसडी या बेस ऑयल के घर्षण-रोधी और घर्षण-रोधी गुणों को बेहतर बनाने के लिए उपयोगी पाए गए हैं। अध्ययनरत मल्टीफंक्शनल एडिटिव्स के बीच कुछ उदाहरणों ने बेस ऑयल में कार्बन कालिख पर मिश्रणों की महत्वपूर्ण फैलाव दक्षता दिखाई है और वाणिज्यिक एडिटिव की तुलना में बेहतर गतिविधि प्रदर्शित की है। परिणाम थीसिस के अध्याय 3 और 4 में शामिल हैं। अध्याय 5 में, बाहरी दाताओं के रूप में सिलोक्सेन/अल्कोक्सीसिलेन की भूमिका को समझने पर जोर देने के साथ ZN उत्प्रेरक का उपयोग करके विशिष्ट गुणों वाले पॉलीप्रोपाइलीन को संश्लेषित किया गया है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

General Abbreviations

ULSD	Ultra-Low Sulfur Diesel	ENDO	Endotherm
EU	European Union	EXO	Exotherm
MASCD	Maximum Allowed Permissible Sulfur Content in Diesel	Cat.	Catalyst
FAME	Fatty Acid Methyl Ester	CSTR	Continuous Stirring Tank Reactor
HFRR	High-Frequency reciprocating rig	ED	External donor
FBWT	Four Ball Wear Test		
SRV	Schwingung (Oscillating), Reibung (Friction), Verschleiß (Wear)	ID	Internal Donor
WSD	Wear Scar Diameter	I.I	Isotactic Index
TOFA	Tall Oil Fatty acids	PP	Polypropylene
COF	Coefficient Of Friction	XS	Xylene Soluble
LCN	Light Cracked Naphtha	TEAL	Triethylaluminum
PIB	Polyisobutylene	EDX	Energy Dispersive X-Ray
PIBSA	Poly(isobutylene succinic anhydride)	VI	Viscosity Index
PIBSI	Poly(isobutylene succinic imide)	KV	Kinematic Index
EC	Ethylene Carbonate	DV	Dynamic Viscosity
ZN	Ziegler Natta	ESI	Electrospray Ionization
ASTM	American Society for Testing and Materials	Mn	Number average molecular weight
NACE	National Association of Corrosion Engineers	Mw	Weight average molecular weight
XPS	X-Ray Photoelectron Spectroscopy	FT	Fourier Transformation
EDS	Energy-Dispersive X-ray spectroscopy	DSC	Differential Scanning Calorimetry

GPC	Gel Permeation Chromatography	PDI	Poly Dispersity Index
NMR	Nuclear Magnetic Resonance	MFI	Melt Flow Index
SEM	Scanning Electron Microscope	IR	Infra-Red
AW	Anti-Wear	BLI	Blend Lubricity Improver
LA	Lubricant Additive	BCP	Blend Commercial PIBSI
EAME	Eleostearic Acid Methyl Ester	EDA	Ethylenediamine
MA	Maleic Anhydride	TBA	Tert-butylamine
BTA	Benzotriazole	PY	Pyrogallol
BHT	Butylated-hydroxy-toluene	T_m	Melting Temperature
nBA	n-butylamine	T_c	Crystallization Temperature
X	Crystallinity		

General Units of measurements

eV	Electron Volt	ppm	Parts per million
keV	Kilo Electron Volt	µm	micrometers
nm	Milimeter	°	Degree
s	seconds	Δ	Difference
rpm	Rotation Per Minute	Å	Angstrom
ν	wavenumber	λ	Wavelength
Kv mm^2	Kilo Volt Mili Meter Square	N	Newtons