

**SURFACTANT-FREE ALCOHOL-DIESEL-WATER
MICROEMULSION FUELS FOR COMPRESSION
IGNITION ENGINES**

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**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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MICROEMULSION FUELS FOR COMPRESSION
IGNITION ENGINES**

**by
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Department of Chemical Engineering

Submitted
in partial fulfilment of the requirements of the degree of Doctor of Philosophy
to the



**INDIAN INSTITUTE OF TECHNOLOGY DELHI
MAY 2020**

***DEDICATED TO MY FAMILY
AND FRIENDS***

CERTIFICATE

This is to certify that the thesis entitled “**Surfactant-free alcohol-diesel-water microemulsion fuels for compression ignition engines**” being submitted by **Ms. Iyman Abrar** to the Department of Chemical Engineering, Indian Institute of Technology Delhi, for the fulfillment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering, is a record of bonafide work carried out by her. She has worked under my guidance and supervision and has fulfilled the requirements, which, to my knowledge, have reached the requisite standard for the submission of the thesis.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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ABSTRACT

Compression ignition (CI) engine is an extensively used diesel-driven internal combustion engine, with a better fuel economy and efficiency as compared to a spark ignition (SI) engine. However, particulate matter (PM) and NO_x emissions generated from diesel fuel have serious environmental and health concerns, which led an interest in the diesel alternatives. Most common diesel alternatives developed till date are either uneconomical or require modifications in current engines and infrastructure. For example, hydrotreated vegetable oil requires high temperature and pressure, thus making the process uneconomical. Similarly, ethanol, another renewable alternative, used in dual-fuel mode, requires separate injection system and fuel tank. Microemulsification is a promising technique of developing economical alternative fuels. It does not require any changes in the existing systems and is environmental friendly in terms of simultaneous reduction of PM and NO_x emissions. However the high percentage of surfactants used to reduce the interfacial tension between the polar and non-polar phases in the microemulsions renders these fuels uneconomical.

This research was focused on developing surfactant-free water-in-diesel microemulsion fuels, using alcohol as co-surfactant as an economical alternative to diesel for the CI engines. The surfactant-free microemulsions could only be formulated in HLB range of 6.27 to 7.76. The effect of different surfactants and alcohols on water solubilization in alcohol-diesel-water system was also studied. Butanol-diesel-water (BDW) microemulsions with HLB of 7.0 were able to incorporate the maximum percentage of water. Moreover, butanol can be derived from a renewable route, and has properties close to diesel, when compared to other lower alcohols. Hence, BDW microemulsions are more promising as compared to other surfactant-free microemulsions.

The BDW microemulsions with 12.9 to 40.0 % (v/v) butanol, 57.8 to 87.0 % (v/v) diesel, and 0.1 to 2.2 % (v/v) water satisfied the ASTM standard specifications of diesel fuel oil, and were compatible with the existing engine and infrastructure. Further, the microemulsion sample with 19.6 % (v/v) butanol, 80.0 % (v/v) diesel, and 0.4 % (v/v) water had 15.7% reduction in brake specific fuel consumption and 24.7% increase in brake thermal efficiency at load of 3.34 kW with respect to diesel, and the cost was 1.9% lower than that of diesel. Moreover, the microemulsion sample with 35.0 % (v/v) butanol, 64.4

% (v/v) diesel, and 0.6 % (v/v) water had 50.0%, 34.4%, 26.6%, and 49.0% reduction in CO, HC, CO₂, and NO_x, respectively, and the cost was 3.4% lower than that of diesel.

The BDW microemulsions exhibited lower fuel consumption, higher thermal efficiency, and lower emissions of CO, HC, CO₂, and NO_x when compared to petro-diesel, with upto 3.4% reduction in cost. Hence, BDW microemulsions present optimal, economical and cleaner alternative to diesel.

सार

संपीडन इग्निशन (CI) इंजन एक बेहतर ईंधन की अर्थव्यवस्था और दक्षता के साथ एक स्पार्क इग्निशन (SI) इंजन की तुलना में एक व्यापक रूप से इस्तेमाल डीजल चालित आंतरिक दहन इंजन है। हालांकि, डीजल ईंधन से उत्पन्न पार्टिकुलेट मैटर (PM) और NO_x उत्सर्जन में गंभीर पर्यावरणीय और स्वास्थ्य संबंधी चिंताएं हैं, जिसने डीजल विकल्पों में रुचि पैदा की। अब तक विकसित किए गए अधिकांश सामान्य डीजल विकल्प या तो असंवैधानिक हैं या वर्तमान इंजन और बुनियादी ढांचे में संशोधनों की आवश्यकता है। उदाहरण के लिए, हाइड्रोट्रीटेड वनस्पति तेल को उच्च तापमान और दबाव की आवश्यकता होती है, इस प्रकार यह प्रक्रिया को अनौपचारिक बना देता है। इसी तरह, दोहरे ईंधन मोड में उपयोग किए जाने वाले एक अन्य अक्षय विकल्प, एथेनॉल को अलग इंजेक्शन प्रणाली और ईंधन टैंक की आवश्यकता होती है। माइक्रोइमल्शन किफायती वैकल्पिक ईंधन विकसित करने की एक आशाजनक तकनीक है। इसे मौजूदा प्रणालियों में किसी भी बदलाव की आवश्यकता नहीं है और PM और NO_x उत्सर्जन में एक साथ कमी के संदर्भ में पर्यावरण के अनुकूल है। हालांकि, माइक्रोइमल्शन में ध्रुवीय और गैर-ध्रुवीय चरणों के बीच पारस्परिक तनाव को कम करने के लिए इस्तेमाल किए जाने वाले सर्फैक्टेंट का अधिक प्रतिशत इन ईंधन को अलाभकर बनाता है।

यह शोध CI इंजनों के लिए डीजल के किफायती विकल्प के रूप में एल्कोहल का सह-सर्फैक्टेंट के रूप में सर्फैक्टेंट-मुक्त पानी-इन-डीजल माइक्रोइमल्शन ईंधन विकसित करने पर केंद्रित था। सर्फैक्टेंट-फ्री माइक्रोइमल्शन केवल HLB रेंज में 6.27 से 7.76 तक हो सकते हैं। एल्कोहल-डीजल-पानी प्रणाली में पानी के घोल पर विभिन्न सर्फैक्टेंट और एल्कोहल के प्रभाव का भी अध्ययन किया गया था। 7.0 के HLB के साथ ब्यूटेनॉल-डीजल-पानी (BDW) सूक्ष्मजीव पानी के अधिकतम प्रतिशत को शामिल करने में सक्षम थे। इसके अलावा, ब्यूटेनॉल को एक अक्षय मार्ग से प्राप्त किया जा सकता है, और अन्य कम एल्कोहल की तुलना में

डीजल के जैसे गुण हैं। इसलिए, अन्य सर्फैक्टेंट-फ्री माइक्रोइमल्शन की तुलना में BDW माइक्रोइमल्शन अधिक आशाजनक होते हैं।

12.9 से 40.0% (v/v) ब्यूटेनॉल, 57.8 से 87.0% (v/v) डीजल, और 0.1 से 2.2% (v/v) पानी के साथ BDW माइक्रोइमल्शन, मौजूदा इंजन और बुनियादी ढांचे के संगत होने के साथ ही, डीजल ईंधन तेल के ASTM मानक विनिर्देशों को संतुष्ट करता है। इसके अलावा, 19.6% (v/v) ब्यूटेनॉल, 80.0% (v/v) डीजल, और 0.4% (v / v) पानी के साथ माइक्रोइमल्शन नमूना में ब्रेक विशिष्ट ईंधन की खपत में 15.7% की कमी और ब्रेक थर्मल दक्षता में 24.7% की वृद्धि हुई थी। डीजल के संबंध में 3.34 किलोवाट का भार, और लागत डीजल की तुलना में 1.9% कम थी। इसके अलावा, 35.0% (v/v) ब्यूटेनॉल, 64.4% (v / v) डीजल, और 0.6% (v / v) पानी के साथ माइक्रोइमल्शन का नमूना में CO, HC, CO₂, और NO_x में क्रमशः 50.0%, 34.4%, 26.6% और 49.0% की कमी आई थी, और लागत डीजल की तुलना में 3.4% कम थी।

BDW माइक्रोइमल्शन ने पेट्रोल-डीजल की तुलना में कम ईंधन खपत, उच्च तापीय क्षमता और CO, HC, CO₂ और NO_x के कम उत्सर्जन को प्रदर्शित किया, जिसकी लागत में 3.4% की कमी आई। इसलिए, BDW माइक्रोइमल्शन डीजल के लिए इष्टतम, किफायती और स्वच्छ विकल्प प्रस्तुत करते हैं।

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LIST OF ABBREVIATIONS

ABE	Acetone-butanol-ethanol
ADW	Alcohol-diesel-water
ASTM	American society for testing and materials
BSEC	Brake specific energy consumption
BDW	Butanol-diesel-water
BSFC	Brake specific fuel consumption
BTE	Brake thermal efficiency
CHAPS	3-[(3-cholamidopropyl)dimethylammonio]-1-propanesulfonate
CI	Compression ignition
CO	Carbon monoxide
CO ₂	Carbon dioxide
CPP	Critical packing parameter
CTAB	Cetyl trimethyl ammonium bromide
DLS	Dynamic light scattering
DTBP	Di-tert-butyl peroxide
EGBE	Ethylene glycol butyl ether
EGT	Exhaust gas temperature
FT	Fischer-Tropsch
GHG	Green house gases
HC	Hydrocarbon(s)
HLB	Hydrophilic-lipophilic balance
HVO	Hydrotreated vegetable oil
IS	Indian standards
NO _x	Nitrogen oxides
PAHC	Polycyclic aromatic hydrocarbons
PDW	Propanol-diesel-water
PIT	Phase inversion temperature
PM	Particulate matter
SI	Spark ignition
SLS	Sodium lauryl sulphate
SO _x	Sulfur oxides

TEM	Transmission electronic microscope
ULSD	Ultra low sulfur diesel